Response to Anonymous Referee #2

We thank the reviewer for the constructive suggestions/comments. Below we provide a point-by-point response to individual comment (Reviewer comments and suggestions are in italics, responses and revisions are in plain font; revised parts in responses are marked with red color; page numbers refer to the modified ACPD version).

Comments and suggestions:

This manuscript reports on observations of VOCs during an ambient field-based study of the physiological partitioning of compounds to and from a sterilized soil surface. The authors use a coated flow tube referenced to a soil free ambient air cell to determine the directionality and strength of VOC fluxes. The study concludes that for all VOCs observed the net flux is a soil surface sink, whereas formic acid production is consistently observed. This is a well-organized, well-written work and clearly presents the results from these experiments. It is my opinion that this work does fit within the scope of ACP and should be accepted with the addition of minor additional discussion and edits.

Responses and Revisions:

Thanks for the positive comments and feedback from the reviewer.

Comments and suggestions:

Briefly, there seems to be a general lack of justification for the identification of several of the key ideals presented in the manuscript. (1) there is a strong push by the authors that this sterile soil system is representative of natural processes that seems to be weakly supported.

Responses and Revisions:

Thanks for the reviewer's comments.

In this manuscript we used sterilized soil to investigate the physicochemical processes of different VOC species on soil surfaces. As the reviewer pointed out, it is true that the sterilized soil system cannot totally represent natural processes. Because we all know that the natural processes on soil involve both biotic and abiotic activities/reactions, and the intrinsic mechanisms can become more complicated with all the factors (biotic and abiotic) involved. From a point view of research methodology, if we want to know the role that each part plays (i.e., biotic processes versus abiotic processes) we first need to investigate them separately. Therefore, here we tried to preclude the influence of biotic activities and only focus on the abiotic reactions (i.e., physicochemical processes). The advantage of our soil system was that it allowed real ambient air react with sterilized soil for a very long time period (one month). The exchange properties we observed here can generally reflect the physicochemical aspect on bare soil.

Comments and suggestions:

(2) there is a large jump evoking heterogeneous chemistry that is not obvious to the reader with the only evidence being emission versus uptake.

Responses and Revisions:

Thanks for the reviewer’s comments.

Heterogeneous chemistry/reactions involve species that are distributed in different phases or are occurring at an interface (Ravishankara, 1997;Rossi, 2003). In our study, we investigated the exchange characteristics of VOCs at the atmosphere-soil interface. By using our coated-wall flow tube technique, the observed VOC uptake and emission on soil provided us direct evidence that some VOC species migrated from the atmosphere/soil into the soil/atmosphere through potential physicochemical processes on soil surfaces. In this way, we classified the physicochemical processes on soil that we found here into heterogeneous chemistry.

Comments and suggestions:

(3) a focus is placed on formaldehyde oxidation to formic acid when all observed VOC species are anticorrelated with the only species emitted, formic acid. In fact on that last point there are two compounds that anticorrelate with formic acid better than formaldehyde (figure 9). The authors should return to the manuscript and provide better justification on why these hypotheses are being made. The leap to these conclusions may be obvious to the authors however, I believe better justification is necessary for the benefit of the reader.

Responses and Revisions:

The reviewer is right. According to the VOC exchange correlation analysis in the manuscript (Sect. 3.6), we found several species (i.e., acetone, isoprene, formaldehyde, styrene and methanol) showed high anti-correlation with formic acid. Without direct experiment/field observation evidence showing the emission of formic acid is only due to the heterogeneous transformation of formaldehyde, we should be more strict to our wording in the manuscript. We have rearranged the context in Sect. 3.6 and Sect. 4.1 in the manuscript to provide better justification.

The rearranged Sect. 3.6 and Sect. 4.1 are as follows:

“3.6 VOC exchange correlation analysis

As discussed above, the uptake dynamics of one individual VOC species may be biased, either (i) by competitive co-absorption of other VOCs or trace gases from ambient air (Lichtin et al., 1996;Ao et al., 2004), or (ii) by formation on the soil through heterogeneous conversion of precursor compounds that have been absorbed earlier (Ammann and Pöschl, 2007;Pöschl et al., 2007), or (iii) by depletion of the individual VOC species due to heterogeneous degradation. To explore potential interactions/interferences of VOC species among each other, correlation analyses of the exchange rates (i.e., the concentration difference between the reference channel and the sample channel $C_r - C_s$ times the volumetric flow rate F) of measured VOC species are conducted for each pair of species. The results are presented in Fig. 9 in terms of Pearson correlation coefficients, together with the molecular structure of each investigated species. The interplay of sorption, heterogeneous reactions and desorption kinetics of VOCs is complex, and heterogeneous reactions may require time periods from milliseconds to weeks or even months to reach equilibrium (Xing and Pignatello, 1996;Ammann and Pöschl, 2007). Hence, to also account for slow kinetics, the correlation analysis in Fig. 9 is based on daily integrals. VOC exchange rates instead of uptake coefficients are used to allow for a budget approach. Positive correlations are indicated in red colors, and some pairs of VOC species show high positive correlation (deep red color code in Fig. 9), suggesting they have similar exchange characteristics. For example, MVK and MACR are the first generation oxidation products of isoprene (Jordan et al., 2009). Thus, the observed high correlation coefficient between MVK+MACR and isoprene can be explained by their similar molecular structures shown in Fig. 9. The same holds for the strong correlation between methanol and formaldehyde, methanol and acetone, as well as for MEK and acetone: similar molecular structures and functional groups result in analogous exchange and reaction mechanisms on soil.

Negative correlations in Fig. 9 are indicated in blue colors. As aforementioned, formic acid is at the very end of the VOC oxidation chain, and is exclusively emitted from the soil sample while all other VOCs tend to be taken up. Thus, correlations of formic acid with other VOCs are negative as such (blue in Fig. 9). High negative correlation coefficients are obtained between formic acid and some species (i.e., acetone, isoprene, formaldehyde, styrene and methanol), indicative of possible generation and emission of formic acid due to heterogeneous transformation of these deposited compounds.

4. Implications for atmospheric chemistry

4.1 Formic acid formation through heterogeneous transformation of deposited VOCs

We know from the above discussions that several VOC species including acetone, isoprene, formaldehyde, styrene and methanol show high anti-correlation with formic acid, suggesting the existence of one or several pathways for formic acid formation through heterogeneous reactions of these VOC precursors.

In the atmosphere, photo-oxidation of acetone contributes to the abundance of formic acid, and the dominant pathway for formic acid formation via acetone photo-oxidation is the reaction of OH radical with acetone-derived formaldehyde (Chattopadhyay et al., 2015). Formic acid production through photo-oxidation of isoprene has been found under high NO_x circumstances (Paulot et al., 2009). Under ambient conditions, gas phase reactions of styrene with OH radical and O_3 can occur respectively, with formaldehyde and benzaldehyde as major products and formic acid as the minor (Tuazon et al., 1993). Methanol has been reported to play an important role in upper tropospheric photo-oxidation chemistry via its contribution to the HO_x budget after its oxidation to formaldehyde (Tie et al., 2003;Singh et al., 1995;Singh et al., 2000;Singh et al., 2004;Colomb et al., 2006). Notably, formaldehyde is an important intermediate of VOC oxidation and a direct precursor of formic acid (Adewuyi et al., 1984;Chameides, 1984). Moreover, the results in Sect. 3.2 and Sect. 3.3 tell us that formaldehyde shows continuous and even increasing uptake during the whole field measurement (see Fig. 5A and 6A). All these results evidence formaldehyde may act as the best candidate for heterogeneous formation of formic acid on soil.

In terms of physicochemistry, formaldehyde is much less stable than formic acid (~ 1 day versus ~ 25 days of mean atmospheric chemical lifetime, see Millet et al., 2015), which indicates its faster turnover rates also on soil surfaces. Moreover, the mean retention coefficient of formaldehyde has been shown to be considerably higher than for formic acid in cloud/ice water (Jost et al., 2017), inferring a reasonable explanation for the preferential release of the organic acid from the soil. Furthermore, aldehydes in general undergo accretion reactions (i.e., aldol condensation type reactions) in acidic media and similar chemistry has been shown to occur on mineral oxides (Li et al., 2001), therefore mineral-rich bare soils can serve as a sink for these compounds. According to our results, formaldehyde is a relatively reactive short-term intermediate for formic acid production, rather than being directly released to the atmosphere under authentic ambient air oxidizing conditions in Beijing city. In general, a catalytic effect of soil can be anticipated by its composition of a variety of mineral oxides (silicon oxide, iron oxide and titanium oxide, etc.). Therefore, our soil sample may serve as a catalytic surface for degradation of the deposited precursors with formaldehyde as the most important intermediate, which can be further oxidized to build up formic acid by heterogeneous reactions on the soil, followed by formic acid emission. This catalytic effect may be further enhanced by the co-existence of other deposited oxidants (O_3, OH radical, NO_2 and peroxides, etc.) on the soil surfaces. More research is needed to confirm the speculation made here.”

Comments and suggestions:

The strength of the arguments here would have been significantly enhanced by using a third cell comparing sterile soil to a representative soil sample that had not been autoclaved, perhaps the authors have results from experiments like that? Without those comparisons, I would like to see additional discussion in the conclusions section comparing similar VOC study observations to the results observed here in detail. The previous studies performed on this topic, many of which were cited, observe dramatic differences in VOC flux directionality with the addition of a litter layer, or microbes/fungi. Putting these results in context, more so than has already been done, will allow the reader to better determine the representativeness of these results and therefore the potential impact.

Responses and Revisions:

Thanks for the reviewer's comments.

As mentioned in the manuscript, our study was aimed to investigate the physicochemical background of VOC exchange on soil independently from biological activity. We agree with the reviewer's suggestion that a comparison between sterilized soil and naturally non-sterilized soil would definitely enhance the strength of our arguments. As we didn't perform the experiments using non-sterilized soil during the field measurement, here we have added additional discussions in the conclusion section:

"…At ambient atmospheric conditions, both the relatively low uptake coefficients derived for the majority of VOC species and the emission of formic acid from the soil to some extent challenge the applicability of models using uptake coefficients derived from laboratory-based uptake measurements, where single VOC species or simple mixtures are supplied using purging air devoid of oxidizing agents. Field measurements as presented here, with all relevant parameters changing in concert, may call attention for the existence of yet unknown interferences or synergetic effects.

As our soil sample is sterilized, the uptake and emission characteristics observed in this study can reflect the contribution of abiotic processes in soil regarding VOC exchange at the atmosphere-soil interface. However, natural soils are a complex ecosystem including leaf litter, plant roots, microorganisms and soil particles. Taking the biotic processes and different soil types into account may produce different results from we observed here. Previous studies have shown that soil can be a source of short-chain oxygenated VOCs and terpenes due to emissions of soil vegetation (e.g., grass and crops), degradation of leaf litter and other activities of soil living organisms (Schade and Goldstein, 2001;Hayward et al., 2001;Gray et al., 2010;Chen et al., 2004;Lin et al., 2007;Scholler et al., 2002;Rossabi et al., 2018). For example, Leff and Fierer (2008) found that litter samples could produce more types of VOCs than the soil samples without litter covers, indicating degradation of soil litter can be an important source of VOC emission. On the other hand, other studies have observed deposition of several categories of VOCs (e.g., alcohols, aldehydes and monoterpenes) on various types of soils (Asensio et al., 2007;Asensio et al., 2008;Aaltonen et al., 2013;Gray et al., 2014). Considering that the results obtained in the present study can only address the effects of physicochemical processes on VOC exchange, follow-up studies are needed to explore the contribution of soil living organisms (e.g., bacteria, fungi) to VOC exchange at the soil-atmosphere interface."

Comments and suggestions:

As is, I am not sure that the physiological processes observed here will be paramount to the biological processing of VOCs, and thus the question, will these mechanisms even matter in a real soil situation or be diluted or obscured by other more dominant processes. That discussion is necessary to justify the exercise of scaling up the rates of formic acid emission observed here in an attempt to establish the importance of this 'new' source of formic acid. One could very easily make the argument that instead of VOCs undergoing heterogeneous oxidation to formic acid on a sterile medium, those VOCs will be consumed by microbes/fungi removing precursor material and thereby terminate the formic acid production scheme introduced here. At a minimum the authors should more clearly indicate the limitations of this study in this context and the assumptions being made to justify scaling of this potential formic acid source.

Responses and Revisions:

Thank the reviewer for pointing this issue out.

In a real soil situation, the physicochemical (abiotic) processes are often combined with biotic processes. The dominance of one over the other is influenced/controlled by changing environmental factors (i.e., temperature, relative humidity and photochemistry) and/or soil types. As discussed in the manuscript, soils can be either sources or sinks for different kinds of VOCs. This difference of soils' role in affecting the exchange properties of VOCs is likely due to varying soil vegetation and/or microbial communities in different soil types. However, here we assume that physicochemical processes on soil surfaces (more likely on soil solid phase through heterogeneous chemistry) can be a common phenomenon, which is occurring in parallel with biotic processes. Because the solid phase of soil, which includes minerals and organic matter (with minerals content much higher than organic matter), are generally stable in nature (https://www.ctahr.hawaii.edu/mauisoil/a_comp.aspx). We think that the results obtained in our study can address the potential contribution of soil particles to formic acid budget from a physicochemical (heterogeneous chemistry) point of view, especially when the soil is dry and the microbial activities are low under some specific situations. We believe our study can provide helpful information or a valuable reference for related model calculation and field campaign studies involving formic acid budget analysis. For example, in a recent campaign in the high Arctic, Mungall et al. (2018) speculated that heterogeneous chemistry could act to oxidize organic molecules present on soil surfaces and serve as a source for formic and acetic acid. Unfortunately, due to the lack of information, they couldn't assess the extent of the contribution of heterogeneous oxidation processes to the observed formic and acetic acid.

Following the review's suggestions, we have added additional discussions in the Sect. 4.2:

"…Note that the magnitude of the emission rate here used for calculation also depends on the mixing ratio levels of ambient VOC precursors and other environmental parameters such as temperature, relative humidity and photochemistry on soil surfaces. Due to the design of our experimental setup, no sunlight reaches the soil surfaces (see Sect. 2.2). But one can imagine that the existence of sunlight would enhance the catalytic effect of soil minerals (e.g., titanium oxide) and, the soil surface will become hotter and thus make soil dry out faster. These changes may influence the exchange rates of the examined VOCs through the following ways: (1) high catalytic efficiency may accelerate transformations of deposited VOC precursors and the formation/emission of formic acid; (2) high temperatures of soil may let more adsorbed VOC molecules escape from soil surfaces through evaporation and decrease their uptake; (3) low amounts of water on soil may increase the uptake of some hydrophobic VOC species and decrease the uptake of some hydrophilic VOCs. The combined effect of these three aspects may even tell another different story, which deserves further studies. In a real soil situation, the physicochemical (i.e., abiotic) processes are often combined with biotic processes. The dominance of one over the other is influenced/controlled by changing environmental factors (i.e., temperature, relative humidity and photochemistry) and/or soil types. However, here we assume that physicochemical processes on soil surfaces (more likely on soil solid phase through heterogeneous chemistry) can be a common phenomenon, which is occurring in parallel with biotic processes. Because the solid phase of soil, which includes minerals and organic matter (with minerals' content much higher than organic matter), are generally stable in nature (https://www.ctahr.hawaii.edu/mauisoil/a_comp.aspx). We think the results obtained in our study can provide a helpful reference regarding the potential contribution of soil particles to formic acid budget from a physicochemical (heterogeneous chemistry) point of view, especially when the soil is dry and the microbial activities are low under some specific situations. Considering the still poorly understood budget of formic acid (Millet, 2012;Paulot et al., 2011), more investigations are needed to quantify the contributions of different types of soil as a potential source of formic acid under different environmental conditions."

Comments and suggestions:

It may be worth discussing the effect that RH has on the mobility of a given molecule with respect to diffusion into the bulk soil sample. This could explain the counterintuitive dependence of hydrophobic molecules on RH, where by surface sites become 'washed' meaning molecules are drawn into the bulk of the soil sample leaving additional bonding sites on the surface thereby increasing the rate of uptake. When the soil dries presumably VOCs that have been washed into the bulk of the soil sample will remain there as the diffusion timescales will be considerably longer. This surface absorbed water also has the potential to promote aqueous reactions that may produce products are a higher rate that simple gas phase heterogeneous reactions. This could be of particular importance to the formic acid source that is implied from your observations.

Responses and Revisions:

Thanks for the reviewer's comments.

As proposed by the reviewer, the effect that RH has on the mobility of hydrophobic molecules is a good point worth discussing in the manuscript.

Therefore, we have added more discussions concerning the RH dependence in Sect. 3.5:

"…However, the uptake coefficients of hydrophobic isoprene and its primary degradation products (i.e., MVK+MACR) also increase at high RH. This counterintuitive dependence may also be explained in another way: more water molecules can push more hydrophobic species into the soil bulk, leaving additional adsorption sites on soil surfaces and thereby increasing its uptake; As the soil becomes dry, the VOC molecules in the soil bulk will remain in situ considering that the timescales of soil bulk diffusion are considerably longer than on soil surfaces. From the physical perspective of vapor pressure, increased temperature leads to decreased trace gas uptake and increased emission. This is in line with the decreased uptake of isoprene at higher temperatures shown in Fig. 8. However, the uptake coefficients of acetaldehyde show a slight increasing trend as a function of T."

Comments and suggestions:

Presumably, from the setup described, there is no light reaching the soil surface. Do the authors have any comments as to how the lack of light on the soil surface would change the partitioning and potential chemistry that would have otherwise been occurring. It would seem that soils would have dried out faster, local soil surface temperatures would have been hotter, and a few other important changes. It would be beneficial to this manuscript to discuss this aspect of the work as the authors do heavily rely on these results being as field representative as possible.

Responses and Revisions:

Thanks for the reviewer’s comments.

Concerning the potential effect of sunlight on VOC exchange at the atmosphere-soil interface, we have added relevant discussions in Sect. 4.2:

“…Note that the magnitude of the emission rate here used for calculation also depends on the mixing ratio levels of ambient VOC precursors and other environmental parameters such as temperature, relative humidity and photochemistry on soil surfaces. Due to the design of our experimental setup, no sunlight reaches the soil surfaces (see Sect. 2.2). But one can imagine that the existence of sunlight would enhance the catalytic effect of soil minerals (e.g., titanium oxide) and, the soil surface will become hotter and thus make soil dry out faster. These changes may influence the exchange rates of the examined VOCs through the following ways: (1) high catalytic efficiency may accelerate transformations of deposited VOC precursors and the formation/emission of formic acid; (2) high temperatures of soil may let more adsorbed VOC molecules escape from soil surfaces through evaporation and decrease their uptake; (3) low amounts of water on soil may increase the uptake of some hydrophobic VOC species and decrease the uptake of some hydrophilic VOCs. The combined effect of these three aspects may even tell another different story, which deserves further studies.”

Comments and suggestions:

Just an idea, there may be a promotion of the uptake rate for acetaldehyde with increasing mixing ratios if the acetaldehyde dimer were involved in a reaction.

Responses and Revisions:

Thanks for the reviewer’s comments.

Following the other reviewer’s suggestions, we have made a new figure as a replacement of the original Fig. 8 in the manuscript. In the new figure, we show the RH and T dependence of uptake coefficients of the VOC species when they have a small variation of their ambient mixing ratios C, assuming that this small variation of C would not have a big effect on gamma. Moreover, the C dependence is shown when the RH is constant at 50%. In the new Fig.8, the uptake coefficients of acetaldehyde show a slight decreasing trend as a function of its mixing ratios. This dependence is contrary to that we had in the previous version. But here as we check the C dependence when RH is constant, this dependence should more precisely reflect the effect of mixing ratios on its uptake rate.

The new Fig. 8 is as follows:

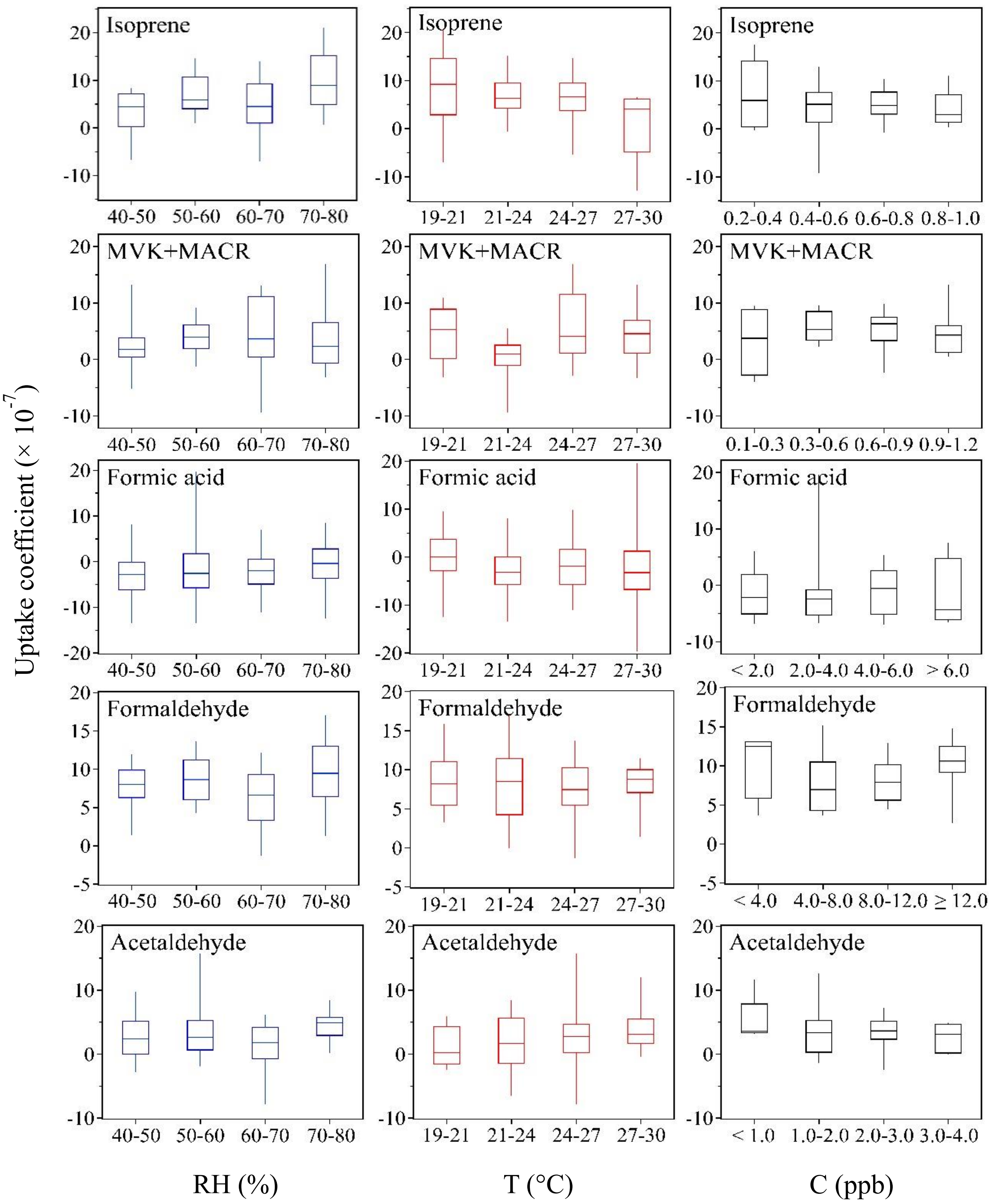

Figure 8. Dependence of uptake coefficients on ambient relative humidity (RH), temperature (T) and mixing ratios (C). Minimum, 25th, 50th, 75th percentile and maximum of the box-and-whisker plots are indicated by bars. The uptake coefficient dependence is based on the hourly averaged data, and the RH and T dependences are plotted when C is varied within a very narrow range (nearly constant) and C dependence is plotted when RH equals to 50%. Note that negative uptake coefficients indicate emission. For details see text.

Comments and suggestions:

On page 12 a large leap is made when the idea of surface reactions of VOCs is thrust into this manuscript seemingly without justification or evidence that these types of reactions are occurring. What evidence is there for soil surface reactions at this point in the paper?

Responses and Revisions:

Thanks for the reviewer’s comments.

We have added more discussions in Sect. 3.3 (page 13), to show the evidence:

“The observed uptake/emission in Fig. 6 can be caused by pore diffusion and soil surface processes (i.e., adsorption/desorption equilibrium and chemical reactions). As aforementioned, the time scale of VOC diffusion through soil pores is around 25 min. This time scale is several orders less than our whole field campaign time period (i.e., 1 month), suggesting that pore diffusion is not the limiting factor of the uptake/emission found here. After the significant absorption saturation on soil in the first few days (see Fig. 6A), the subsequent relatively stable uptake for most of the VOC species can be due to chemical reactions on soil surfaces. Our previous laboratory study of formaldehyde uptake on soil has proved that the observed uptake is a combination of adsorption/desorption equilibrium and chemical reactions (Li et al., 2016). …”

Comments and suggestions:

The paragraph on page 12, line 19 is very difficult to understand. The first sentence is confusing introducing surface reaction, but only instead of diffusion into pores? This section needs to be clarified.

Responses and Revisions:

Thanks for the reviewer’s comments.

In order to let the readers easily understand the chemical reactions on soil surfaces mentioned in the paragraph on page 12 (now on page 13 of the modified version), we added more discussions in front of the paragraph:

“The observed uptake/emission in Fig. 6 can be caused by pore diffusion and soil surface processes (i.e., adsorption/desorption equilibrium and chemical reactions). As aforementioned, the time scale of VOC diffusion through soil pores is around 25 min. This time scale is several orders less than our whole field campaign time period (i.e., 1 month), suggesting that pore diffusion is not the limiting factor of the uptake/emission found here. After the significant absorption saturation on soil in the first few days (see Fig. 6A), the subsequent relatively stable uptake for most of the VOC species can be due to chemical reactions on soil surfaces. Our previous laboratory study of

formaldehyde uptake on soil has proved that the observed uptake is a combination of adsorption/desorption equilibrium and chemical reactions (Li et al., 2016). From a perspective of kinetic gas theory, the derived uptake coefficients can be further used to determine VOC surface reaction rates on soil which are only caused by reactions on soil surface instead of diffusion into soil pores under steady state conditions (i.e., after significant absorption saturation of the soil sample in the first few measurement days in Fig. 6A). … ”

Comments and suggestions:

Page 7, line 29: "basing" should be 'based'.

Responses and Revisions:

Corrected.

Comments and suggestions:

Page 8, line 12: what does "During the field measurement, the system was running in multiple ion mode" mean? Is this meaning the PTR-MS was using H3O+ and O2+ or NO+? Or is this just referring to stepping through the masses using the quadrupole. Because of the context, and what is currently being done in the PTR-MS/PTR-TOF field with multiple reagent ion modes, this needs to be explicitly stated.

Responses and Revisions:

Thanks for the reviewer's comments.

The system was running in multiple ion mode refers to stepping through the masses using the quadrupole. We have made an explicit statement concerning the multiple ion mode in Page 8:

"During the field measurement, the system was running in multiple ion mode, where the quadruple switched between the selected masses."

Comments and suggestions:

Page 8, line 17: I would rewrite this sentence as such, 'Uncertainties of measured species were about 5% - 15%, with the notable exception of formaldehyde, formic acid and acetic acid.'

Responses and Revisions:

Corrected.

Comments and suggestions:

Page 8, line 26: I suggest rewriting "the atmospheric abundance of ethanol and dimethyl ether is supposed to be low" to 'the atmospheric abundance of ethanol and dimethyl ether in similar urban site has previously been found to be low. "Supposed to be low" is very nonscientific way of saying something.

Responses and Revisions:

Corrected.

Comments and suggestions:

Page 8, line 29: The line "The influences were corrected by introducing the m/z = 89 in the calculations (Yuan et al., 2013)" does not provide many details as to what was done. I do realize that they are in this publication but another half or full sentence on this would be helpful to the reader. As is this line reads as a fragment of an idea, e.g. what is m/z 89 and what calculation are you talking about?

Responses and Revisions:

Thanks for the reviewer's comments.

We have rephrased this sentence to make it provide more details and the new sentence is as follows:

"…Therefore, during calculations of acetic acid concentration the m/z = 89 (attributed to ethyl acetate) was introduced to correct for the influences (Yuan et al., 2013)."

Comments and suggestions:

Page 8, line 32: You need to define what CKD stands for here.

Responses and Revisions:

Corrected.

Comments and suggestions:

Page 9, line 32: I think the mention of Eqs. 19.14 and 19.17 is referring to equations in Seinfeld and Pandis 2016. It would be more appropriate to reprint these equations here is they are used in this work and cite them in full.

Responses and Revisions:

Corrected.

Comments and suggestions:

Page 14, line 6: This "On one hand"…"On the other hand" phrasing is suggestive of two contrasting ideas in competition. In your case these are additive issues/assumptions that limit the interpretation of these result. I would therefore recommend removing that phrasing scheme.

Responses and Revisions:

We thank for the review's correction. We have removed the phrasing scheme.

Comments and suggestions:

Page 15, line 7: Acetaldehyde is not a hydrophobic molecule, and is in fact soluble in water in all proportions.

Responses and Revisions:

Thanks for the reviewer's comments.

Following the other reviewer's suggestions, we have made a new figure as a replacement of the original Fig. 8 in the manuscript. And therefore the text in Sect. 3.5 has been revised accordingly. The sentence that the reviewer mentioned has been removed from Sect. 3.5.

Comments and suggestions:

Page 17, line 3: It is stated that "formaldehyde uptake reveal a relatively high correlation with formic acid emission", however, I am not sure that his has been shown effectively. I also believe that there is a large anticorrelation of those two species not a correlation. Point number two should have a reference to the reaction of formaldehyde to formic acid. A bit later you need to change the word "evidence" to a more fitting verb, like 'suggest'.

Responses and Revisions:

Thanks for the reviewer's comments.

We have rearranged the text in Sect. 3.6 and 4.1. In the new Sect. 4.1, we use "anti-correction" to replace "correlation" to show the relation between formaldehyde uptake and formic acid. The word "evidence" has been changed into "suggest". The modified text in Sect. 4.1 is as follows:

"**4.1 Formic acid formation through heterogeneous transformation of deposited VOCs**

We know from the above discussions that several VOC species including acetone, isoprene, formaldehyde, styrene and methanol show high anti-correlation with formic acid, suggesting the existence of one or several pathways for formic acid formation through heterogeneous reactions of these VOC precursors.

In the atmosphere, photo-oxidation of acetone contributes to the abundance of formic acid, and the dominant pathway for formic acid formation via acetone photo-oxidation is the reaction of OH radical with acetone-derived formaldehyde (Chattopadhyay et al., 2015). Formic acid production through photo-oxidation of isoprene has been found under high NO_x circumstances (Paulot et al., 2009). Under ambient conditions, gas phase reactions of styrene with OH radical and O_3 can occur respectively, with formaldehyde and benzaldehyde as major products and formic acid as the minor (Tuazon et al., 1993). Methanol has been reported to play an important role in upper tropospheric photo-oxidation chemistry via its contribution to the HO_x budget after its oxidation to formaldehyde (Tie et al., 2003;Singh et al., 1995;Singh et al., 2000;Singh et al., 2004;Colomb et al., 2006). Notably, formaldehyde is an important intermediate of VOC oxidation and a direct precursor of formic acid (Adewuyi et al., 1984;Chameides, 1984). Moreover, the results in Sect. 3.2 and 3.3 tell us that formaldehyde shows continuous and even increasing uptake during the whole field measurement (see Fig. 5A and 6A). All these results suggest formaldehyde may act as the best candidate for heterogeneous formation of formic acid on soil."

Comments and suggestions:

Page 17, line 9: "indicates its faster turnover rates also on soil surfaces" should be reworded.

Responses and Revisions:

Thanks for the reviewer's suggestion.

The sentence has been reworded as follows:

"In terms of physicochemistry, formaldehyde is much less stable than formic acid (~ 1 day versus ~ 25 days of mean atmospheric chemical lifetime, see Millet et al., 2015), indicating its faster turnover rates on soil surfaces."

Comments and suggestions:

Page 17, line 14-19: Here you are identifying ambient constituents that could be used to support or contradict your proposed mechanism. You elude to SO2 observations on page 10, so does formic acid formation seem to be suppressed during periods of high SO2 as was found in AO et al. 2004? What about promotion by high NO? The soil is sterile so it should not be producing NO however there is ambient NO that should be interacting with the soil surface, is the formic acid formation rate increased with high ambient NO? If there is no evidence for these correlations than why believe that these mechanisms are occurring?

Responses and Revisions:

Thanks for the reviewer's comments.

Based on our observation data, we checked the relation between the formation rate of formic acid and the ambient mixing ratios of SO_2 and NO. We didn't find these lab-observed phenomena as reported by Ao et al. (2004). Therefore, the related discussion regarding the work of Ao et al. (2004) has been removed from our manuscript.

Comments and suggestions:

Page 17, line 23: I think you really need to better justify the statement "formaldehyde as the most important intermediate". It would seem to me that you are forcing a conclusion here when many of the organics being absorbed have the potential to oxidize and produce formic acid as an end product of oxidation.

Responses and Revisions:

Thanks for the reviewer's comments.

Here the statement of "formaldehyde as the most important intermediate" is referring to the discussion we have in the some section (modified Sect. 4.1):

"...In the atmosphere, photo-oxidation of acetone contributes to the abundance of formic acid, and the dominant pathway for formic acid formation via acetone photo-oxidation is the reaction of OH radical with acetone-derived formaldehyde (Chattopadhyay et al., 2015). Formic acid production through photo-oxidation of isoprene has been found under high NO_x circumstances (Paulot et al., 2009). Under ambient conditions, gas phase reactions of styrene with OH radical and O_3 can occur respectively, with formaldehyde and benzaldehyde as major products and formic acid as the minor (Tuazon et al., 1993). Methanol has been reported to play an important role in upper tropospheric photo-oxidation chemistry via its contribution to the HO_x budget after its oxidation to formaldehyde (Tie et al., 2003;Singh et al., 1995;Singh et al., 2000;Singh et al., 2004;Colomb et al., 2006). Notably, formaldehyde is an important intermediate of VOC oxidation and a direct precursor of formic acid (Adewuyi et al., 1984;Chameides, 1984)..."

Comments and suggestions:

Page 18: It seems a large stretch to indicate that the physiochemical properties of this soil sample used here, a completely sterilized medium with no ground cover, litter or impurities would be a good model for even barren land. Even in barren land such as Saharan soil samples there are microbes capable of interacting with the absorbed organics to alter the emission properties of the soil. It is necessary to mention the extent of the assumptions here to give an honest review of the potential impact of this suggested source.

Responses and Revisions:

Thanks for the reviewer’s comments.

We have added more discussions in Sect. 4.2 to try to give an honest review of the potential impact of this suggested source:

“…To the best of our knowledge, this study is the first trial to evaluate the potential contribution of physicochemical processes on soil under real ambient conditions to the atmospheric budget of formic acid. Assuming the heterogeneous formation of formic acid also applies to other bare soil types around the globe, a global formic acid source strength of ~ 0.24 Tg yr^{-1} can be estimated using the average emission rate obtained here and a global barren land (i.e., bare soil and land with very sparse vegetation) surface area of ~ 2.8 × 10^{7} km^{2} (Roser and Ritchie, 2018). This source strength due to heterogeneous reactions on bare soils is comparable to that from anthropogenic and biofuel emissions (0.4 Tg yr^{-1} by Millet et al., 2015) but still much less than the missing source strength. Note that the magnitude of the emission rate here used for calculation also depends on the mixing ratio levels of ambient VOC precursors and other environmental parameters such as temperature, relative humidity and photochemistry on soil surfaces. Due to the design of our experimental setup, no sunlight reaches the soil surfaces (see Sect. 2.2). But one can imagine that the existence of sunlight would enhance the catalytic effect of soil minerals (e.g., titanium oxide) and, the soil surface will become hotter and thus make soil dry out faster. These changes may influence the exchange rates of the examined VOCs through the following ways: (1) high catalytic efficiencies may accelerate transformations of deposited VOC precursors and the formation/emission of formic acid; (2) high temperatures of soil may let more adsorbed VOC molecules escape from soil surfaces through evaporation and decrease their uptake; (3) low amounts of water on soil may increase the uptake of some hydrophobic VOC species and decrease the uptake of some hydrophilic VOCs. The combined effect of these three aspects may even tell another different story, which deserves further studies. In a real soil situation, the physicochemical (i.e., abiotic) processes are often combined with biotic processes. The dominance of one over the other is influenced/controlled by changing environmental factors (i.e., temperature, relative humidity and photochemistry) and/or soil types. However, here we assume that physicochemical processes on soil surfaces (more likely on soil solid phase through heterogeneous chemistry) can be a common phenomenon, which is occurring in parallel with biotic processes. Because the solid phase of soil, which includes minerals and organic matter (with minerals’ content much higher than organic matter), are generally stable in nature (https://www.ctahr.hawaii.edu/mauisoil/a_comp.aspx). We think the results obtained in our study can provide a helpful reference regarding the potential contribution of soil particles to formic acid budget from a physicochemical (heterogeneous chemistry) point of view, especially when the soil is dry and the microbial activities are low under some specific situations. Considering the still poorly understood budget of formic acid (Millet, 2012;Paulot et al., 2011), more investigations are needed to quantify the contributions of different types of soil as a potential source of formic acid under different environmental conditions.”

Comments and suggestions:

Page 19, line 29: change "oxidizing" to 'oxidized'.

Responses and Revisions:

Corrected.

Comments and suggestions:

In your conclusions you state that "The emission of formic acid is solely due to physicochemical processes (i.e., heterogeneous transformations of absorbed VOC precursors)" however there could also be a component that is due to reversible uptake of formic acid on the soil surface. Is it not possible that the formic acid is being taken up on the surface of the soil until the pH or water content reaches a particular turning point then it is volatilized to the atmosphere? You can say there is no net uptake of formic but you cannot say that none the molecules that are coming off the surface were previously in the gas phase. You are looking at the net process.

Responses and Revisions:

We thank the reviewer for pointing this out.

The reviewer is right. The observed emission of formic acid can be due to its previous uptake and then re-emitted to the atmosphere as the soil pH or water content reaches a particular turning point. Yes, here in the conclusion we are talking about the net process.

We have modified the statement in the conclusion part:

"…The net emission of formic acid is solely due to physicochemical processes (i.e., heterogeneous transformations of absorbed VOC precursors) on soil, which represents an additional ground-based source of this organic acid."

Comments and suggestions:

Page 20, line 12: change "for" to 'to'. Also, I am not sure as to what the sentence is referring. There was no mention of interferences in the manuscript. Are the synergetic effects the formation of formic from VOC precursors?

Responses and Revisions:

Thanks for the reviewer's comments.

The “for” has been changed into “to” in the manuscript. Here we say “the existence of yet unknown interferences or synergetic effects” aiming to highlight the difference between ambient field measurements and laboratory experiments. Under ambient conditions, the air is a mixture including various trace gases (e.g., VOCs, oxidants, radicals) and aerosols, and all the environmental parameters change simutaneously. When we look at the exchange behavior of one VOC species at the atmosphere-soil interface, the other species (one or several) existed in the ambient air may interfere or have a synergetic effect on the observed exchange properties, making it different from those obtained from laboratory studies.

References

Aaltonen, H., Aalto, J., Kolari, P., Pihlatie, M., Pumpanen, J., Kulmala, M., Nikinmaa, E., Vesala, T., and Bäck, J.: Continuous VOC flux measurements on boreal forest floor, Plant and Soil, 369, 241-256, 10.1007/s11104-012-1553-4, 2013.

Adewuyi, Y. G., Cho, S.-Y., Tsay, R.-P., and Carmichael, G. R.: Importance of formaldehyde in cloud chemistry, Atmospheric Environment (1967), 18, 2413-2420, https://doi.org/10.1016/0004-6981(84)90011-8, 1984.

Ammann, M., and Pöschl, U.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions – Part 2: Exemplary practical applications and numerical simulations, Atmos. Chem. Phys., 7, 6025-6045, 10.5194/acp-7-6025-2007, 2007.

Ao, C. H., Lee, S. C., Zou, S. C., and Mak, C. L.: Inhibition effect of SO2 on NOx and VOCs during the photodegradation of synchronous indoor air pollutants at parts per billion (ppb) level by TiO2, Applied Catalysis B: Environmental, 49, 187-193, https://doi.org/10.1016/j.apcatb.2003.12.011, 2004.

Asensio, D., Penuelas, J., Filella, I., and Llusia, J.: On-line screening of soil VOCs exchange responses to moisture, temperature and root presence, Plant and Soil, 291, 249-261, 2007.

Asensio, D., Penuelas, J., Prieto, P., Estiarte, M., Filella, I., and Llusia, J.: Interannual and seasonal changes in the soil exchange rates of monoterpenes and other VOCs in a Mediterranean shrubland, European Journal of Soil Science, 59, 878-891, 2008.

Chameides, W. L.: The photochemistry of a remote marine stratiform cloud, Journal of Geophysical Research: Atmospheres, 89, 4739-4755, 10.1029/JD089iD03p04739, 1984.

Chattopadhyay, A., Chatterjee, P., and Chakraborty, T.: Photo-oxidation of Acetone to Formic Acid in Synthetic Air and Its Atmospheric Implication, The Journal of Physical Chemistry A, 119, 8146-8155, 10.1021/acs.jpca.5b04905, 2015.

Chen, F., Ro, D. K., Petri, J., Gershenzon, J., Bohlmann, J., Pichersky, E., and Tholl, D.: Characterization of a root-specific Arabidopsis terpene synthase responsible for the formation of the volatile monoterpene 1,8-cineole, Plant Physiology, 135, 1956-1966, 2004.

Colomb, A., Williams, J., Crowley, J., Gros, V., Hofmann, R., Salisbury, G., Klüpfel, T., Kormann, R., Stickler, A., Forster, C., and Lelieveld, J.: Airborne Measurements of Trace Organic Species in the Upper Troposphere Over Europe: the Impact of Deep Convection, Environmental Chemistry, 3, 244-259, https://doi.org/10.1071/EN06020, 2006.

Gray, C. M., Monson, R. K., and Fierer, N.: Emissions of volatile organic compounds during the decomposition of plant litter, Journal of Geophysical Research-Biogeosciences, 115, 2010.

Gray, C. M., Monson, R. K., and Fierer, N.: Biotic and abiotic controls on biogenic volatile organic compound fluxes from a subalpine forest floor, Journal of Geophysical Research-Biogeosciences, 119, 547-556, 2014.

Hayward, S., Muncey, R. J., James, A. E., Halsall, C. J., and Hewitt, C. N.: Monoterpene emissions from soil in a Sitka spruce forest, Atmospheric Environment, 35, 4081-4087, 2001.

Jost, A., Szakáll, M., Diehl, K., Mitra, S. K., and Borrmann, S.: Chemistry of riming: the retention of organic and inorganic atmospheric trace constituents, Atmos. Chem. Phys., 17, 9717-9732, 10.5194/acp-17-9717-2017, 2017.

Leff, J. W., and Fierer, N.: Volatile organic compound (VOC) emissions from soil and litter samples, Soil Biology and Biochemistry, 40, 1629-1636, https://doi.org/10.1016/j.soilbio.2008.01.018, 2008.

Li, P., K. A. Perreau, E. Covington, C. H. Song, G. R. Carmichael, and Grassian, V. H.: Heterogeneous reactions of volatile organic compounds on oxide particles of the most abundant crustal elements: Surface reactions of acetaldehyde, acetone, and propionaldehyde on SiO2, Al2O3, Fe2O3, TiO2, and CaO, Journal of Geophysical Research: Atmospheres, 106, 5517-5529, doi:10.1029/2000JD900573, 2001.

Lichtin, N. N., Avudaithai, M., Berman, E., and Grayfer, A.: TiO2-photocatalyzed oxidative degradation of binary mixtures of vaporized organic compounds, Solar Energy, 56, 377-385, https://doi.org/10.1016/0038-092X(96)00014-X, 1996.

Lin, C., Owen, S. M., and Penuelas, J.: Volatile organic compounds in the roots and rhizosphere of Pinus spp., Soil Biology & Biochemistry, 39, 951-960, 2007.

Millet, D. B.: Atmospheric chemistry: Natural atmospheric acidity, Nature Geosci, 5, 8-9, 2012.

Mungall, E. L., Abbatt, J. P. D., Wentzell, J. J. B., Wentworth, G. R., Murphy, J. G., Kunkel, D., Gute, E., Tarasick, D. W., Sharma, S., Cox, C. J., Uttal, T., and Liggio, J.: High gas-phase mixing ratios of formic and acetic acid in the High Arctic, Atmos. Chem. Phys., 18, 10237-10254, 10.5194/acp-18-10237-2018, 2018.

Paulot, F., Crounse, J. D., Kjaergaard, H. G., Kroll, J. H., Seinfeld, J. H., and Wennberg, P. O.: Isoprene photooxidation: new insights into the production of acids and organic nitrates, Atmos. Chem. Phys., 9, 1479-1501, 10.5194/acp-9-1479-2009, 2009.

Paulot, F., Wunch, D., Crounse, J. D., Toon, G. C., Millet, D. B., DeCarlo, P. F., Vigouroux, C., Deutscher, N. M., González Abad, G., Notholt, J., Warneke, T., Hannigan, J. W., Warneke, C., de Gouw, J. A., Dunlea, E. J., De Mazière, M., Griffith, D. W. T., Bernath, P., Jimenez, J. L., and Wennberg, P. O.: Importance of secondary sources in the atmospheric budgets of formic and acetic acids, Atmos. Chem. Phys., 11, 1989-2013, 10.5194/acp-11-1989-2011, 2011.

Pöschl, U., Rudich, Y., and Ammann, M.: Kinetic model framework for aerosol and cloud surface chemistry and gas-particle interactions – Part 1: General equations, parameters, and terminology, Atmos. Chem. Phys., 7, 5989-6023, 10.5194/acp-7-5989-2007, 2007.

Ravishankara, A. R.: Heterogeneous and Multiphase Chemistry in the Troposphere, Science, 276, 1058-1065, 10.1126/science.276.5315.1058, 1997.

Rossabi, S., Choudoir, M., Helmig, D., Hueber, J., and Fierer, N.: Volatile Organic Compound Emissions From Soil Following Wetting Events, Journal of Geophysical Research: Biogeosciences, 123, 1988-2001, doi:10.1029/2018JG004514, 2018.

Rossi, M. J.: Heterogeneous reactions on salts, Chem Rev, 103, 4823-4882, 10.1021/cr020507n, 2003.

Schade, G. W., and Goldstein, A. H.: Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation, Journal of Geophysical Research-Atmospheres, 106, 3111-3123, 2001.

Scholler, C. E. G., Gurtler, H., Pedersen, R., Molin, S., and Wilkins, K.: Volatile metabolites from actinomycetes, Journal of Agricultural and Food Chemistry, 50, 2615-2621, 2002.

Singh, H., Chen, Y., Tabazadeh, A., Fukui, Y., Bey, I., Yantosca, R., Jacob, D., Arnold, F., Wohlfrom, K., Atlas, E., Flocke, F., Blake, D., Blake, N., Heikes, B., Snow, J., Talbot, R., Gregory, G., Sachse, G., Vay, S., and Kondo, Y.: Distribution and fate of selected oxygenated organic species in the troposphere and lower stratosphere over the Atlantic, Journal of Geophysical Research: Atmospheres, 105, 3795-3805, 10.1029/1999JD900779, 2000.

Singh, H. B., Kanakidou, M., Crutzen, P. J., and Jacob, D. J.: High concentrations and photochemical fate of oxygenated hydrocarbons in the global troposphere, Nature, 378, 50, 10.1038/378050a0, 1995.

Singh, H. B., Salas, L. J., Chatfield, R. B., Czech, E., Fried, A., Walega, J., Evans, M. J., Field, B. D., Jacob, D. J., Blake, D., Heikes, B., Talbot, R., Sachse, G., Crawford, J. H., Avery, M. A., Sandholm, S., and Fuelberg, H.: Analysis of the atmospheric distribution, sources, and sinks of oxygenated volatile organic chemicals based on measurements over the Pacific during TRACE-P, Journal of Geophysical Research: Atmospheres, 109, n/a-n/a, 10.1029/2003JD003883, 2004.

Tie, X., Guenther, A., and Holland, E.: Biogenic methanol and its impacts on tropospheric oxidants, Geophysical Research Letters, 30, n/a-n/a, 10.1029/2003GL017167, 2003.

Tuazon, E. C., Arey, J., Atkinson, R., and Aschmann, S. M.: Gas-phase reactions of 2-vinylpyridine and styrene with hydroxyl and NO3 radicals and ozone, Environmental Science & Technology, 27, 1832-1841, 10.1021/es00046a011, 1993.

Xing, B., and Pignatello, J. J.: Time-dependent isotherm shape of organic compounds in soil organic matter: Implications for sorption mechanism, Environmental Toxicology and Chemistry, 15, 1282-1288, 10.1002/etc.5620150805, 1996.