Interactive comment on "Heterogeneous uptake of amines onto kaolinite in the temperature range of 232-300 K" by Y. Liu et al.

Y. Liu et al.

Referee #2

Using a Knudsen cell reactor and ATR-FTIR, Liu et al. investigated the heterogeneous reactions of methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA) with kaolinite (as a surrogate of mineral dust) and the effect of temperature. Both amines and mineral dust are important components in the troposphere, and their reactions have not been examined yet. This manuscript fits the scope of ACP well and the results are quite new. The kinetic data present by this work would help us better understand the tropospheric sinks of amines and the aging processes of mineral dust particles. This manuscript can be published after the following comments are addressed

Response: Thank you for your positive comments.

Major comments:

Line 133-136: Prior to the uptake measurement, the reaction chamber was passivated with amines to reduce/minimize the wall effect. The sample chamber also has some (though smaller compared to the reaction chamber) wall effect. Is this significant compared to the uptake by kaolinite? I believe this can be determined by background experiments in which no dust is deposited onto the sample holder.

Response: Thank you for your comment. We have performed blank experiments for all of these amines. Figure R1 shows the results (raw data) of the blank experiments for MA and TMA. This experiment was carried out at 232 K. When the steady state of TMA signals was reached (both m/z 59 and 58), the Teflon sampler (without particles) was exposed to TMA vapor by opening the sample lid. No changes in TMA signals were observed. This means the contribution of the fresh surface to the uptake of amines

by kaolinite is negligible.

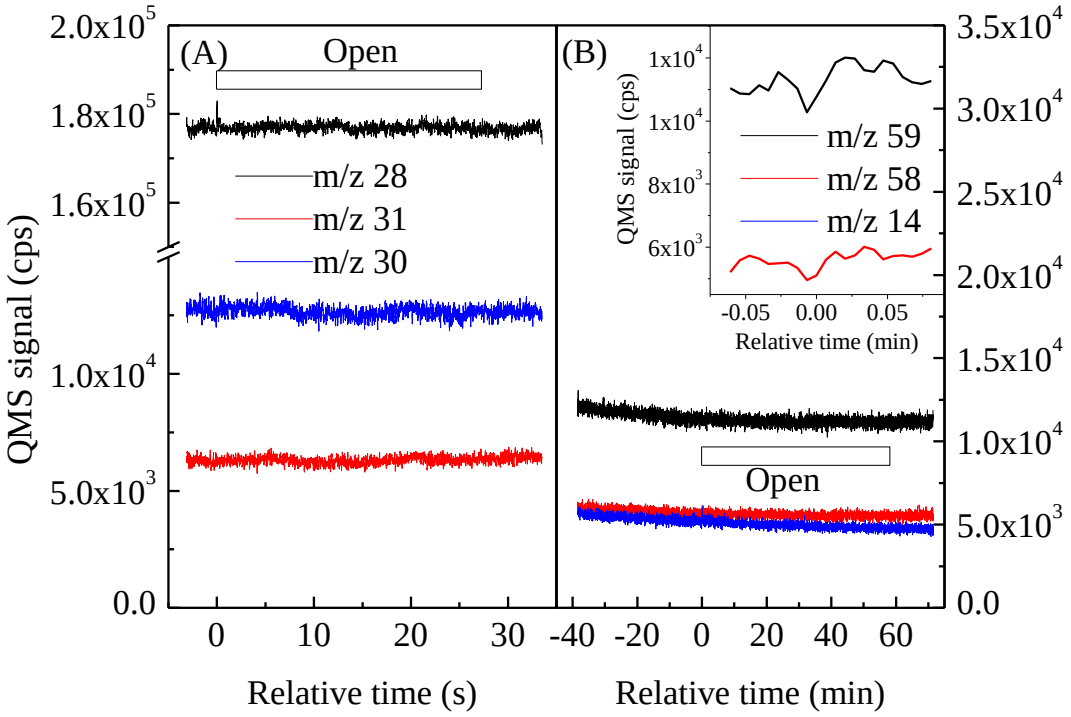

Fig. R1. Blank experiments (raw data) for (A) MA and (B) TMA at 232 K.

Line 429-438: While I agree with the authors that heterogeneous reactions with mineral dust can be an important sink for these amines in the troposphere, I also two comments: 1) the effect of gas phase diffusion needs to be discussed (Tang et al., 2015), especially for large particles (e.g., mineral dust) and fast uptake (which is also the case in this study); 2) only extreme conditions with very high dust loadings are discussed; to understand the general role of these reactions, the authors should also discuss the lifetimes under typical atmospheric conditions. By the way, the dust loading unit used in this manuscript is μm^2 cm^{-3}; while this is convenient to calculate the lifetime using Eq. (16), the corresponding mass concentration (which is more widely used) should also be provided.

Response: Thank you for your suggestion. We agree with you that gas-phase diffusion would be an important issue if the uptake experiments were not performed in a free molecular flow. Thus, a diffusion correction was required using the empirical formula for experiments carried out at ambient pressure (Fuchs and Sutugin, 1970;Worsnop et

al., 2002;Widmann and Davis, 1997). However, the pressure in the reactor was ~3.5×10^{-4} Torr in this study. Thus, the mean free path of gas was 12 cm even at 232 K. This value was greater than the reactor dimensions (5.6 cm), which will be summarized in **Table S1** (Table R1, here). Therefore, a diffusion correction was not necessary in this study when calculating the effective uptake coefficient.

Table R1. The parameters of the Knudsen cell reactor.

Parameter	value
V (cm^3)	93.90
A_w (cm^2)	116.20
Φ(cm)	5.60
H(cm)	3.50
A_s (cm^2)	3.26
A_h (N_2, mm^2)	0.90 ±0.15
k_{esc} (N_2, s^{-1})	1.14 ±0.14
F of amines (molecules s^{-1})	~1.2×10^{13}
MS sensitivity of amines (3σ, molecules s^{-1})	~1.1×10^{12} (MA), ~1.4×10^{12} (DMA), ~1.7×10^{12} (TMA)
Dp of kaolinite (μm)	0.56

Of course, diffusion should be considered in modelling studies to assess the impact of heterogeneous uptake on the sink of amines. Because the diffusion effect depends on the size distribution of particles, it cannot be estimated in Eq. (16) at the present time. Using Eq. (16), we can only roughly estimate the lifetimes of amines via heterogeneous uptake. In the manuscript, the following paragraph will be added to clarify the influence on diffusion of lifetime estimation "It should be pointed out that the diffusion effect of amines from the gas phase to the particle surface at ambient pressure will decrease the apparent loss rate of amines (Tang et al., 2015), and consequently enhance their lifetimes in the atmosphere. This was not considered in Eq. (16). Therefore, modelling studies considering this influence are necessary in the future for fully understanding the impacts of heterogeneous uptake on the sink of amines".

With the average density (1.5 g cm^{-3}) of atmospheric particles (Kannosto et al., 2008), the surface concentration of particles can be converted to the mass concentration;

150 μm^2 cm^{-3} corresponds to 259 $\mu g \cdot cm^{-3}$. This will be added in the manuscript as "If we assume that all mineral dust is in the form of kaolinite, and the dust loading is 150 μm^2 cm^{-3} (de Reus et al., 2000; Frinak et al., 2004), which corresponds to 259 $\mu g \cdot cm^{-3}$ with an average density of atmospheric particles of 1.5 g cm^{-3} (Kannosto et al., 2008), under extreme conditions". The lifetimes of amines by heterogeneous uptake under a typical particle concentration (80 $\mu g \cdot cm^{-3}$) (He et al., 2014) have also been estimated. Their lifetimes were 49.4, 56.6 and 18.6 h, respectively. This will also be added in the manuscript as "Under the typical particle concentration in Beijing (80 $\mu g \cdot cm^{-3}$) (He et al., 2014), their lifetimes were 49.4, 56.6 and 18.6 h, respectively" and "Under the typical particle concentration in Beijing, the contribution of heterogeneous uptake to the sink of amines should also be considered".

Line 467-468: It is stated that physical adsorption takes place between amines and kaolinites, but no direct experimental evidence is provided. As I understand, both Knudsen cell reactor and ATR-FTIR can be used to examine whethere a gas-surface reaction is reversible. I would suggest that another 1-2 figures with experimental data should be included to clarify this issue.

Response: Thank you for your suggestion. Repeat uptake experiments were carried out after the used sample was evacuated overnight at 300 K. The uptake curve in the second run coincided very well with that in the first run (Fig. R2). This means that uptake of amines on kaolinite is reversible. This figure will be added as Fig. S4.

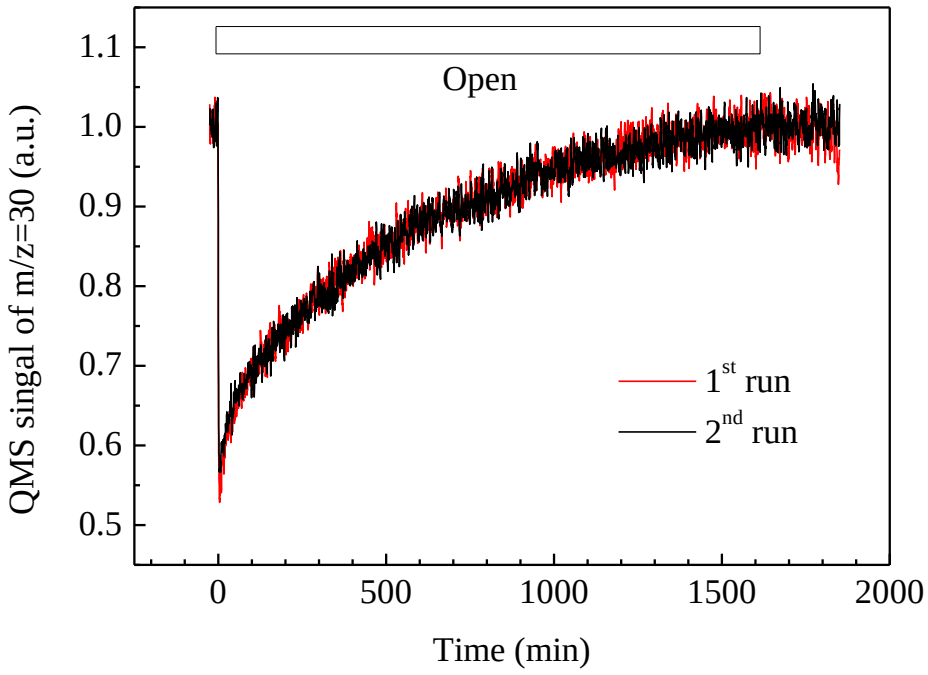

Fig. R2. Repeat uptake curves of MA after the used sample was evacuated overnight at 300 K. The sample mass was 19.8 mg.

Minor comments:

Line 4: I should suggest that "amines" should be changed to "methylamine, dimethylamine, and trimethylamine (TMA)" to be specific.

Response: Thank you. The "amines" in the title will be replaced with "methylamine, dimethylamine, and trimethylamine" in the manuscript.

Line 24-25: This statement is incorrect. The uptake coefficients were directly derived from the experimental data as discussed in Sections 3.1 and 3.2, and mass accommodation coefficients are used to derive enthalpies and entropies (Section 3.3).

Response: Thank you. This sentence will be revised as "The uptake coefficients (γ) were mainly determined by mass accommodation coefficients based on the temperature dependence of the γ" in the manuscript.

Line 49: please also provide the concentrations in pptv.

Response: Thank you. The stated concentration range corresponds to 20−340 pptv.

This will be added as "Amines, whose atmospheric concentrations are typically 1~14 nmol N m^{-3} (or 20−340 pptv)…" in the manuscript.

Line 81: The review paper by Crowley et al. (2010) should also be cited here together with Usher et al. (2003).

Response: These two references will be cited in the manuscript.

Line 312: I believe "γeff" should be "γeff/γobs".

Response: Thank you. It will be corrected in the manuscript.

Line 339-343: It should be further explained why the study by Wang et al. (2010a) explained the difference between Liu et al. (2012a) and Qiu et al. (2011). For the current manuscript, it is not clear to me.

Response: The temperature was 298 K in our previous work, while it was 293 K in Qiu's work. This was partially responsible for the smaller uptake coefficient in our work. We will added this reason in the manuscript as "This might partially explain the difference in the measured γ of MA on $(NH_4)_2SO_4$ between our previous work (Liu et al., 2012) and Qiu's work (Qiu et al., 2011) because the temperature was 5 K lower in their work than ours".

Line 457-463: the effects of heterogeneous reactions on the chemical composition and IN activity of mineral dust particles is mentioned here. I do believe that it should also be mentioned in the introduction. Besides, many papers have discussed the effects of heterogeneous reaction on the hygroscopicity and CCN and IN activities of mineral dust, including those by Cziczo et al. (2009), Sullivan et al. (2009), Ma et al. (2012), Tobo et al. (2012) and Tang et al. (2016), just to name a few.

Response: Thank you for your suggestion. A paragraph will be added in the manuscript as "In addition, mineral dust including kaolinite has been well recognized as effective ice nuclei (IN) (Wex et al., 2014;Salam et al., 2006). Surface coatings from heterogeneous reaction may modify the hygroscopicity (Ma et al., 2012), the cloud

condensation nuclei (CCN) activity (Sullivan et al., 2009) and the ice nuclei (IN) activity (Cziczo et al., 2009;Tobo et al., 2012) of mineral dust. Thus, it is necessary to investigate the heterogeneous reaction between amines and kaolinite for understanding the climatic effect changes of kaolinite during atmospheric transformation."

Figure 5: It will improve the readability of this figure to move ΔH and ΔS values to the figure caption instead.

Response: Thank you. These values will be moved to the figure caption as "The Δ*H* of MA, DMA and TMA are -11.2 ±0.6, -15.8 ±3.4 and -12.1 ±1.2 kJ mol^{-1}, while the Δ*S* are -97.5 ±2.4, -111.8 ±13.0 and -90.4 ±4.9 J $mol^{-1}K^{-1}$, respectively."

References:

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