Response to Anonymous Referee #1

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:

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 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.

Responses and Revisions:

Thanks for the positive comments and feedback from the reviewer.

Comments and suggestions:

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 coefficient 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.

Responses and Revisions:

Good suggestion.

We have made a new plot as a replacement of the original Fig. 8 in the manuscript. In the new plot, 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%. As the reviewer suggested, we also tried to create 3-D plots for the different VOCs. Unfortunately, the data set is not large enough to allow us to do this.

The revised part is as follows:

“3.5 VOC exchange dependence on environmental parameters

In order to explore potential effects of environmental factors on the exchange of these VOC species at the atmosphere-soil interface, the relation between uptake coefficients and ambient relative humidity (RH), temperature (T) and mixing ratio (C) is further examined, and those VOC species showing relatively significant dependencies are shown in Fig 8. To interpret the uptake coefficient dependence on a single parameter, the others should remain constant. Under ambient conditions, however, all the environmental parameters change simutaneously and some of them are even closely related (e.g., between RH and T, see Fig. 5). Therefore in Fig. 8 we present the RH/T dependence as the C varies within a narrow range (i.e., this range can be considered constant when compared with the whole variation scope of C during the entire measurement time period). The C range for the species in Fig. 8 is: 0.5-0.6 for isoprene, 0.8-1.0 for MVK+MACR, 2.0-6.0 for formic acid, 8.0-12.0 for formaldehyde and 1.5-2.5 for acetaldehyde. These ranges are determined following the criterion of A ± B, where A means the one-month-average of the ambient mixing ratios of each species and B is determined by using two criteria: (1) it should be as small as possible; (2) the selected range can provide a data set large enough for plotting the RH/T dependence box chart. Regarding the C dependence in Fig. 8, only the data is adopted when RH equals to 50%.

RH affects the amount of surface-adsorbed water and can accelerate or slow down trace gas uptake rates (Crowley et al., 2010). High-RH induced condensed water may attract water-soluble or hydrophilic gas species and hence enhance their uptake (Pei and Zhang, 2011), or decrease their net emission. This mechanism applies, e.g., to hydrophilic formaldehyde and formic acid (see Table S.3 for respective Henry’s law constants). On the other hand, more water molecules on soil surfaces tend to repel the hydrophobic species more strongly or reduce gas uptake by means of competitive adsorption effects between water molecules and gas species (Ruiz et al., 1998;Goss et al., 2004;Donaldson et al., 2014a;Li et al., 2016). 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.

Even though the calculation of uptake coefficients intrinsically accounts for the gas phase mixing ratios, higher mixing ratios have been shown to reduce uptake coefficients (Sassine et al., 2010;Wang et al., 2012). A negative effect of increased mixing ratios on uptake coefficients is also observed for isoprene and acetaldehyde in Fig. 8. The negative effect of mixing ratios on uptake coefficients can be understood as competition among the individual VOC molecules for reactive uptake sites, or with other VOCs whose mixing ratios show a simultaneous increase (Li et al., 2016). Our previous laboratory experiments on formaldehyde (Li et al., 2016) showed that this trend was more pronounced under dry conditions (RH = 0%) than under humid conditions (RH = 40%), in agreement with the formaldehyde pattern shown here."

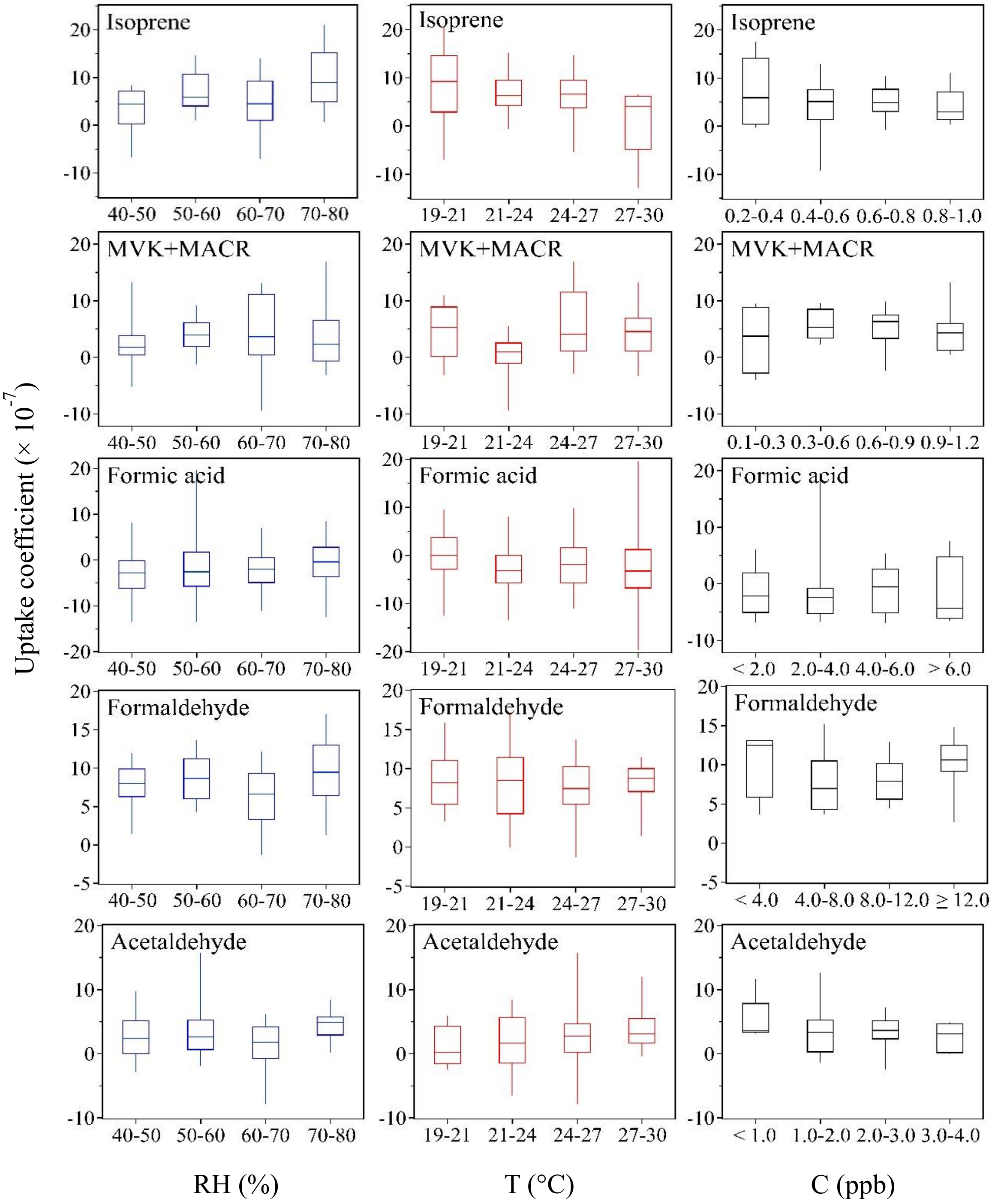


Figure 8. Dependence of uptake coefficients on ambient relative humidity (RH), temperature (T) and mixing ratios (C). Minimum, 25th, 50th, 75th percentile and maximum of the box-and-whisker plots are indicated by bars. The uptake coefficient dependence is based on the hourly averaged data, and the RH 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:

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).

Responses and Revisions:

Good suggestion.

An explicit mention of the estimation of the missing source of formic acid would be very helpful for the readers. Unfortunately, the studies of Millet et al. and Paulot et al. didn't provide such an explicit number for this missing source. According to the statement on line 648, we can have a general range of this missing source around 40 – 90 Tg yr^{-1}.

We made a correction in this part, shown as follows:

"4.2 Physicochemical reactions on bare soil and soil-derived dust may act as a potential source of formic acid

… Modelled budget analyses implicate the existence of one or more large missing sources for formic acid, i.e., the annually produced formic acid (100 - 120 Tg yr^{-1}) is two to three times that can be explained based on the current understanding of primary and secondary (gas phase) atmospheric processes and aqueous-phase cloud/rain chemistry, …"

Comments and suggestions:

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 nontransparent 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 ransmit 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.

Responses and Revisions:

Thanks for the reviewer's comments.

The PTFE film has a thickness of ~ 0.5 mm, which is much thicker than the normally used transparent PTFE film. The film we had for our flow tube system is a PTFE film coated with an aluminum foil (nontransparent), so it can reflect the sunlight very effectively. This kind of film is commercially available and especially used for blocking the sunlight and insulating the heat going into the sampling box. For our case, we can say there was no light in the sampling box or the light intensity was extremely low during daytime. Therefore, our flow tube system didn't suffer from diurnal light fluctuations.

To let the readers understand our flow tube system more easily, we have modified the statement as follows:

"**2.2 Measurement site, experimental setup and operation**

…Two openings on the sampling box allowed for direct access of ambient air into the flow tube system. The sampling box was covered with a non-transparent PTFE film (coated with an aluminium foil and with a total thickness of ~ 0.5 mm) that functioned as both a reflector for sunlight and a shelter from rainwater. The flow tube system consisted of a sample channel and a reference channel."

Comments and suggestions:

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?*

Responses and Revisions:

Thanks for the reviewer's comments.

The autoclaving method shows the strongest effect on eliminating biotic activities compared with other sterilization methods, as proved by previous studies (Razavi darbar and Lakzian, 2007). Razavi darbar and Lakzian found that the colony forming unit (CFU, a unit used to estimate the number of viable bacteria or fungal cells in a sample) of the soil sample after autoclaving was less than 0.5% of that of the unsterilized soil sample, suggesting very small fraction of living or dormant microbes was left after the sterilization treatment. During the one-month field campaign, a PTFE membrane filter was installed upstream of the flow tube system and this operation could prevent the bacteria in the ambient air from inhabiting on the soil sample during the field measurement. Unfortunately, we didn't do further RNA analysis or enzyme assays to check the microbial activities before and after the campaign. But we assumed that in our case the microbial effects were unsignificant compared with the physicochemical processes. For the whole measurement time period, we only used one single sterilized soil sample to simulate/reflect the long time interaction between soil and the atmosphere in the real world. As mentioned in the manuscript, prior to the VOC exchange experiment under ambient conditions the freshly coated tube was flushed with N_2 to scrub potential VOC impurities from the soil and this procedure could provide adsorption-sites devoid of reversibly absorbed VOCs on the soil surface as well as within the soil pores, and therefore allow focus on uptake kinetics from the initial phase (VOCs-free soil) of the exchange experiment. Therefore, along with the field measurement the soil sample would gradually get saturated and this could definitely contribute to the observed decrease of the uptake coefficients. More details regarding soil saturation can be found in Sect. 3.3 in the manuscript.

Comments and suggestions:

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 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.*

Responses and Revisions:

Thanks for the reviewer's comments.

Here we first give a brief introduction of the working principle of a PTR-MS. After having a general idea of the working principle, our responses to the reviewer's comments can be more easily understood.

Within a PTR-MS instrument, one part called ion source can generate hydronium ions (H_3O^+) with high purity. These hydronium ions then go to a drift tube to have proton transfer reactions. In the drift tube, the species (R) with a higher proton affinity than H_2O can have proton transfer reactions with H_3O^+ :

$R + H_3O^+ \rightarrow RH^+ + H_2O$

The product ions RH^+ will then go through ion interfaces and finally be detected by a mass analyzer in the PTR-MS (Bin et al., 2017). Therefore, only the protonated molecules (i.e., ions) can be detected by a PTR-MS. PTR-MS only obtains the mass-to-charge ratios (*m/z*) of the ions and does not provide a priori information on the compounds contributing to a particular *m/z* (Bin et al., 2017).

The *m/z* of 47 can be attributable to several species including formic acid, ethanol and dimethyl ether. The potential interference of nitrious acid to measurement of formic acid by the PTR-MS technique cannot be possible, because the *m/z* of protonated nitrious acid ($H_2NO_2^+$) would be 48.

During the field measurement, unfortunately, we didn't measure the ambient concentrations of ethanol and dimethyl ether. However, the atmospheric abundance of ethanol and dimethyl ether in similar urban site has previously been found to be low (Good et al., 1998;Monod et al., 2003;Jia et al., 2012), giving rise to a measurement uncertainty within ± 30%.

Comments and suggestions:

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?

Responses and Revisions:

Thanks for the reviewer's comments.

The measurement uncertainties of the presented VOCs (as shown in Figure 5a) can be found in the manuscript (Sect.2.2):

"…Uncertainties of measured species except for formaldehyde, formic acid and acetic acid were about 5% - 15%."

The measurement uncertainties of the presented inorganic air pollutants (as shown in Figure 4a) have been added in Sect. 2.2:

"…In addition to measurements of VOC species by the PTR-MS, several common air pollutants were also monitored by Thermo Scientific analyzers: O_3 (Model 49*i*, UV photometric O_3 analyzer), CO (Model 48*i*, trace-level-enhanced gas filter correlation CO analyzer), NO_x (Model 42*i*, trace level chemiluminescence NO-NO_2-NO_x analyzer) and SO_2 (Model 43*i*, trace-level-enhanced pulsed fluorescence SO_2 analyzer). These analyzers were calibrated every three days and uncertainties of these measured air pollutants were less than 5%."

In Figure 5a, the dotted lines have been changed into black solid lines to make them more visible. The modified Figure 5 is as follows:

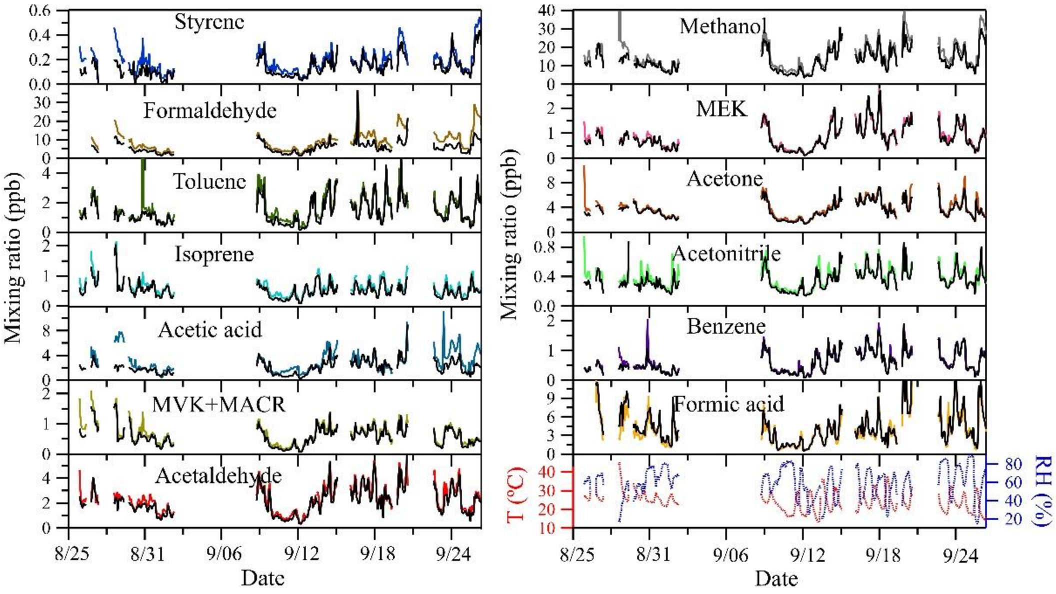


Figure 5. (A)

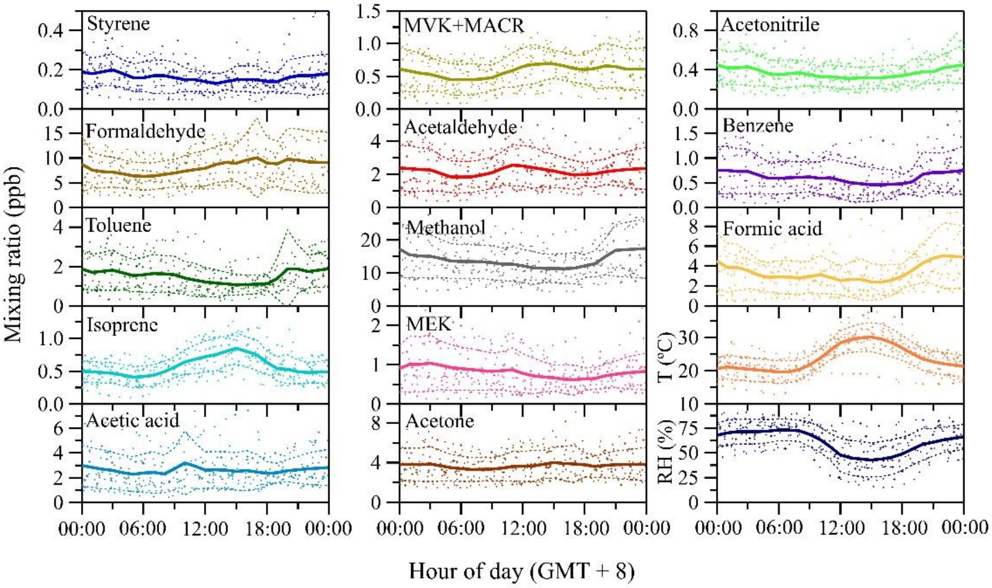
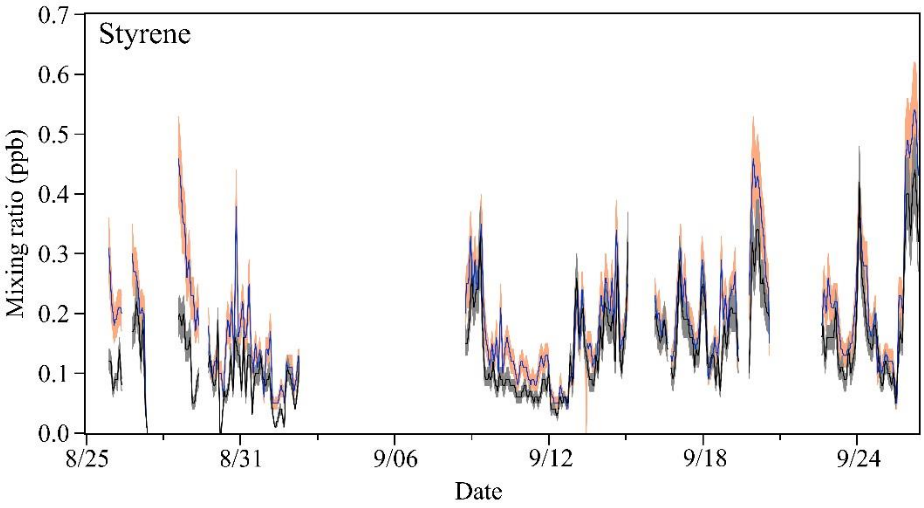
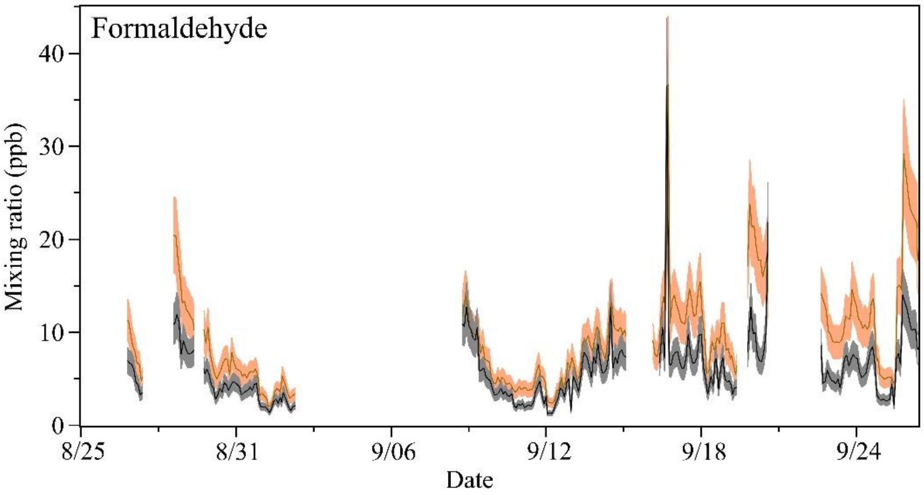


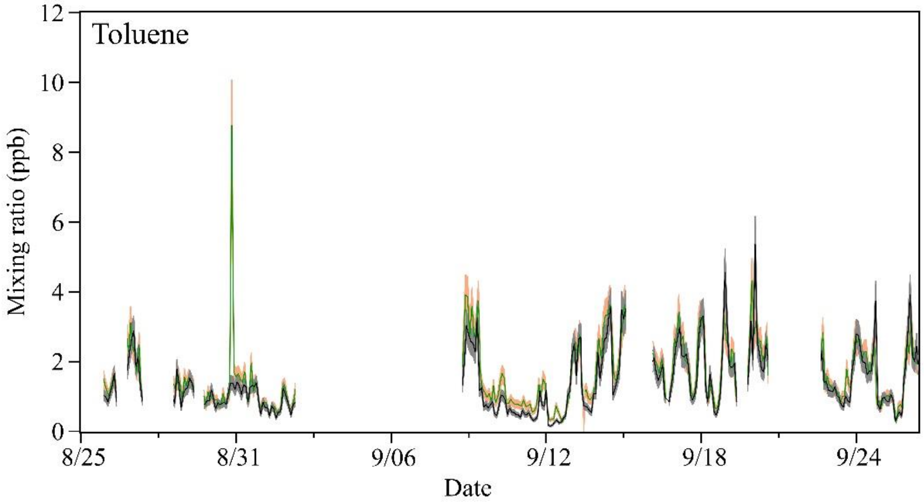
Figure 5. (B)

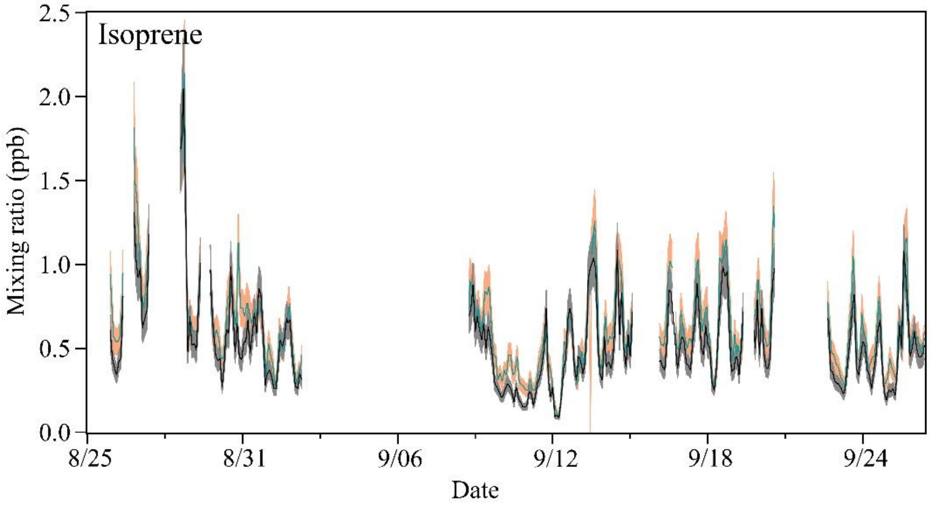
Figure 5. Time series of observed ambient air mixing ratios of VOCs and air temperature and relative humidity (A), and respective mean diel courses (B). Colorful lines in (A) denote ambient air mixing ratios at the outlet of the reference tube C_r, and black lines at the outlet of the sample tube C_s. In (B), symbols denote individual hourly averaged data, and the thick solid lines respective mean diel profile. Thin dashed lines represent one standard deviation (± 1 SD) from the mean value.

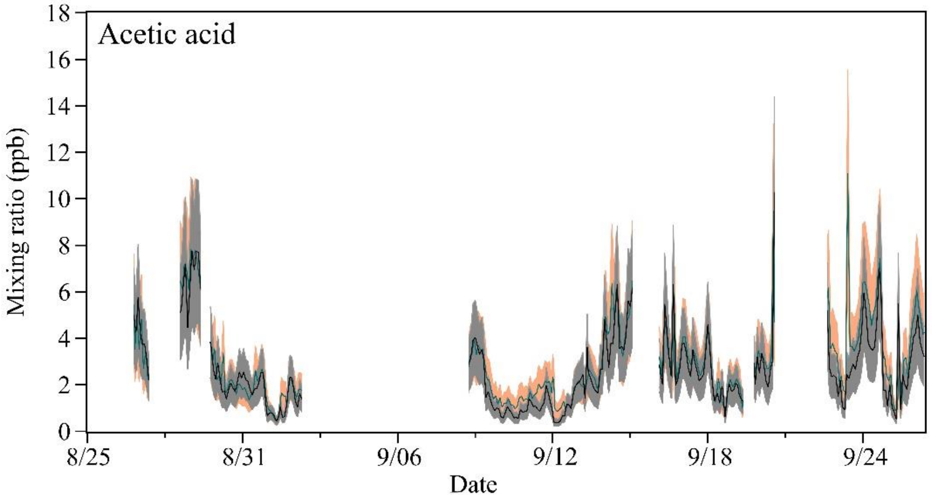
In order to clearly see the confidence bands for each data set, we have shown the confidence bands of each VOC species in Fig. S.2 in the supplement:

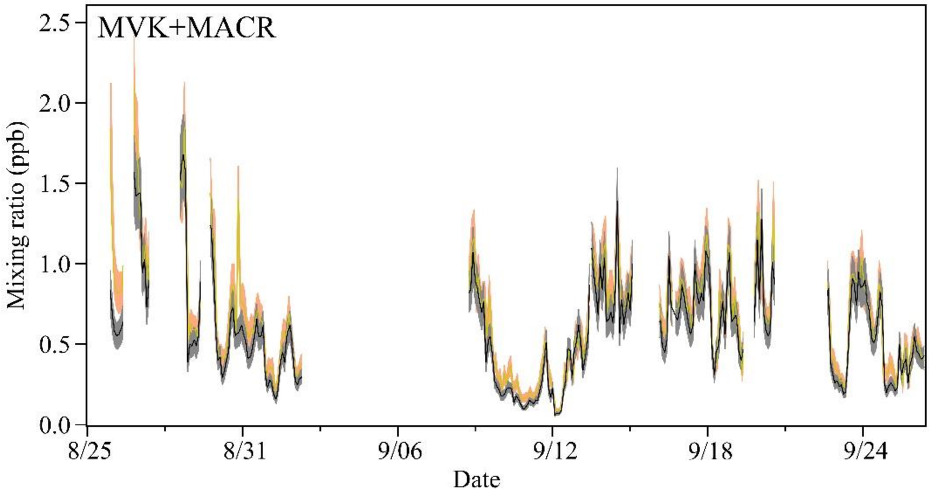

Styrene
Mixing ratio (ppb)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
8/25
8/31
9/06
9/12
9/18
9/24
Date

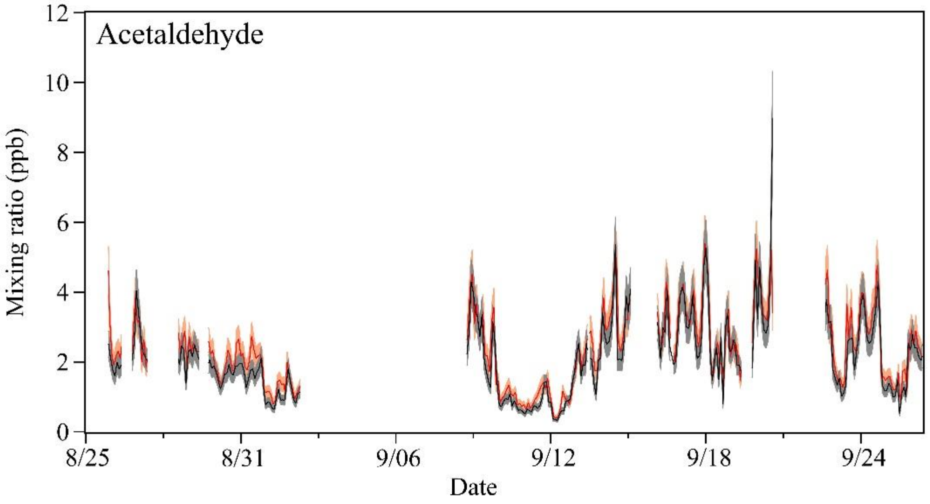

Formaldehyde
Mixing ratio (ppb)
0
10
20
30
40
8/25
8/31
9/06
9/12
9/18
9/24
Date

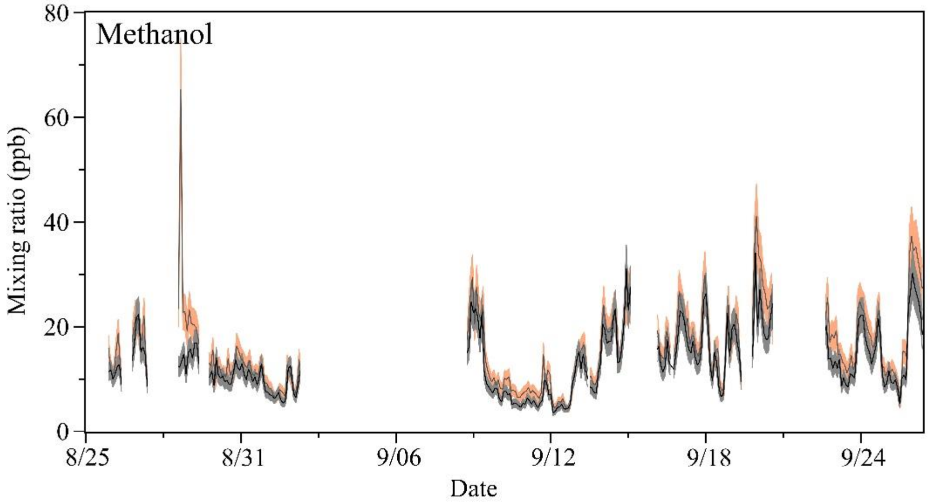

Toluene
Mixing ratio (ppb)
0
2
4
6
8
10
12
8/25
8/31
9/06
9/12
9/18
9/24
Date

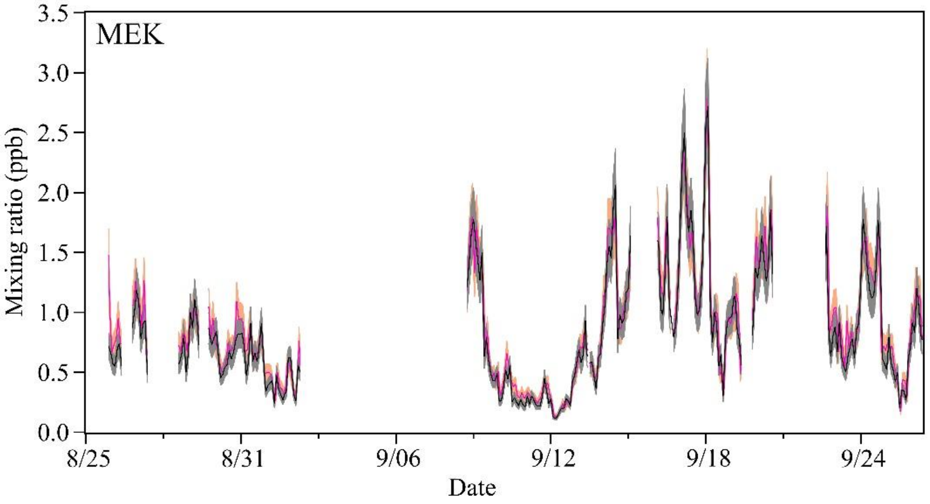

Isoprene
Mixing ratio (ppb)
2.5
2.0
1.5
1.0
0.5
0.0
8/25
8/31
9/06
9/12
9/18
9/24
Date

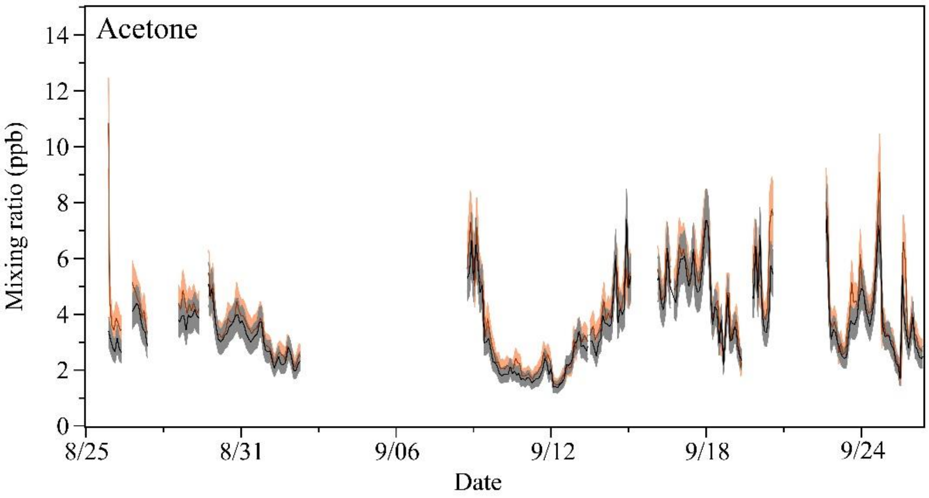

Acetic acid
Mixing ratio (ppb)
18
16
14
12
10
8
6
4
2
0
8/25
8/31
9/06
9/12
9/18
9/24
Date

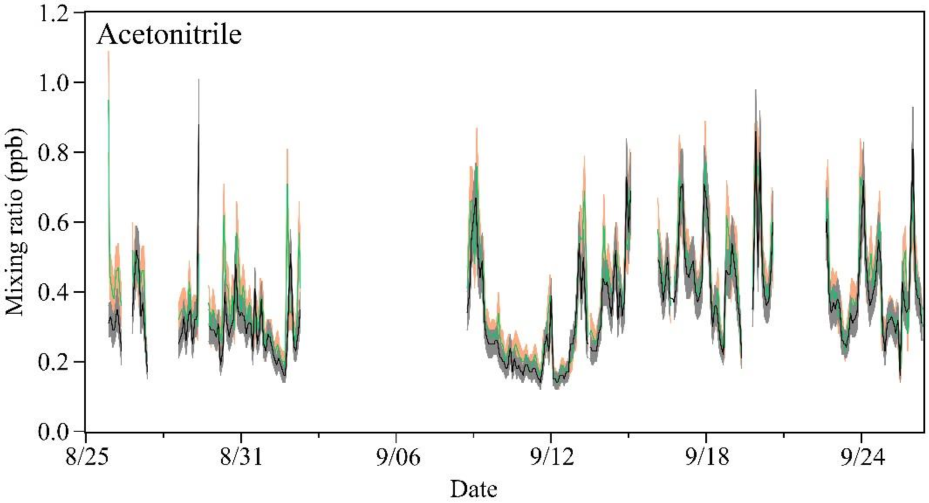

MVK+MACR
Mixing ratio (ppb)
2.5
2.0
1.5
1.0
0.5
0.0
8/25
8/31
9/06
9/12
9/18
9/24
Date

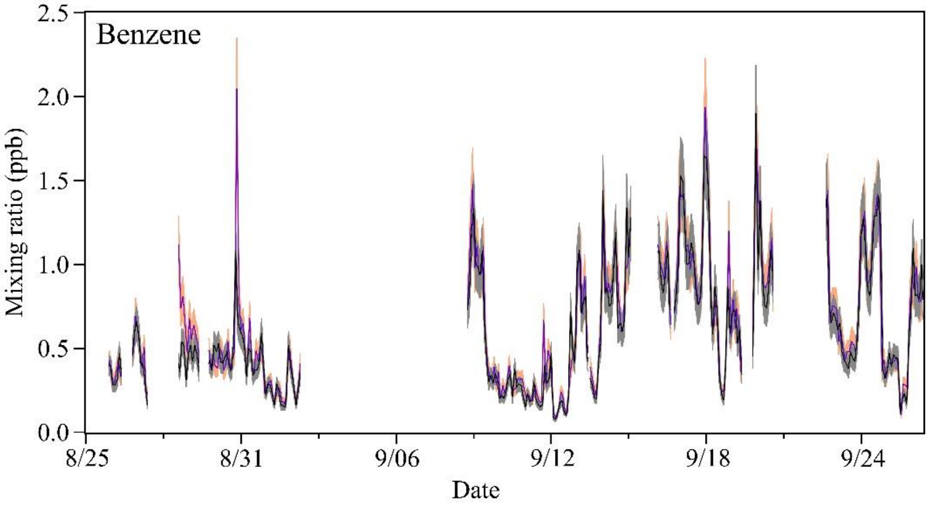

Acetaldehyde
Mixing ratio (ppb)
0
2
4
6
8
10
12
8/25
8/31
9/06
9/12
9/18
9/24
Date


Methanol
Mixing ratio (ppb)
0
20
40
60
80
8/25
8/31
9/06
9/12
9/18
9/24
Date


MEK
Mixing ratio (ppb)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
8/25
8/31
9/06
9/12
9/18
9/24
Date


Acetone
Mixing ratio (ppb)
0
2
4
6
8
10
12
14
8/25
8/31
9/06
9/12
9/18
9/24
Date


Acetonitrile
Mixing ratio (ppb)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
8/25
8/31
9/06
9/12
9/18
9/24
Date


Benzene
Mixing ratio (ppb)
0.0
0.5
1.0
1.5
2.0
2.5
8/25
8/31
9/06
9/12
9/18
9/24
Date

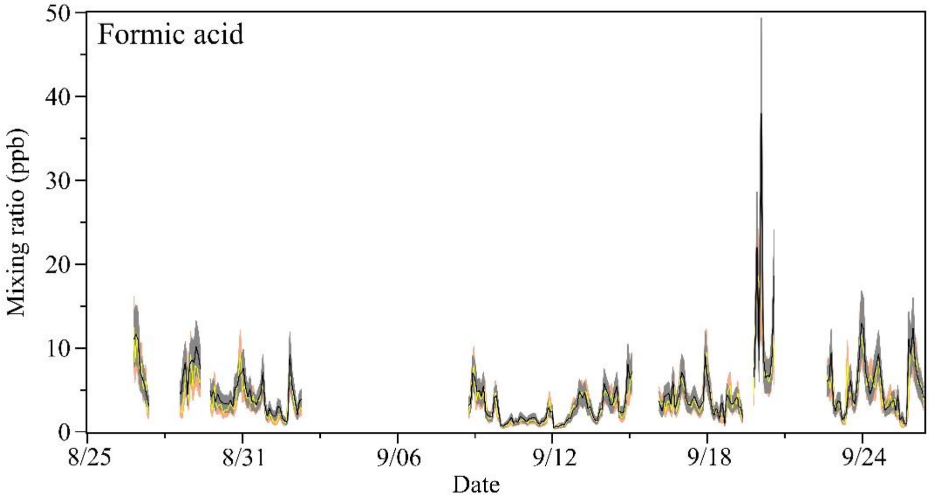


Figure S.2. Time series of ambient air mixing ratios of the examined VOCs. The lines mean the best estimation by the PTR-MS: colorful lines denote C_r and black lines denote C_s. The confidence bands (best estimate ± measurement uncertainties) are shown as the orange shaded areas (for C_r) and gray shaded areas (for C_s).

Comments and suggestions:

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.

Responses and Revisions:

Thanks for the reviewer’s comments.

We have defined the terms *Ra*, *Rb* and *Rc* in the caption of Figure 3.

The modified figure caption is as follows:

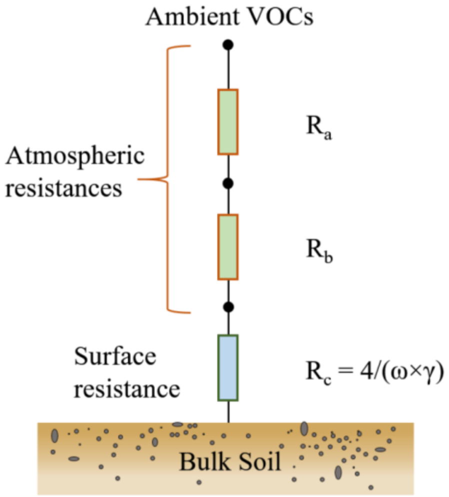


Figure 3. Schematic of the resistance model for VOC species dry deposition on soil. R_a: aerodynamic resistance; R_b: quasi-laminar layer resistance; R_c: soil surface resistance.

References

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