

Interactive comment on “Laboratory study on heterogeneous decomposition of methyl chloroform on various standard aluminosilica clay minerals as a potential tropospheric sink” by S. Kutsuna et al.

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Major revised points: We have done the following two major revisions:

1. The wrong numbers in Eqs.16 and 17 (p.1864, lines 12 and 17) are corrected.
2. Physical meaning of k_1 and how to estimate lifetime using k_1 are described.

Details of these two main revisions are as follows.

M1. The wrong numbers in Eqs.16 and 17 are corrected (p.1864, lines 12 and 17):

The wrong factor of $1.17\text{E-}22$ in Eq. 16 is corrected to $1.66\text{E-}24$. The number of $4.53\text{E-}13$ in Eq.17 is corrected to $6.43\text{E-}15$. Lifetimes derived in the 3.4.1 and 3.4.2

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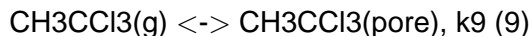
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sections are not changed because these lifetimes had been calculated with the correct equations.

M2. Physical meaning of k_1 and how to estimate lifetime using k_1 are described:

We assume that all the processes concerned can be approximated by linear processes under the steady state. This assumption seems to apply for illite (API no.35*), judging from the relation between the amount of CH_3CCl_3 adsorbed and the partial pressure of gaseous CH_3CCl_3 as shown in the 3.3.1 section.

In the 3.2.2 section, the activity of clay materials is compared via k_1 and k_1/s . The k_1/s value represents a flux of gaseous CH_3CCl_3 to unit area of the clay surface. To simplify an explanation, only reactions on the surface in pores are considered. This simplification is reasonable because the surface area in pores is much larger than the surface area outside pores of most clay materials examined. The following reaction scheme will be used in the revised manuscript instead of the scheme (9)-(11) (p.1862, lines 9-11).



where k_9 is a constant originating from diffusion of CH_3CCl_3 in pores; K_{10} is the adsorption equilibrium coefficient of CH_3CCl_3 in pores; k_{11} is the first-order surface reaction rate constant in pores; $\text{CH}_3\text{CCl}_3(\text{g})$ and $\text{CH}_3\text{CCl}_3(\text{pore})$ are gaseous CH_3CCl_3 outside and in pores, respectively; $\text{CH}_3\text{CCl}_3(\text{ad})$ is CH_3CCl_3 adsorbed on the surfaces in pores; and $\text{CH}_2=\text{CCl}_2(\text{ad})$ and $\text{HCl}(\text{ad})$ are $\text{CH}_2=\text{CCl}_2$ and HCl , respectively, adsorbed on the surfaces in pores.

Since the k_{11} value is much smaller than the adsorption rate and the desorption rate, equilibrium of CH_3CCl_3 between in air and on the surface can be estimated to be determined by K_{10} . The steady state flux of CH_3CCl_3 to pores by diffusion (F) is

represented by Eq.(S1).

$$F = k_9(\text{PMC}(\text{g}) - \text{PMC}(\text{pore})) \quad (\text{S1}),$$

where $\text{PMC}(\text{g})$ and $\text{PMC}(\text{pore})$ are partial pressure of gas-phase CH_3CCl_3 (outside clay samples) and equilibrium partial pressure of CH_3CCl_3 adsorbed in pores. It is assumed that CH_3CCl_3 in pores is removed according to first-order kinetics by reactions on the inner surface of pores of clay minerals by Eq.(S2).

$$d\text{PMC}(\text{pore})/dt = -k_d \text{PMC}(\text{pore}) \quad (\text{S2}),$$

where $k_d = k_{11} K_{10}$.

Since $F = -d\text{PMC}(\text{pore})/dt = -k_1 \text{PMC}(\text{g})$ at steady state, Eq.(S3) is obtained.

$$1/k_1 = 1/k_9 + 1/k_d \quad (\text{S3}).$$

The k_9 value is estimated to be $>1\text{E-}3 \text{ s}^{-1}$ at 313 K, because CH_3CCl_3 decayed according to first-order kinetics after 14 min-reaction period. In addition, the formation rate of $\text{CH}_2=\text{CCl}_2$ is measured to be almost same as the decay rate of CH_3CCl_3 except for the initial period after changing the gas-circulating route. These facts indicate that $k_1 \ll k_9$ and that k_1 is nearly equal to k_d . Physical meaning of k_1 is represented by Eq.(S3) on the assumption of the steady state and linear processes.

The lifetime cannot be calculated directly from the k_1 value, because the k_1 value is nonlinearly dependent on density of clay minerals. The k_{clay} and f_{MC} are needed to estimate lifetime of CH_3CCl_3 . The k_{clay} is the overall first-order rate constant of CH_3CCl_3 in and on the clay material and it is defined by Eq.(S4).

$$dM(\text{clay})/dt = -k_{\text{clay}} M(\text{clay}) \quad (\text{S4}),$$

where $M(\text{clay})$ represents total amount of CH_3CCl_3 adsorbed on the surface and in the pores of the clay material. When the $M(\text{clay})$ value is proportional to partial pressure of gaseous CH_3CCl_3 , the k_{clay} and f_{MC} value are represented by Eqs. (S5) and (S6) in the steady state.

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$$k_{\text{clay}} = \{(1 + f_{\text{MC}}) / f_{\text{MC}}\} k_1 \quad (\text{S5}),$$

$$f_{\text{MC}} = f_{\text{MC}}' n_s \quad (\text{S6}),$$

where f_{MC} is the mole fraction of CH_3CCl_3 adsorbed on the surface and in the pores of the clay material to CH_3CCl_3 in air (outside the clay material); and n_s in m^{-1} is the surface area of clay minerals per unit volume of air.

In the 3.2.2 section, the $k_{\text{clay}} = \{(1 + K) / K\} k_1$, which is briefly described (p. 1855, line 6), is obtained by approximating f_{MC} by K . On the other hand, in the 3.3.1 section, f_{MC}' is experimentally determined on the basis of the data shown in Fig. 11, and k_{clay} is calculated from the experimentally determined f_{MC}' and k_1 . The experimentally determined f_{MC}' and k_{clay} for illite (API no.35*) in the 3.3.1 section are used to estimate lifetime of CH_3CCl_3 in the 3.4.1 and 3.4.2 sections. In Eq. 16 (p. 1864, line 12) in the 3.4.1 section, $f_{\text{MC}}' = K_{\text{AMC}} R T$.

to Specific comments

1. Pressure drop

(a) In our experimental set-up, clay samples have been set in the removable cell and they are in one atmospheric air without exposure to a CH_3CCl_3 -air mixture. Partial pressure drop in CH_3CCl_3 due to the change in the circulating route cannot be reduced by inserting a dummy volume in the by-pass route, because a CH_3CCl_3 -air mixture is mixed with the air in the removable cell. This experimental set-up is not suitable for measuring rapid change in partial pressure because the mixing time of a gas mixture is 1 min or longer as follows (1(b)).

(b) The gas mixture is circulated with a magnetic-driven glass pump ($0.7 \text{ dm}^3 \text{ min}^{-1}$). Since the volume of the reactor is 0.85 dm^3 , it takes about 1.2 min for one round. About three times the total reactor volume is required for circulating all the gas mixture through these cells. Hence it takes about 3-4 min to circulate all the gas mixture through the closed-circulation reactor. These facts will be mentioned in the Experimental section

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of the revised manuscript.

(c) Time-course of CH_3CCl_3 in the absence of clay samples is added to Fig. 3A.

(d) The x-axis intercept ($-\text{dPMC}$) means a real loss of CH_3CCl_3 . It takes about 3–4 minutes till the equilibrium of the system is achieved after changing the route as described above (1(b)). The equilibrium is confirmed in the experiment in the absence of clay samples as mentioned in 1(c). This will be mentioned in the Experimental section of the revised manuscript. However, in fact, it took longer time till the equilibrium of the system was achieved. We consider this period as the time required for achieving a steady state between partial pressures of CH_3CCl_3 outside and inside clay materials as shown in Eq. 9 in M2. These will be discussed in the 3.3.1 section of the revised manuscript.

2. Decay of CH_3CCl_3

(a) The large deviation from the first order kinetics at 34 min (4 min after changing the route) is mainly a consequence of the partial pressure drop and subsequent mixing and diffusion in pores. After at 44 min (14 min after changing the route), the deviation from first-order-kinetics is a consequence of the linear process approximation such as deactivation due to HCl produced.

(b) p.1853, lines 20-21: P_0 is the pressure at 30 min (0 min after changing the route) extrapolated from the fit. In the revised manuscript, this will be clearly described in the 3.2.1 section.

(c) p.1853, lines 18-20; Figs. 8A and 8B; p. 1853, lines 13-14: As mentioned in 1(d), it took ca. 14 min at $T = 313 \text{ K}$ to come to first-order kinetics because of diffusion of CH_3CCl_3 in the pores and/or on the surfaces of the clay material. At 298 and 283 K, the steady state can be achieved after longer time. Figure 11 shows that $a\text{MC}$ is proportional to PMC except for the initial data (gray symbols). The number of the data that is not proportional to PMC is larger at 283 and 298 K than at 313 K.

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(d) Mono-explanation fits are applied to the data when the steady state seems to be achieved. The related processes are approximated to be linear processes at the steady state. As described in the major revision [M2], the competition between surface reaction and system equilibration are modeled by the scheme containing diffusion from outside to inside clay materials and subsequent removal on the inner pores of clay minerals. Errors of this approximation will be discussed only about the data for illite (API no. 35*) in the revised manuscript.

3. Photodecomposition of $\text{CH}_2=\text{CCl}_2$

(a) HCl was less than expected from stoichiometry of $\text{CH}_2=\text{CCl}_2$ loss.

(b) We think that heterogeneous photodecomposition of $\text{CH}_2=\text{CCl}_2$ proceeds via two schemes: heterogeneous photodecomposition of $\text{CH}_2=\text{CCl}_2$ and the reaction of $\text{CH}_2=\text{CCl}_2$ with Cl atoms that are released from $\text{CH}_2=\text{CCl}_2$. We reported this scheme for heterogeneous photodecomposition of $\text{CCl}_2=\text{CCl}_2$ on clay minerals [Kutsuna et al., 2000b]. HCl would be produced via addition reaction of Cl to $\text{CH}_2=\text{CCl}_2$ and subsequent decomposition reactions on the surface and in air. This discussion will be added in the 3.2.2 section of the revised manuscript.

(c) CO and COCl_2 were produced in some experimental runs.

4. Clay samples used in the previous study (Experimental section):

The montmorillonite sample used in the previous study [Kutsuna et al., 2000a] is not identical to either one of the samples used in the present study or the API standard clay minerals. The other three clay samples used in the previous study were not API standard samples, either. These facts will be clearly described in the Experimental section of the revised manuscript.

5. Uptake coefficient

(a) The g value was calculated to be $(9 \pm 1) \times 10^{-10}$. Errors represent only \pm s in fitting the data by a line through the origin in Fig. 5A. As mentioned in the main revision

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M2, the k_1 value depends on fMC and the $k_{\text{clay}} \text{fMC} / s$ values are more suitable for estimating g . Since fMC is approximated by K in the 3.2.2 section, $k_{\text{clay}} \text{fMC} = k_1 (1 + K)$ is obtained by Eq. (S5) in M2. Therefore, in the revised manuscript, the g value is calculated from the $k_1 (1 + K) / s$ slope in Fig. 5C. The g value was calculated to be $(1.0 \pm 0.1) \text{E-9}$. Errors represent only $\pm s$ in fitting the data by a line through the origin in Fig. 5C.

(b) The g value obtained here is about one order of magnitude smaller than that for halloysite-p and allophane-p given in Kutsuna et al., 2000a. In the previous study, the analysis was based on the Langmuir type reaction scheme and the parameters such as surface reaction rate constants were obtained by a simulation for all the data at different initial partial pressures. We found in the previous study that the g value increased with decreasing initial partial pressure of CH_3CCl_3 . Lack of considering a non-linear adsorption is a reason why the g value in this study is smaller than in the previous study. On the other hand, in the 3.4.1 and 3.4.2 sections, lifetime of CH_3CCl_3 is deduced from the data for illite (API no. 35*). A linear adsorption of CH_3CCl_3 is confirmed for illite (API no. 35*) under the experimental conditions examined.

(c) In the 3.3.1 and 3.4.1 sections, the mole fraction of CH_3CCl_3 in the pores and/or on the surface of illite (35*) to CH_3CCl_3 in air (fMC) at 313 K are determined from Figure 10. The fMC is determined to be 0.145. As mentioned in M2, the fMC in Table 1 is assumed to be equal to K (0.26 ± 0.09). The difference in fMC gives different g values. The g value is determined to be $(1.3 \pm 0.4) \text{E-9}$ from $\text{fMC} = 0.145$, while the g value in Table 1 of the revised manuscript is $(1.4 \pm 0.6) \text{E-9}$. Errors represent standard deviation of the mean value for the five measurements. The value of $t_{\text{dustlocal}}$ calculated from $g = 1.4 \text{E-9}$ is $(1.3/1.4)$ times the values in Table 3. The $t_{\text{groundtropos}}$ cannot be estimated from only g values because fMC is needed in calculating the chemical removal efficiency (a) in Eq. 21 (p.1866, line 23).

The errors of the g values obtained in this study come from a linear process approximation, estimation of mean molecular velocity of CH_3CCl_3 in pores and estimation of

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mole equilibrium between inside and outside clay materials as described in M2.

6. Release of water and CH_3CCl_3 from clay materials by photoillumination (p.1859, lines 2-27):

(a) It is difficult to determine water vapor in our experimental set-up. The water release was not determined. The adsorption of CH_3CCl_3 is expected to increase when the water is released. But, as shown in Fig. 3A, the increase in the adsorption by photoillumination was not found.

(b) Direct evidence of desorption of CH_3CCl_3 is not obtained. The increase in CH_3CCl_3 by photoillumination tends to be small, when the adsorption on clay minerals is small.

7. The uncertainty in aMC due to the pressure drop / system equilibrium (Fig.11, pp.1861-1862):

The partial pressure drop was estimated to be a factor of 0.23 ± 0.01 . Since the initial partial pressure of CH_3CCl_3 is about 16 Pa, the uncertainty in aMC due to the pressure drop is 0.16 Pa in gaseous CH_3CCl_3 , which corresponds to 3.3×10^{16} molecules in aMC. The gray symbols in Fig.11 are not used in calculating KHMC. The gray symbols are the data at 4 min reaction at 313 K, the data at 4 - 24 min reaction at 298 K and the data at 4 - 54 min reaction at 283 K.

8. The factors in Eqs.13 and 16 and derivation of Eq.13:

1) about Eq.13 (p. 1862, line 15)

Eq.13 is reduced by Eq. (S5) shown in the main revision M2.

In the revised manuscript, k_{sr} in Eq.13 is replaced by k_{clay} , which is defined as Eq. (S4) in M2. The k_1 value is related to the k_{clay} value as follows:

$k_1 = \{f_{MC} / (1 + f_{MC})\} k_{clay}$ (S7),

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where fMC is the mole fraction of CH₃CCl₃ in the pores and/or on the surface of clay minerals to CH₃CCl₃ in air as mentioned in M2. fMC is represented by Eq. (S8) from Eq. 8 (p. 1862, line 2).

$$fMC = m S KHMC R T / (NA V) \text{ (S8)},$$

where m and S are the weight and the BET specific surface area of illite (API no.35*), respectively; V is the volume of the reactor used (0.85 in dm³); NA is the Avogadro's number (6.02E23); R is the gas constant (8.31 in Pa m³ K⁻¹); and Ta is the temperature of most parts of the reactor (room temperature, 298 in K). Substitution of m = 0.05 in g and S = 70.6 m² g⁻¹ into Eq. (S8) gives Eq. (S9).

$$fMC = 1.71E-17 KHMC \text{ (S9)}.$$

Combining Eq. (S3) with Eq. (S5) gives Eq. 13.

2) about Eqs. 16 (p.1864, line 12) and 17 (p.1864, line 17) As mentioned in M1, the following mistakes are corrected.

1, The value "1.17E-22" in Eq. 16 is replaced by "1.66E-24".

2, The value "4.53E-13" in Eq. 17 is replaced by "6.43E-15".

These mistakes arose by calculating the value of S (70.6 in m² g⁻¹) twice, since the S had been eliminated from Eq. 16 in the older version of the manuscript. This correction will not change the estimated lifetimes in the text (Tables 3 and 4) because the lifetime had been calculated from the corrected value of KAMC.

The value of 1.66E-24 is equal to 1/NA, where NA is the Avogadro's number (6.02E23).

Technical corrections

1, Eqs. 14, 17: Unit of T is described as follow:

page 1862, line 24: The k_{clay}(T) value in s⁻¹ at temperature T in K was expressed by Eq. 14.

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page 1864, line 15: The KAMC value in $\text{m}^{-2} \text{Pa}^{-1} \text{mol}$ at temperature T in K is expressed by Eq. 17.

2, Large size of characters were used in Table 1, Figures 5, 8 and 11.

3, p. 1859, lines 13 and 16: "most of" is corrected to "most".

4, The distinction between "adsorption constant in Langmuir form" and "equilibrium constant" is noted. In the revised manuscript, the distribution between outside and inside clay materials is considered. The "equilibrium constant" will be used for distribution between outside and inside clay materials.

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