Response to Anonymous Referee #1

We thank the reviewer for the constructive suggestions/comments. Below we provide a point-by-point response to individual comments (reviewer comments and suggestions are in italics, responses and revisions are in plain font; revised sections in the manuscript text in response to the comments are marked with red color; page numbers refer to the ACPD version; figures and tables used in the responses are labeled as Fig. R1, Table R1, …).

Comments and suggestions:

In order to improve the clarity of the article, a more comprehensive description of the statistical methods used for data analysis would be helpful, especially how many replicates were used to determine the error bars.

Responses and Revisions:

Good suggestion. We have revised the captions of Figure 5 and Figure 6 (as Fig. R5 and Fig. R6, respectively), and indicated the number of replicate experiments used for error bars:

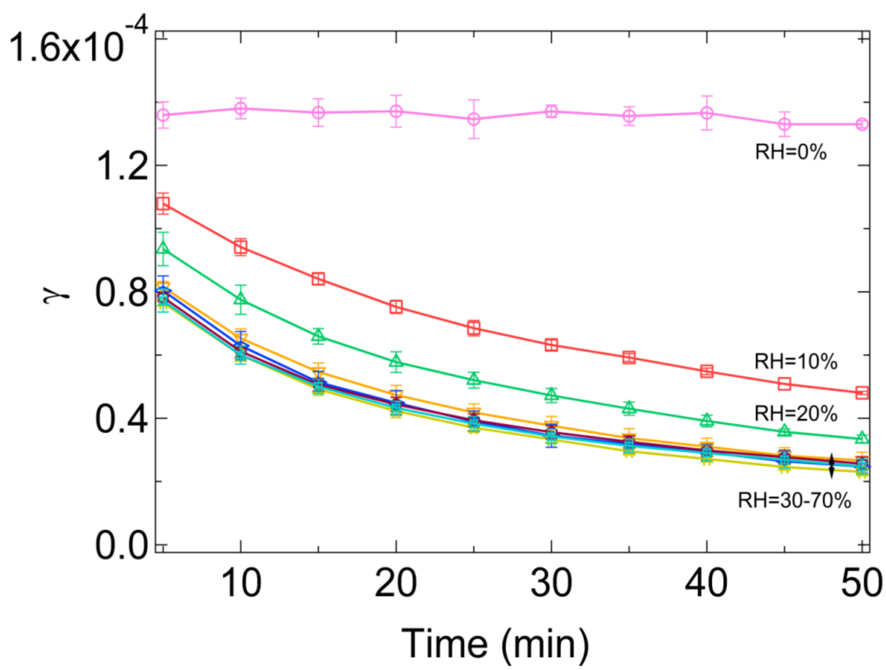

Figure R5. Uptake coefficients variation as a function of uptake time, under different RHs. The error bars represent the standard deviation of three replicate experiments.

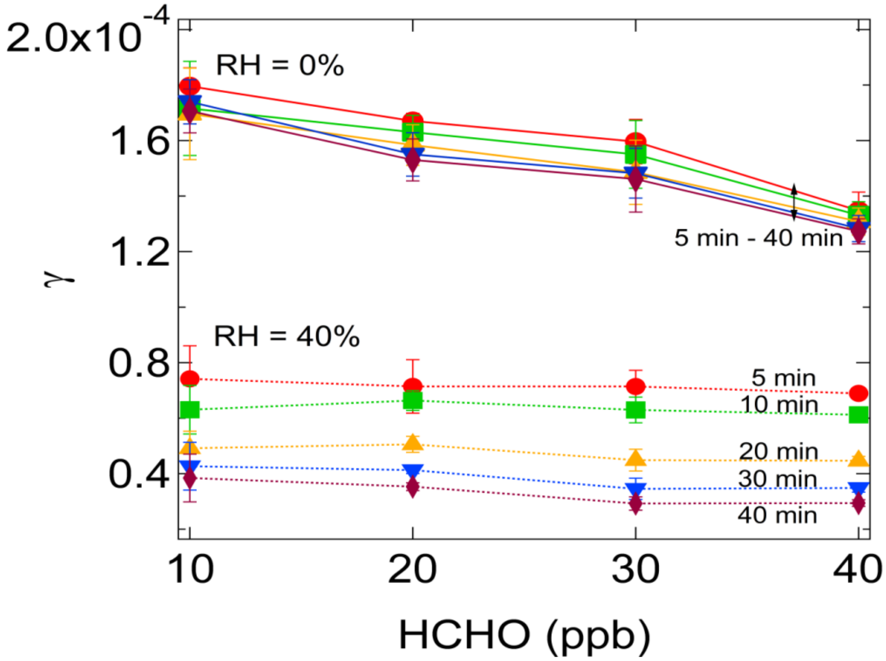

Figure R6 (A).

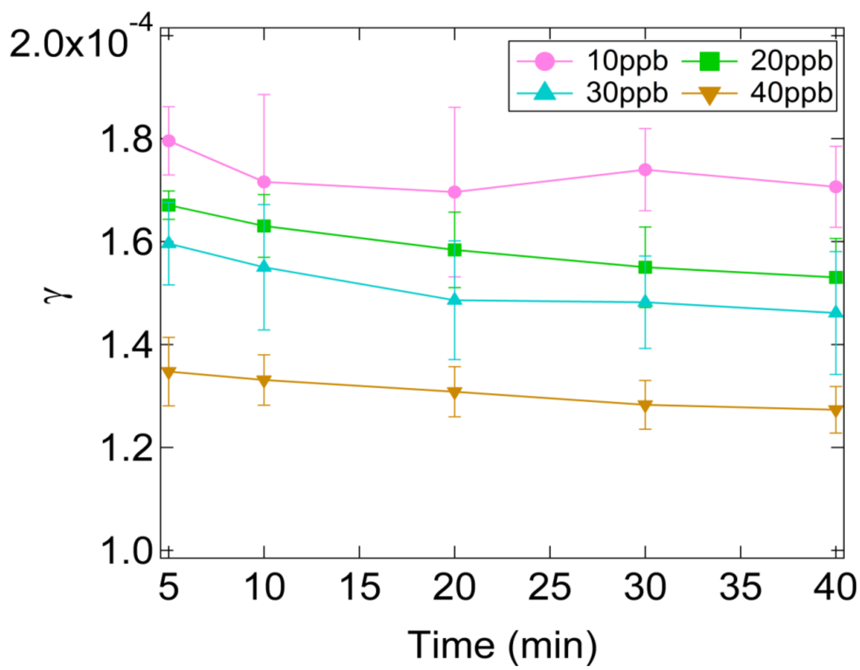

Figure R6 (B).

Figure R6. Dependence of uptake coefficients on initial HCHO concentrations at 0% and 40% RH, after uptake time periods of 5 min (red), 10 min (green), 20 min (orange), 30 min (blue) and 40 min (purple) (A); and uptake coefficients as a function of uptake time period at 0% RH (B);

both under ambient pressure and 296 K. The error bars represent the standard deviation of three replicate experiments.

Comments and suggestions:

Also, a table of the uptake coefficients would further extend the utility of the paper as it would allow others to easily use this data for modeling.

Responses and Revisions:

Good suggestion. We have summarized the uptake coefficients in a table in the supplemental information (Table S.1.) to allow others to easily use the data for modeling, which is now referred to on page 6, line 22:

"…In order to facilitate modelling, the calculated uptake coefficients as a function of initial HCHO concentration, relative humidity and uptake time period are summarized in Table S.1."

Initial HCHO con. C_{in} (ppb)	RH (%)	$\gamma^a \times 10^{-5}$	$\gamma^b \times 10^{-5}$	$\gamma^c \times 10^{-5}$	$\gamma^d \times 10^{-5}$	$\gamma^e \times 10^{-5}$	$\gamma^f \times 10^{-5}$
10	0	17.9 ± 0.7	17.2 ± 1.7	17.0 ± 1.6	17.4 ± 0.8	17.1 ± 0.8	16.7 ± 1.3
10	40	7.4 ± 1.2	6.3 ± 0.9	4.9 ± 0.6	4.3 ± 0.8	3.8 ± 0.9	3.5 ± 0.8
20	0	16.7 ± 0.3	16.3 ± 0.6	15.8 ± 0.7	15.5 ± 0.8	15.3 ± 0.8	15.4 ± 0.4
20	40	7.2 ± 1.0	6.6 ± 0.4	5.1 ± 0.3	4.1 ± 0.1	3.5 ± 0.1	3.2 ± 0.1
30	0	16.0 ± 0.8	15.5 ± 1.2	14.8 ± 1.2	14.8 ± 0.9	14.6 ± 1.2	14.2 ± 0.9
30	10	11.6 ± 0.3	9.4 ± 0.3	7.5 ± 0.2	6.3 ± 0.2	5.5 ± 0.1	4.8 ± 0.1
30	20	10.4 ± 0.5	7.8 ± 0.5	5.8 ± 0.3	4.7 ± 0.2	3.9 ± 0.2	3.3 ± 0.1
30	30	9.4 ± 0.3	6.5 ± 0.3	4.7 ± 0.3	3.8 ± 0.3	3.1 ± 0.3	2.7 ± 0.2
30	40	7.1 ± 0.6	6.3 ± 0.5	4.5 ± 0.4	3.4 ± 0.4	2.9 ± 0.2	2.5 ± 0.2
30	50	7.6 ± 0.3	6.0 ± 0.2	4.2 ± 0.2	3.3 ± 0.1	2.7 ± 0.1	2.3 ± 0.1
30	60	7.8 ± 0.1	6.1 ± 0.2	4.4 ± 0.2	3.6 ± 0.2	3.0 ± 0.2	2.6 ± 0.2
30	70	7.7 ± 0.4	6.0 ± 0.3	4.3 ± 0.2	3.4 ± 0.2	2.9 ± 0.2	2.5 ± 0.2
40	0	13.5 ± 0.7	13.3 ± 0.5	13.1 ± 0.5	12.8 ± 0.5	12.7 ± 0.4	12.7 ± 0.3
40	40	6.9 ± 0.1	6.1 ± 0.2	4.5 ± 0.2	3.5 ± 0.2	2.9 ± 0.1	2.5 ± 0.1

[a]Uptake coefficients at uptake time period of 5 min. [b]10 min. [c]20min. [d]30min.[e]40min.[f]50min.
The error bars represent one standard deviation of three replicates.

Table R.S.1. Calculated HCHO uptake coefficients as a function of initial HCHO concentration, relative humidity and uptake time period.

Comments and suggestions:

p. 7, line 29: "They both gave explanations based on the Langmuir-Hinshelwood mechanism." A brief description of the Langmuir-Hinshelwood mechanism would be helpful here for the broad readership of ACP.

Responses and Revisions:

Good suggestion. It is necessary to give a description of the Langmuir-Hinshelwood mechanism to help the broad readership understand it more easily. Therefore, we have added a brief description concerning this mechanism on page 8, line 23:

"…They both gave explanations based on the Langmuir-Hinshelwood mechanism, in which gas molecules compete for the adsorption sites and the adsorbed molecules undergo following reactions. At higher HCHO concentrations (20 – 40 ppb) or/and higher water vapour partial pressure (RH = 40%), the soil surface becomes more easily covered by adsorbed HCHO or/and H_2O molecules that had not yet reacted, resulting in lower probability of successful collisions between HCHO and the soil surface and thus a lowering of the uptake coefficient."

Comments and suggestions:

p. 8, line 34: "Among the inorganic oxides, silicon oxide is most abundant followed by oxides of aluminum, calcium and iron, with their contents (wt%) being ~64%, ~13%, ~6.3% and ~5.7%, respectively." I recommend rephrasing to be more cautious with assignments. EDX data is insufficient for determining mineralogical composition. Did the authors have other data to suggest that the Si, Al, Ca and Fe are due to oxides of these elements? Some of these elements can be present as carbonates or other minerals as well.

Responses and Revisions:

The reviewer was right. The elements of Si, Al, Ca and Fe can be present as several different forms (i.e., as oxides, carbonates or other minerals). Unfortunately, we do not have any further information on the determination of mineralogical composition. So we have rephrased this section to be more scientifically rigorous (page 9, line 27):

"…As shown in Fig. S.2, inorganic elements (mainly exist as minerals) dominate the soil composition and the low fraction of carbon is consistent with the measurement of soil organic matter (Sect. 2.1). Among the inorganic elements, silicon is most abundant followed by aluminium, calcium and iron, with their contents (wt%) being ~64%, ~13%, ~6.3% and ~5.7%, respectively. The partial reversibility can be interpreted by the different uptake ability of various components. Carlos-Cuellar et al.(2003) reported that HCHO uptake was completely reversible on SiO_2 but only partly (< 1~15%) reversible on α-Al_2O_3 and α-Fe_2O_3. Xu et al. (2011) investigated the heterogeneous reactions of HCHO on the surface of γ-Al_2O_3 particles and concluded that the adsorbed HCHO was firstly oxidized to dioxymethylene and further to formate. The fraction of silicon of ~70% (silicon content divided by the total amount of all inorganic elements) in the soil investigated here closely resembles the fraction of HCHO desorbed ((70 ± 15)%) from soil at zero air conditions.

Since mineral particles occupy the major volume (approximately 45% - 49%) of soils (DeGomez et al., 2015) and silicon minerals (e.g., silicon oxides) are fairly common in mineral particles, the partial reversibility of HCHO uptake as shown in Fig. 7 may be expected as a general feature for other similar types of soils.

Comments and suggestions:

p. 10, line 15: One monolayer at 30% RH was also reported by Donaldson et al., 2014, so there is general agreement across very different soil types.

Responses and Revisions:

Good suggestion. We have added Donaldson's paper as a reference and found the fact that one monolayer formed around 20-30% RH could apply across very different soil types (page 11, line 12):

"…Based on our BET experiment, one water monolayer forms at ~30% RH (Fig. 8) which is consistent with those values (20%-30%) reported by Donaldson et al. (2014), Lammel (1999) and Goss (1993) retrieved across different soil types."

Comments and suggestions:

Figure 3 would be clearer if it was a plot of uptake coefficient vs. time displaying all three experiments on the same axes.

Responses and Revisions:

Good suggestion. We have re-plotted Figure 3 in a form of uptake coefficient vs. time and displayed all three experiments on the same axes. Also, the uptake time of each experiment has been stated in page 7, line 14:

"As shown in Fig. 3, almost identical uptake coefficients are determined from three experiments (each lasted for 50 minutes) at RH of 50% and HCHO concentration of ~35 ppbv."

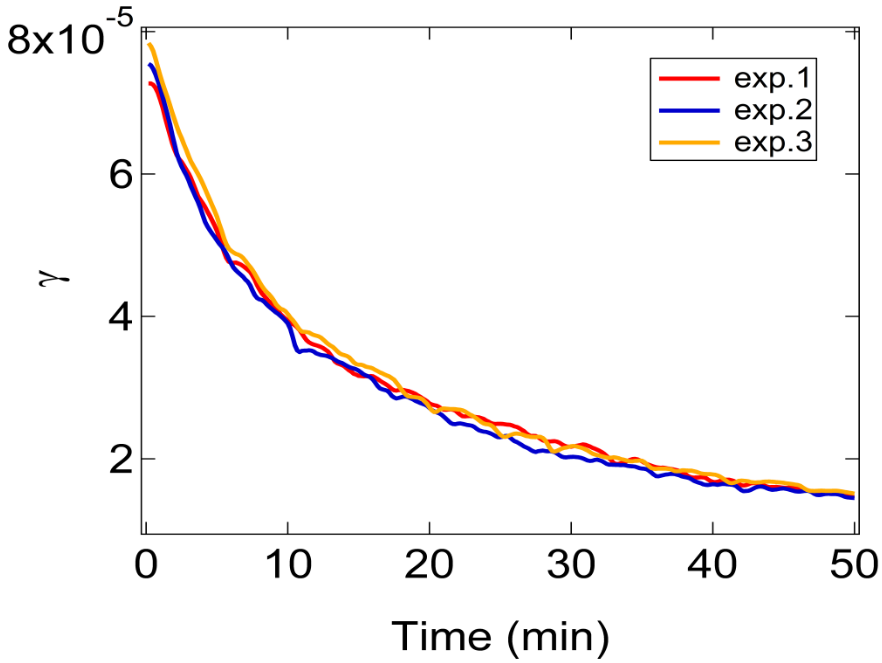

Figure R3. Effect of repeated uptake and emission on soil uptake coefficients within the uptake time range of 50 min at 50% RH.

Comments and suggestions:

Figure 4 might be better displayed as four separate plots instead of two compound plots as the uptake coefficient data is buried in the formaldehyde trace.

Responses and Revisions:

We thank the reviewer's good suggestion. The uptake coefficient data shown in Figure 4 is tended to indicate its variation trend as a function of uptake time (see the results and discussion part). As we have further provided an uptake coefficient table (according to the reviewer's suggestion), the exact uptake coefficient values are now available for readers who are interested in using the data. In this sense, we would like to keep Figure 4 in its original version.

Comments and suggestions:

Figure 6A seems to display too much data. If the authors could make two graphs like part B, one for 0% RH and one for 40% RH, that would be easier to compare.

Responses and Revisions:

We thank the reviewer's good suggestion. Figure 6A is aimed to compare the dependence of uptake coefficient on initial HCHO concentration between dry and humid (RH=40%) conditions. It is more comparable, in our opinion, if both conditions are shown in one plot, as we can also see the effect of water vapor on decreasing the uptake coefficient. For the case of RH=0% in Figure 6A, the symbols are overlapped and the respective information can be retrieved in Figure 6B. So we would tend to keep Figure 6A in its original version.

References:

Carlos-Cuellar, S., Li, P., Christensen, A. P., Krueger, B. J., Burrichter, C., and Grassian, V. H.: Heterogeneous uptake kinetics of volatile organic compounds on oxide surfaces using a Knudsen cell reactor: Adsorption of acetic acid, formaldehyde, and methanol on alpha-Fe2O3, alpha-Al2O3, and SiO2, J Phys Chem A, 107, 4250-4261, 2003.

Basic Soil Components: http://articles.extension.org/pages/54401/basic-soil-components, 2015.

Donaldson, M. A., Berke, A. E., and Raff, J. D.: Uptake of Gas Phase Nitrous Acid onto Boundary Layer Soil Surfaces, Environ Sci Technol, 48, 375-383, 2014.

Goss, K. U.: Effects of Temperature and Relative-Humidity on the Sorption of Organic Vapors on Clay-Minerals, Environ Sci Technol, 27, 2127-2132, 1993.

Lammel, G.: Formation of Nitrous Acid: Parameterisation and Comparison with Observations.286, 1999.

Xu, B. Y., Shang, J., Zhu, T., and Tang, X. Y.: Heterogeneous reaction of formaldehyde on the surface of gamma-Al2O3 particles, Atmos Environ, 45, 3569-3575, 2011.