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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 #1

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Overall Comments. The manuscript by Li et al. describes a novel field experiment used to study the uptake of ambient VOCs on soil surfaces. The study represents a test of a new system for measuring VOC uptake coefficients on soil under ambient conditions and in ambient air masses with all their complexity. It is comprised of two flow tubes (one is Teflon, the other is coated with sterilized soil) that are exposed to ambient air, the output of which is flowed into a proton-transfer mass spectrometer (PTR-MS). The main advantage of the technique is it allows simultaneous measurements of multiple reactants under ambient conditions. The potentially large data sets can allow calculation of uptake parameters of multiple species as a function of various ambient conditions (e.g., VOC concentration, T, RH, light intensity, etc.). Some of the

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most meaningful results using this method stem from the correlations that can be drawn between chemical fluxes measured in the flow tube. One of the stories to evolve out of such analysis is the anti-correlation between formaldehyde and formic acid fluxes in the soil-coated tube, which led to the conclusion that formaldehyde was oxidized to formic acid on the soil surface. This is important for understanding the missing source of formic acid to the atmosphere that has been highlighted by numerous field studies. The disadvantages include the fact that both the surface and the gaseous reactant mixture are comprised of multiple components. This increases the complexity of the system to levels that may preclude understanding a system in detail. Indeed, some effects could be masked by cooperative effects, one may not be able to disentangle physical and chemical processes. However, I still think the advantages outweigh these problems. If one clearly understands these caveats, and the authors certainly do, then one can use this system to provide an exploratory view of a certain suite of VOCs and can provide a springboard into more targeted experiments done on single components on simplified model surfaces, if interesting and unexplained behavior is observed. I support publication of the manuscript after the following points are addressed. It will be a valuable contribution to our knowledge of VOC uptake and provides the community with a new approach to studying this important topic.

Specific Comments. While the ambient flow tube method is useful as an exploratory tool to study uptake behavior under ambient conditions, it is very difficult to use this method to extract detailed mechanistic information and it is hard to put any weight behind the interpretation of trends observed in Figures 8. All else being equal, the most influential variables determining the uptake coefficients for the VOCs studied here are concentration of the VOC and the relative humidity. As noted by the authors, uptake coefficients increase with decreasing gas phase reactant concentration; uptake coefficients can be high if the gas reacts with bare mineral surface and can decrease or increase (depending on its solubility in water/Henry's law coefficient) as water coverage increases. Temperature, RH, and VOC concentration constantly vary during the ca. month-long measurement campaign. The authors tried to show how uptake coef-

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ficients depend on relative humidity, temperature, and VOC concentration in Figure 8. However, I don't think this is the best way to display the data. For example, the gamma vs. RH data is comprised of data from the entire range of T and VOC concentration data (i.e., one independent variable is plotted although two other confounding variables are also varying). To truly understand how RH affects the gamma value, one needs to produce graphs where RH is the only independent variable (i.e., T and VOC concentration are constant). Can the authors do this? Alternatively, one can create 3-D plots: For example, gamma vs. concentration vs. RH. The surface produced could potentially better display important trends. This could allow the authors to take representative slices along the gamma-concentration or gamma-RH space to show trends where the other variable is held constant. I would be interested to know if there is enough data to do this and what the outcome would be. Without such control on variables, I would be reluctant to interpret the data in Figure 8.

In Section 4.2, the authors state on line 648 that "annual produced formic acid (100-120 Tg/y)" and mention that there is a significant missing source. The missing source is stated as being two or three times larger than can be explained based on current understanding of primary and secondary atmospheric processes and aqueous-phase cloud/rain chemistry. Besides saying that it is two or three times than expected, I am missing explicit mention of what that estimate is? Do Millet or Paulot etc. provide an explicit number in Tg/y or nmol/m2/s for that missing source? If so, please include so the reader can compare your later estimates (e.g., line 663).

I also had several questions about the experimental system. First, the authors mention that the sampling box sheltering the flow tube system is covered with a "thin non-transparent PTFE film that functioned as both a reflector for sunlight and a shelter form rainwater." How thin is the film? The word film suggests this is very thin and thin PTFE is often used as a diffuser to transmit light evenly to optical sensors/detector chips, for example. I wonder if any light is allowed to enter the sampling box? If so, what is the light intensity that the flow tubes are exposed to? If the flow tubes are exposed to diurnal light fluctuations, then there could be the added complexity of heterogeneous photochemistry occurring.

My next questions are related to potential contributions from microbial activity or background. The authors write in Section 2.1 that they sterilized soil using the autoclave technique to eliminate "primary microbial impact on VOC exchange." This technique exposes the sample to high temperature (often with steam) and pressure to destroy microorganisms; often this must be repeated several times. Despite these efforts, it has been shown that the method does not guarantee that all microbes are eliminated since recalcitrant temperature-resistant spores or dormant states protected in the soil matrix may remain viable through this process. Did the authors do anything to verify that the samples were free of microbial activity after the system was autoclaved (e.g., RNA analysis or enzyme assays) or after a full month of experiments had been performed? Related to this, how long was a coated batch of soil in place on the flow tube wall? I may have missed this, but was a single sample present for the entire 1-month field campaign, or was it changed frequently. If so, please indicate how frequently the soil sample was changed. If it was changed, were samples comparable? i.e., was the thickness and coverage the same, etc. Did the uptake coefficients measured for a given compound increase or decrease as the campaign proceeded, indicating possible contribution of surface saturation effects or changes in microbial activity of the soil?

I am not as familiar with the nuances of PTR-MS ion chemistry. The authors used m/z 47 to monitor and quantify formic acid, methanol, and dimethyl ether. Formic acid forms a major part of the story here, so it is important to understand and correct for interferences if they exist. Was the MS of sufficient resolution to discern between these isomers. The authors say the ambient concentrations are supposed to be low at this site, but don't mention if they measured them (e.g., with GC/MS method) during this particular field campaign. With all these interferences, how can the authors be sure that the signal at m/z 47 is entirely due to formic acid? Also, do the authors expect any interferences from nitrous acid at this mass? Over a month of measurement, nitrous

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acid will deposit on all surfaces and eventually outgas in quantities that may pose a serious problem if PTR-MS is sensitive to it. I would be interested in knowing the answer to this as it may impact interpretation of the formic acid data.

I also have a question about the measurement uncertainty present in the raw data depicted in Figure 4a and 5a. In Figure 5a, for example, two data traces are overlaid for each compound measured – one for the coated wall tube and one for the blank Teflon tube (the reference). The difference is used to determine the uptake coefficient. Are the traces in the coated tube and reference tube significantly different (statistically)? Ideally, we would see the confidence intervals on each data point on these graphs so we can tell if the difference between the coated wall and reference tubes is indeed significant? In Figure 5a, is there a way to: (1) make the traces more visible (the dotted line is barely visible), and (2) is there a way to show confidence bands for each data set (coated wall and reference tube) on the same plot. Perhaps this figure could be expanded to take up two pages in the Supplement to show more detail?

Lastly, for Figure 3, I feel that the terms Ra and Rb should be specifically defined (as the aerodynamic and quasilaminar resistance) in the figure caption.

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