

## ***Interactive comment on “Physicochemical uptake and release of volatile organic compounds by soil in coated-wall flow tube experiments with ambient air” by Guo Li et al.***

### **Anonymous Referee #2**

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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. Please find my detailed comments in the following response.

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

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. 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

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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.

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 at a higher rate than simple gas phase heterogeneous reactions. This could be of particular importance to the formic acid source that is implied from your observations.

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.

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.

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

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the paper? 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.

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

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  $H_3O^+$  and  $O_2^+$  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.

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.' 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. 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? Page 8, line 32?: You need to define what CKD stands for here. 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 if they are used in this work and cite them in full. 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 results. I would therefore recommend removing that phrasing scheme. Page 15, line 7: Acetaldehyde is not a hydrophobic molecule, and is in fact soluble in water in all proportions. Page 17, line 3: It is stated that

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“formaldehyde uptake reveal a relatively high correlation with formic acid emission”, however, I am not sure that this 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’. Page 17, line 9: “indicates its faster turnover rates also on soil surfaces” should be reworded. 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 SO<sub>2</sub> observations on page 10, so does formic acid formation seem to be suppressed during periods of high SO<sub>2</sub> 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? 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. 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. Page 19, line 29: change “oxidizing” to ‘oxidized’ 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

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atmosphere? You can say there is no net uptake of formic but you cannot say that none of the molecules that are coming off the surface were previously in the gas phase. You are looking at the net process. 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?

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