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Technical Note: Influence of surface roughness and local turbulence on coated-wall flow tube experiments for gas uptake and kinetic studies

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Abstract

Coated-wall flow tube reactors are frequently used to investigate gas uptake and heterogeneous or multiphase reaction kinetics under laminar flow conditions. Coating surface roughness may potentially distort the laminar flow pattern, induce turbulence and introduce uncertainties in the calculated uptake coefficient based on molecular diffusion assumptions (e.g., Brown/CKD/KPS methods), which hasn't been sufficiently addressed in previous applications. Here we investigate the influence of surface roughness and local turbulence on coated-wall flow tube experiments for gas uptake and kinetic studies. According to laminar boundary theory and considering the specific flow conditions in a coated-wall flow tube, we suggest using a critical height δ_c to evaluate turbulence effects in the design and analysis of coated-wall flow tube experiments. When a coating thickness ε_{max} is larger than δ_c, the roughness elements of the coating may cause local turbulence and result in overestimation of the real uptake coefficient (γ). We collect ε_{max} values in previous coated-wall flow tube studies and evaluate their roughness effects using the criterion of δ_c. In most cases, the roughness doesn't generate turbulence and has negligible effects. When turbulence is generated, the calculated effective uptake coefficient (γ_{eff}) can bear large difference compared to the real uptake coefficient (γ). Their difference becomes less for gas reactants with lower uptake (i.e., smaller γ), or/and for a smaller ratio of the coating thickness ε_{max} to the flow tube radius R_0, (ε_{max}/R_0). On the other hand, the critical height δ_c can also be adjusted by optimizing flow tube configurations and operating conditions (i.e., tube diameter, length and flow velocity), to ensure not only an unaffected laminar flow pattern but also a flexible residence time of gas reactants in flow tube reactors.

1. Motivation

Coated-wall flow tube reactors have been extensively employed for investigations of uptake and reaction kinetics of gases with reactive solid/semi-solid surfaces (Kolb et al., 2010). To simulate various heterogeneous or multiphase reactions relevant to atmospheric chemistry, these coated reactive surfaces can span a broad scale including inorganic salts (Davies and Cox, 1998;Chu et al., 2002;Qiu et al., 2011), organic acids and sugars (Shiraiwa et al., 2012;Steimer et al., 2015), proteins (Shiraiwa et al., 2011), soot (McCabe and Abbatt, 2009;Khalizov et al., 2010;Monge et al., 2010), mineral dust (El Zein and Bedjanian, 2012;Bedjanian et al., 2013), ice (Hynes et al., 2001;Hynes et al., 2002;Bartels-Rausch et al., 2005;Fernandez et al., 2005;McNeill et al., 2006;Petitjean et al., 2009;Symington et al., 2012) and soils (Stemmler et al., 2006;Wang et al., 2012;Donaldson et al., 2014a;Donaldson et al., 2014b;VandenBoer et al., 2015;Li et al., 2016). Due to uptake or chemical reactions of gases at coated tube walls, radial concentration gradients are established within the tube and radial diffusion can be significant. It is therefore necessary to account for this gas-diffusion effect on gas-surface interactions. The most commonly utilized methods for evaluation and correction for gas-diffusion in flow tubes include the Brown method (Brown, 1978), CKD method (Murphy and Fahey, 1987) and a more recently developed simple KPS method (Knopf et al., 2015). All of these methods are derived based on the assumption that gas flow in flow tubes should be well-developed laminar to ensure that the flow velocity profile is parabolic and that the radial transport of gas reactants is solely caused by molecular diffusion.

It is well known that the flow conditions in a tube depend on the Reynolds number, *Re* (Eqn. 1),

$$Re = \frac{\rho \times V_{avg} \times d}{\mu} = \frac{V_{avg} \times d}{v} \qquad (1)$$

where ρ is density of the fluid passing through the tube, V_{avg} is the average velocity of the fluid (i.e., the volumetric flow rate divided by the cross sectional area of the tube), d is diameter of the tube, μ and v are dynamic viscosity and kinematic viscosity of the fluid, respectively. A laminar flow can be expected when *Re* is less than ~ 2000 (Murphy and Fahey, 1987;Knopf et al., 2015). Here, the expression of *Re* quantifies the nature of the fluid itself (i.e., ρ, V_{avg}, μ and v) and the tube geometry (i.e., d), but it does not account for the effects of surface roughness.

Surface roughness effects on flow conditions were firstly discussed by Nikuradse (1950). Based on his work, the Moody diagram has been extensively used in industry to predict the effects of surface roughness (roughness height ε or relative roughness ε/d) on flow characteristics (in terms of friction factor). According to the Moody chart, when the surface roughness is small enough (i.e., $\varepsilon/d \leq 5\%$), the roughness effects within low Reynolds number regime (*Re* < 2000, characteristic of laminar flow) is negligible. Recent experimental and theoretical studies, however, have found significant effects of surface roughness on laminar flow characteristics (e.g., fraction factor, pressure drop, critical Reynolds number and heat transfer etc.) in micro-channels and pipes even under conditions of $\varepsilon/d \leq 5\%$ (Herwig et al., 2008;Gloss and Herwig, 2010;Zhang et al., 2010;Zhou and Yao, 2011). This is because not only the ratio of ε and d but also other factors, such as shape of roughness elements (Herwig et al., 2008;Zhang et al., 2010) and spacing between different roughness elements (Zhang et al., 2010), may determine the influence of surface roughness on the flow conditions.

Moreover, compared to the rough pipe surfaces commonly dealt with in industry (with $0 \leq \varepsilon \leq 50$ μm, see http://mdmetric.com/tech/surfruff.htm), the surfaces used in atmospherically relevant flow tube studies are with much larger surface roughness (e.g., inorganic salts, organic acids and proteins, soot, mineral dust, ice and soils, with $0 \leq \varepsilon \leq$ ~ 650 μm; see

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Fig. 1), and the roughness of these surfaces are sometimes beyond the criterion of $\varepsilon/d \leq \sim 5\%$. The reported specific surface areas of these coatings span a wide range from ~ 20 m^2 g^{-1} to ~ 100 m^2 g^{-1} with a coated film thickness scale from tens of micro-meters to several hundreds of micro-meters (Davies and Cox, 1998;Chu et al., 2002;McCabe and Abbatt, 2009;Khalizov et al., 2010;El Zein and Bedjanian, 2012;Shiraiwa et al., 2012;Wang et al., 2012;Bedjanian et al., 2013;Donaldson et al., 2014a;Donaldson et al., 2014b;VandenBoer et al., 2015), indicating considerable porosity in coating layer and significant roughness on their surfaces.

Although the surface roughness effects can be potentially important, there has been a long-lasting debate on whether the coating surface roughness could disturb the fully developed laminar flow in flow tube kinetic experiments (Taylor et al., 2006;Herwig et al., 2008) and its effects were usually not well-quantified in most of the previous gas uptake or/and kinetic studies (Davies and Cox, 1998;Chu et al., 2002;McCabe and Abbatt, 2009;Khalizov et al., 2010;El Zein and Bedjanian, 2012;Shiraiwa et al., 2012;Wang et al., 2012;Bedjanian et al., 2013;Donaldson et al., 2014a;Donaldson et al., 2014b;VandenBoer et al., 2015). It is, however, conceivable that as the roughness of the coating surfaces increases it would eventually distort the steady laminar regime near tube walls and small-scale eddies would evolve from roughness elements giving rise to local turbulence, and hence corrupt the application of Brown/CKD/KPS methods for the derivation of uptake coefficient. The extent of these effects may depend on the coated film thickness and its surface roughness. It means that the roughness effects on flow conditions to a great extent rely on the various coating techniques applied by different operators, leading to disagreement of the experimental results.

In the present study, the surface roughness effects on laminar flow are quantitatively examined. In view of the special laminar boundary layer structure in flow tubes, we employ a critical height δ_c to evaluate the influence of surface roughness on laminar flow patterns. By taking it into account in flow tube experimental design, it is feasible to satisfy the preconditions of merely radial diffusion of gas reactants existing inside flow tube reactors and therefore validate the application of Brown/CKD/KPS methods. The introduction of δ_c provides an easy way of compromising different flow tube experimental parameters (e.g., tube diameter, tube length and flow velocity etc.) to achieve (1) guaranteed application of diffusion correction methods, and (2) flexible and adjustable flow tube configurations to realize different experiment requirements. Previous flow tube investigations employing various coating materials and thicknesses are summarized and further evaluated by the proposed criterion of δ_c, as an illustration of how this criterion can be applied. For previous experimental configurations, where local turbulence might not have been avoided, a modified CKD method (M-CKD) is developed to estimate the possible maximum error of the calculated effective uptake coefficient (γ_{eff}).

2. Methods

2.1 Influence of surface roughness on laminar flow

According to the proverbial boundary layer theory proposed by Prandtl (1904), when a fluid (normally a gas mixture, a gas reactant mixed with a carrier gas, in uptake kinetic studies) enters the inlet of a flow tube with a uniform velocity, a laminar boundary layer (i.e., velocity boundary layer) will form very close to the tube wall (Fig. 2). This buildup of laminar boundary layer is because of the non-slip condition of the tube wall and the viscosity of the fluid, that is, viscous shearing forces between fluid layers are felt and dominant within the laminar boundary layer (Mauri, 2015). The thickness of laminar boundary layer δ will continuously increase in the flow direction (axial direction in Fig. 2) until at a distance (from the tube entrance) where the boundary layers merge. Beyond this distance the tube flow is entirely viscous, and the axial velocity adjusts slightly further until no changes of velocity along the axial direction. Then, a fully developed velocity profile is formed and this velocity profile is

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parabolic, which is characteristic of well-developed laminar flow (Mohanty and Asthana, 1979;White, 1998). The development and formation of this velocity profile is illustrated in Fig. 2. Normally, for coated-wall flow tube experiments a pre-tube is employed to function as developing a well-developed laminar flow before it entering into the coated tube section.

As demonstrated in previous studies using micro-channels and pipes (Herwig et al., 2008;Gloss and Herwig, 2010;Zhang et al., 2010;Zhou and Yao, 2011), the roughness elements on flow tube coatings can have non-ignorable effects on laminar flow conditions even if these coatings are entirely submerged into the laminar boundary layer. In other words, the disturbance on well-developed laminar flow patterns can be achieved artificially by roughness elements of the tube coating. However, there is a critical height δ_c within which the roughness effects can become ignorable (Achdou et al., 1998).

Figure 3 shows a schematic of the structure of the δ_c and its related flow conditions in a coated-wall flow tube. When a roughness height ε (here in Fig.3, the roughness height ε equates to the coating thickness ε_{max}, see Sect. 3.1 for explanation) is larger than the critical height δ_c, local eddies may occur in the spaces between the neighboring roughness elements (i.e., case 1 in Fig. 3A). Local turbulence induced by these roughness elements will enhance local transport of air masses within the scales of the roughness heights, which invalidates the assumption of solely molecular diffusion of gaseous reactants and the application of diffusion correction methods for the determination of γ (Brown, 1978;Murphy and Fahey, 1987;Knopf et al., 2015). Nevertheless, when a roughness height comes into the critical height δ_c where viscous effects overwhelmingly dominate, the flow very near the rough wall will tend to be Stokes-like or creeping, shown as Case 2 in Fig. 3B. This Stokes-like flow adjacent to the rough surfaces can eventually avoid local turbulence between the roughness elements and guarantee perfect laminar flow regime (i.e., only molecular diffusional transport of gas reactants to rough reactive coatings at the flow tube wall) formation throughout the whole flow tube volume. Thus Case 2 satisfies the prerequisite for the diffusion correction methods used for flow tube experiments, i.e., $\varepsilon/\delta_c < 1$. In the next section, we will show how to derive δ_c.

2.2 δ_c derivation

Achdou et al., (1998) proposed effective boundary conditions for a laminar flow over a rough wall with periodic roughness elements, and observed that when $\varepsilon/L_c < Re^{-1/2}$ (ε: roughness height; L_c: characteristic length, for a tube the characteristic length $L_c = d$) the roughness elements could be contained in the boundary layer. This means that, for their case, the boundary layer thickness is in the order of $L_cRe^{-1/2}$. Within the boundary layer, they found that local turbulence could occur between the roughness elements until $\varepsilon/L_c < Re^{-3/4}$, where the viscous effects became dominated in roughness elements and then the flow near the rough wall tended to be creeping. This result coincides with Kolmogorov's theory (Kolmogorov, 1991), in which the critical length ratios between small scale and large scale eddies is also in the order of $Re^{-3/4}$, even though this theory only applies to turbulent flow with large Reynolds numbers. Here, we adopt this criterion to judge if local eddies could occur in the spaces between neighboring roughness elements. Thus, the critical height δ_c can be expressed as:

$$\delta_c = d \times Re^{-3/4} = d^{1/4} \times \left(\frac{V_{avg}}{v}\right)^{-3/4} \quad (2)$$

where d is the diameter of the flow tube, Re is the Reynolds number, V_{avg} and v are the average velocity and the kinematic viscosity of the fluid, respectively.

With Eqn. (2), for a specified experiment configuration (i.e., flow tube diameter, flow velocity and fluid properties etc.) the critical height δ_c can be determined, and therefore the effects of coating roughness on laminar flow can be estimated provided the roughness height ε is known.

2.3 Error estimation with modified CKD method

The potential effects of coating roughness on laminar flow are described and classified into two cases in Fig. 3 (Sect. 2.1), in which only Case 2 provides the ideal precondition ensuring that the diffusion correction methods (Brown/CKD/KPS methods) can be applied to obtain accurate γ from flow tube experiments. Case 1, however, can be quantitatively simulated because local turbulence is constrained into the scale of the roughness height ε (see Fig. 3A) and the turbulence effects could be quantified by assuming a proper turbulent diffusion coefficient D_t within ε.

Hence, for Case 1, in order to estimate the potential error of the effective uptake coefficient (γ_{eff}) derived from molecular-diffusion-correction using the conventional methods aforementioned (here we adopt the CKD-B method proposed in our previous study Li et al., 2016), we further developed a modified CKD method (M-CKD, illustrated in Fig. 4) to account for local turbulence and therefore derive the real uptake coefficient (γ). In the M-CKD method, the molecular diffusion coefficient D of the gas reactant of interest is used in the main free-stream region (above the rough coating thickness ε_{max}) while a turbulent diffusion coefficient D_t is used in the roughness region to account for local turbulence between coating roughness elements (Fig. 4). The assumption of a whole turbulence layer (no laminar layer) in the roughness region represent an upper limit for the influence of turbulence, which corresponds to a largest uncertainty introduced to the calculation of γ_{eff}. More details about derivation of γ_{eff} and γ by CKD-B and M-CKD can be found in Appendix A.1 and A.2.

The turbulent diffusion coefficient D_t can be approximately estimated by the following equation (Taylor, 1922;Roberts and Webster, 2002):

$$D_t \approx V \times \varepsilon_{max} \quad (3)$$

where V is the flow velocity at the top edge of ε_{max} (blue dashed line in Fig. 4). V is calculated according to the parabolic velocity profile (in tube radial direction) of the main laminar flow in the flow tube. Here the rough coating thickness ε_{max} reflects the largest scale to which a local eddy can develop, because a roughness height ε has the range of $0 \le \varepsilon \le \varepsilon_{max}$. Half of ε_{max} is used as a characteristic diffusion distance in the turbulence-occurred region (Fig. 4).

3. Results and discussion

3.1 Design of coated-wall flow tube experiments

The introduction of the critical height δ_c, into the field of gas uptake or reaction kinetic studies using coated-wall flow tubes, provides us the way for determining when the surface roughness effects can be negligible in flow tube experiments. That is, the roughness height ε of a coating film should be well within the domain of δ_c (Case 2 in Fig. 3B), as only in this case the free molecular diffusion of a gas reactant in the radial direction can be ascertained and thus the Brown/CKD/KPS methods can be safely applied. Note that in real operations of flow tube coating design it is very inconvenient and difficult to precisely measure the surface roughness height ε of the coating film despite several instruments (e.g., stylus profiler, non-contact optical profiler and atomic force microscope etc.) are available for surface roughness examination (Poon and Bhushan, 1995). To simplify the discussion, here, we take the thickness of the coating film ε_{max} as a maximum of its surface roughness (sometimes this case can happen), and use the comparison between ε_{max} and δ_c as a reference for the design of flow tube coating thickness. Such treatment is more suitable for practical applications because determination of coating film thicknesses can be simply achieved either by calculating the coating film volume (coated mass divided by density) or by means of scanning electron microscope technique, and the condition of $\varepsilon_{max}/\delta_c < 1$ can definitely ensure the case of $\varepsilon/\delta_c < 1$.

Larger δ_c would allow a wider range of coating thickness ε_{max} without surface roughness effects. Based on Eqn. (2), larger δ_c can be achieved either by increasing the tube diameter d or by decreasing the fluid average velocity V_{avg}. In most cases, constant residence time of gaseous reactants inside flow tubes is needed to allow for enough uptake/reactions within the coated flow tube volume. This requirement can also be fulfilled by adjusting the coated tube length L, that is, to achieve larger δ_c the influence of decreasing V_{avg} on residence time can be balanced by reducing L.

Figure 5 summarizes and evaluates the potential effects of surface roughness in previous flow tube experiments. From Eqn. (2), kinematic viscosity of a fluid (carrier gas in flow tubes) will affect δ_c. It is therefore necessary to classify the flow tube experiments according to the types of the utilized carrier gases, such as synthetic air (Fig. 5A), nitrogen (Fig. 5B) and helium (Fig. 5C). The calculated δ_c, with varying tube diameter d and average flow velocity V_{avg}, are indicated by dash-dotted contour lines. Various coatings and configurations in previous studies are represented by different symbols and their coating thicknesses ε_{max} are indicated by the color of symbols, see figure caption for details. To reflect the influence of the roughness of flow tube wall itself, for the experiments using rough-wall flow tubes (e.g., sandblasted tubes) the mean wall roughness is also accounted for ε_{max} calculation, for example, the protein coating in Fig. 5A. Meanwhile, for easier comparisons of potential coating roughness effects on laminar flow between different experiment configurations summarized here, calculated δ_c basing on the experimentally adopted d and V_{avg} are further displayed in Fig. A.1.

As shown in Fig. 5, most of the coating thicknesses are well below the calculated values of δ_c (Case 2 in Fig. 3B), implying that their surface roughness effects on laminar flow and on the calculated uptake coefficient are ignorable. A few coating thicknesses, however, are significantly larger than the calculated δ_c, as shown by the green circle (Case 1, soil coating in Fig. 5B) and the blue triangle (Case 1, ice coating in Fig. 5C). These coatings may have a potential influence on laminar flow pattern and local turbulence may occur within the roughness-constructed spaces (see Fig. 4).

For most cases of flow tube experiments design, a coating layer cannot be thin enough due to requirements of reaction kinetics (bulk diffusion and surface reactions can both play important roles) and the thickness of a coating layer had been found to have an influence on gases uptake until a critical threshold was reached (Donaldson et al., 2014a;Li et al., 2016). This means that there is a need to comprehensively consider all the parameters (e.g., coating thickness, tube diameter, tube length, flow velocity etc.) and a compromise of each parameter for the others is necessary to finally ensure both the unaffected laminar flow conditions and the application requirements for diffusion correction methods. For example, to ensure $\varepsilon_{max}/\delta_c < 1$ for a thick coating (large ε_{max}), we can increase δ_c by increasing the tube diameter or decreasing the flow velocity as shown in Fig. 5.

The conditions of $\varepsilon_{max} < \delta_c$ (constraining a coating thickness within the critical height of δ_c, Case 2 in Fig. 3) help to avoid the potential impacts of coating roughness on the laminar flow. During practical operations of flow tube coating and configuration design, however, some exceptional circumstances can still be foreseen (as in Case 1 in Fig. 3). For example, one may encounter the conditions in Case 1 (Fig. 3A) due to the limit of coating techniques or other specific considerations. Then it is critical to make a priori evaluation of potential error of γ due to coating roughness effects in the design of flow tube experiments.

Figure 6 shows the deviation of calculated uptake coefficient γ_{eff} against the real uptake coefficient γ for Case 1. There, three different cases of ε_{max}/R_0 are presented with all the rest experimental configurations being kept the same (see Table A.1). For higher $\varepsilon_{max}/R_{0,}$ the deviation of γ_{eff} is also larger, indicating that a thick coating will result in larger error of the calculated γ_{eff}. Meanwhile, this error is also closely related to the magnitude of γ: at $\gamma < 10^{-5}$ there is almost no difference between γ_{eff} and γ, but at γ beyond 10^{-5} the error is apparent and considerably increases. In the case where local turbulence cannot be avoided (Case 1), Fig. 6 can be used to estimate the error of calculated γ_{eff}. With this error range in mind, the selection of coating techniques or/and parametrization of other experimental conditions can be better constrained, for example, if γ can be assumed to be smaller than 10^{-5} the coating roughness effects become negligible.

3.2 Wall-roughness-induced error of γ_{eff} in Case 1: for previous flow tube studies

Local turbulence caused by rough coatings had not been well-quantified in previous studies. Nevertheless, it may indeed happen and therefore introduce errors in the calculated uptake coefficient derived from the Brown/CKD/KPS methods (i.e., effective uptake coefficient γ_{eff}). It is therefore meaningful too, for previous flow tube designers, to have an estimation of the potential error of the measured γ_{eff} if their experiment conditions match Case 1. We show here an example illuminating how this estimation can be accomplished, by means of simulation under the pre-defined experimental configurations identical with those adopted in the above section.

Figure 7 shows the maximum relative errors that can be expected for a series of γ_{eff} under the three different cases of ε_{max}/R_0 shown in Fig. 6. Similar to the dependence of γ_{eff}/γ on γ (Fig. 6), the increase of γ_{eff} and ε_{max}/R_0 are also accompanied by the increase of γ_{eff}/γ in Fig. 7. The experiment example with coating thickness matching Case 1 (soil coating in Fig. 5B) is examined and the estimated maximum error (i.e., γ_{eff}/γ, γ_{eff} is 5.5×10^{-5}, an average value from the measurements by Li et al., 2016) is ~ 1.5 (red solid circle), implying that the coating roughness has a small effect on laminar flow in their case. But for larger γ_{eff}, γ_{eff}/γ versus a wide range of γ_{eff} (red dotted line in Fig. 7) also gives high values, for example, when $\gamma_{eff} > 10^{-3}$. This simulation further highlights the need to inspect the possible errors of previously measured high γ_{eff} (e.g., $> 10^{-3}$) if their coating roughness is accord with Case 1.

4. Conclusions

In this study, a new criterion is proposed to eliminate/minimize the potential effects of coating surface roughness on laminar flow in coated-wall flow tube experiments and therefore validate the application of conventional diffusion correction methods for uptake coefficient calculations. While keeping a coating film thickness well within the critical height δ_c to exclude potential surface roughness effects, flexible coated-wall flow tube design can also be achieved, i.e., one can increase δ_c by adjusting flow tube geometric parameters (i.e., tube diameter and tube length) or flow velocity V_{avg} to ensure not only an unaffected laminar flow pattern but also a flexible residence time in flow tube reactors. We illustrate the application of this new criterion for previous investigations, and demonstrate its effectiveness in optimizing flow tube design and consolidating kinetic experimental results. Moreover, based on the CKD method, a modified diffusion correction method (M-CKD) is proposed to evaluate the maximum relative error of the effective uptake coefficient γ_{eff}. The error estimation demonstrates that a smaller positive bias of γ_{eff} can be expected for experimental configurations employing gas reactants with lower uptake efficiency or/and smaller relative ratio of ε_{max}/R_0.

5. Data availability

The underlying research data and Matlab code for the M-CKD and CKD-B methods can be accessed upon contact with Yafang Cheng (yafang.cheng@mpic.de), Hang Su (h.su@mpic.de) or Guo Li (guo.li@mpic.de).

Appendix

A.1 Evaluation of the modified CKD method

To have an intuitive feeling of the change of concentration profiles due to local-turbulence-induced enhancement of the uptake coefficient, the CKD-B and the M-CKD have been applied to the experiment configuration of the exampled Case 1 in Fig. 7 (see HCHO in Table A.1), as shown in Fig. A.2. Comparison between Fig. A.2 (A) and (B) shows that local turbulence within the roughness thickness can enhance radial transport of the gas reactant and thus increase the effective uptake coefficient γ_{eff}.

A.2 Derivation procedure of γ_{eff}/γ versus γ or γ_{eff}

Derivation of γ_{eff}/γ versus γ or γ_{eff} is based on a combination of a modified CKD method (M-CKD), assuming that roughness-induced local turbulence occurs within the domain of $0.5\varepsilon_{max}$ (simulation of Case 1), and the CKD-B method (a CKD-based method using Matlab) which was described in our previous study (Li et al., 2016). The respective derivation procedures are shown in Fig. A.3. For one specific experiment configuration, both CKD-B and M-CKD can generate a correlation table with its first column being concentration transmittance (C/C_0) and the second column the corresponding uptake coefficient (γ), and their one-to-one correspondence is indicated by the same subscripts (e.g., k, n, j, m etc.), as shown in Fig. A.3. Under ideal laminar flow conditions (without local turbulence), a concentration transmittance (C/C_0), i.e., the flow tube outlet concentration devided by the inlet concentration, can be obtained from flow tube experiments. With C/C_0, its corresponding real uptake coefficient γ can be determined from the C_B/C_0 versus γ_B table derived from the CKD-B method (Fig. A.3A), i.e., if $(C_B/C_0)_k$ equals to C/C_0 then γ_{Bk} is γ. With this γ (i.e., γ_{Bk}) and the M-CKD method, another $(C_M/C_0)_j$ corresponding to γ can be seeked out from the M-CKD derived table (C_M/C_0 versus γ_M). Then another γ_{Bn} can be found from the C_B/C_0 versus γ_B table, with its corresponding $(C_B/C_0)_n$ equaling to $(C_M/C_0)_j$; this γ_{Bn} is exactly the effective uptake coefficient γ_{eff}. Finally, γ_{eff}/γ versus γ can be derived, that is γ_{Bn}/γ_{Bk} versus γ_{Bk}. These procedures are shown in Fig. A.3A. For local turbulence existing in the domain of $0.5\varepsilon_{max}$, with the experiment-measured C/C_0, its corresponding γ_{eff} and γ can be obtained from the C_B/C_0 versus γ_B table and the C_M/C_0 versus γ_M table, respectively, i.e., if $(C_B/C_0)_k$ equals to C/C_0 then γ_{Bk} is γ_{eff}; if $(C_M/C_0)_j$ equals to C/C_0 then γ_{Mj} is γ. Consequently, γ_{eff}/γ versus γ_{eff} can be derived, that is γ_{Bk}/γ_{Mj} versus γ_{Bk} (see Fig. A.3B).

A.3 Limitations of CKD and KPS methods

Due to the different algorithms employed, the CKD method (Murphy and Fahey, 1987) and the KPS method (Knopf et al., 2015) could derive contrasting γ when turbulence occurs (see Fig. A.4). As shown in Fig. A.4, with ideal laminar flow (without any local turbulence, Case 2) the KPS (with diffusion correction) and CKD show perfect agreement for the derived γ in the C/C_0 range of 0.548 to 1 (shaded area). If C/C_0 is smaller than the critical transmittance value (< 0.548), e.g., because of enhanced mass transport towards the coated-wall due to local turbulence in laminar flow, the KPS results in negative γ (for details, see Knopf et al., 2015) while the CKD has no solutions. For C/C_0 larger than 1, both methods derive negative γ implying emissions of gas reactants from the coating.

Acknowledgments

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Table A.1. Detailed experiment configurations employed for the modified CKD (M-CKD) simulation (Figs. 6 and 7) and for comparison between CKD and KPS derived γ (Fig. A.4).

d (mm)	L (mm)	F (L/min)	T (°C)	Coating material	Gas reactant	Carrier gas	Usage in this paper
7	250	5	25	Not-specified	O_3	nitrogen	for M-CKD simulation, ε_{max}/R_0 = 0.05, 0.10, 0.20
7	250	1	23	soil	HCHO	nitrogen	for M-CKD simulation, ε_{max}/R_0 = 0.15 and for Fig. A.2
17	200	4	23	soil	SO_2	synthetic air	for Fig. A.4

d: flow tube diameter; L: flow tube length; F: volume flow rate; T: temperature

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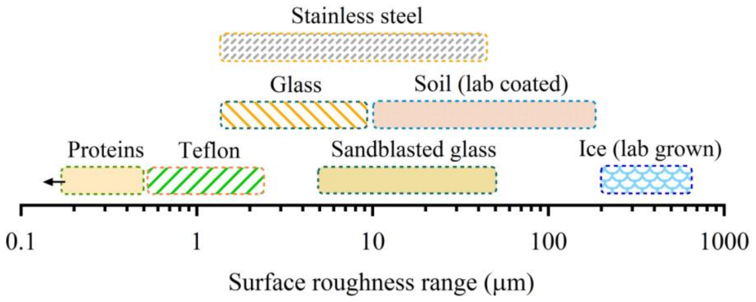


Figure 1. Typical surface roughness for materials commonly used in flow tube gas uptake and kinetic experiments. Data sources: https://neutrium.net/fluid_flow/absolute-roughness/ and http://www.edstech.com/design-tools.html. The soil roughness refers to Li et al., (2016) and the ice roughness refers to Onstott et al., (2013) and Landy et al., (2015).

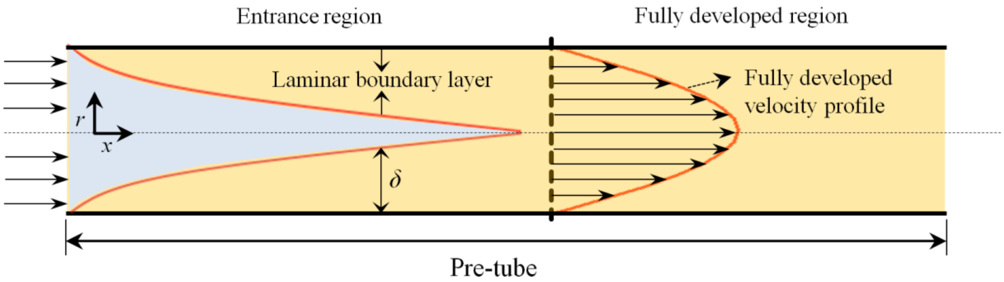
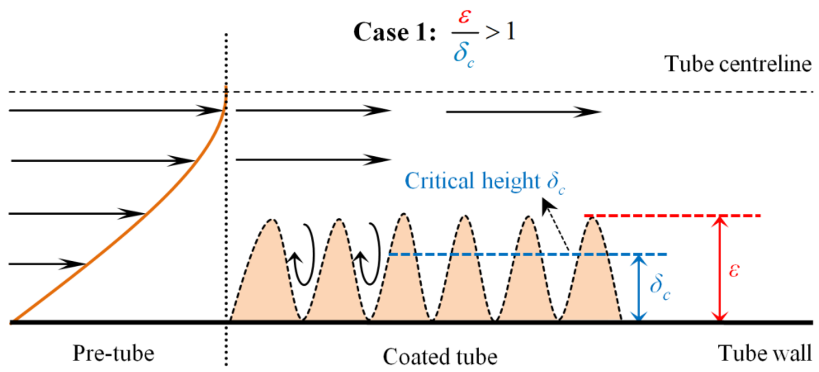
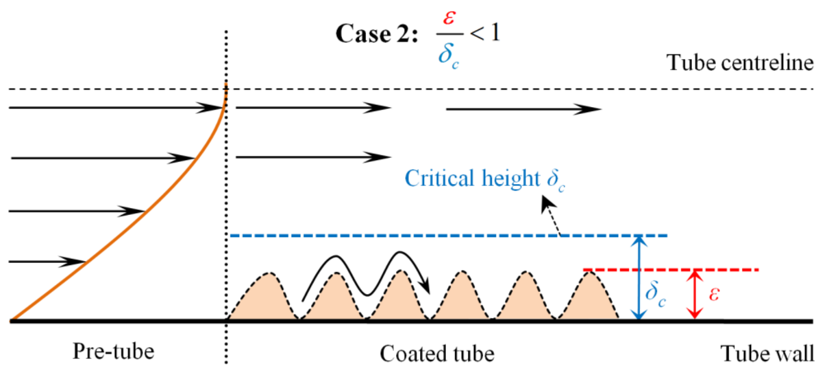


Figure 2. Developments of laminar boundary layer and flow velocity profile within the pre-tube.



(A)



(B)

Figure 3. Schematic of the critical height δ_c and its related flow conditions in a flow tube with rough coatings. Upstream of the coated tube section, a pre-tube is installed to warrant well-developed laminar flow conditions. Two cases of tube coatings reflect different impacts of a roughness element with varying height ε on flow patterns.

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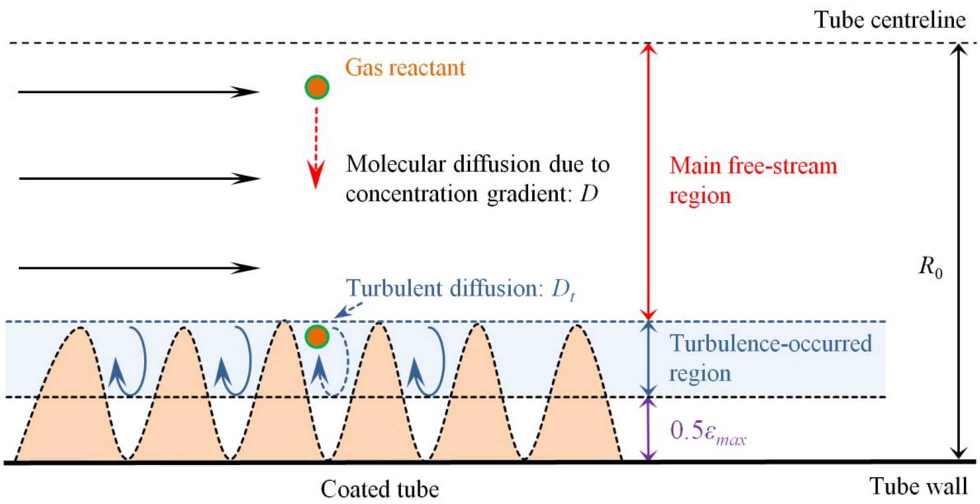

Figure 4. Illustration of the modified CKD method, i.e., employment of molecular diffusion coefficient D of the gas reactant and a turbulent diffusion coefficient D_t in the main free-stream region and turbulence-occurred region, respectively.

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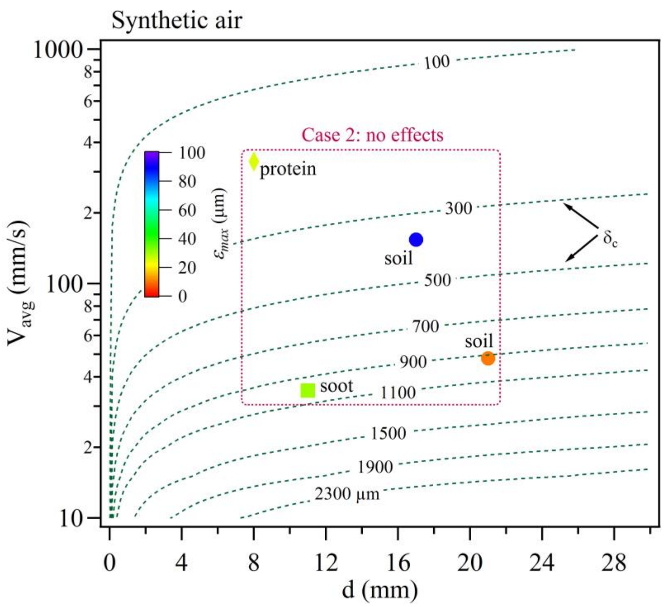
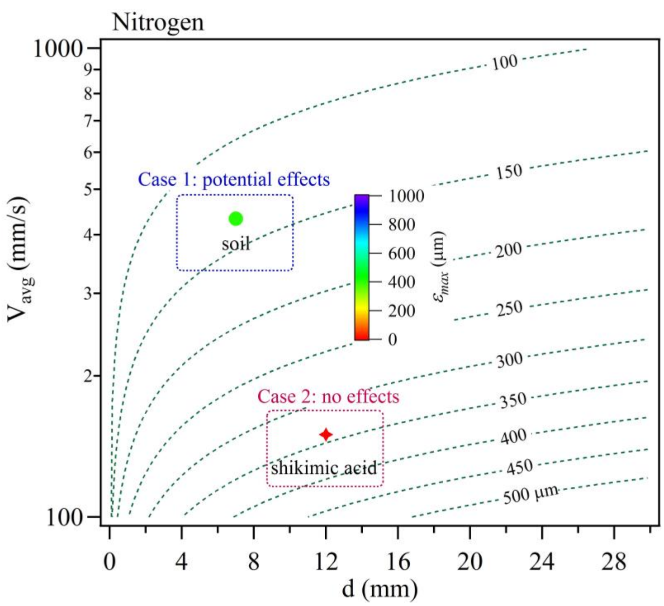


(A)



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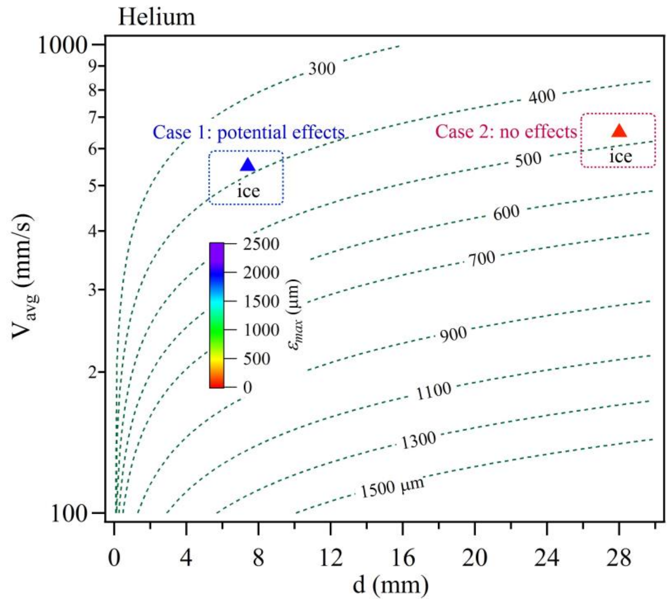

(C)

Figure 5. Calculated critical height δ_c (dash-dotted lines) and representative coating thickness ε_{max} (color coded) adopted from literature, versus varying tube diameter *d* and flow velocity V_{avg} in flow tube experiments with carrier gases of synthetic air (A), nitrogen (B) and helium (C), respectively. References for previously applied coatings summarized here are: diamond (Shiraiwa et al., 2011), square (Monge et al., 2010), upper circle (Donaldson et al., 2014a;Donaldson et al., 2014b) and lower circle in (A) (Wang et al., 2012); circle (Li et al., 2016) and star in (B) (Steimer et al., 2015); blue triangle (McNeill et al., 2006) and light red triangle (Petitjean et al., 2009) in (C).

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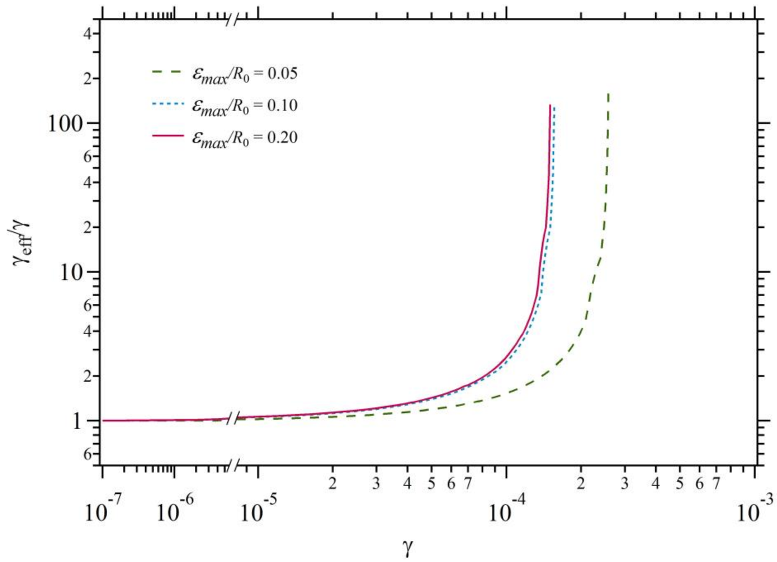

Figure 6. Maximum error of the effective uptake coefficient (γ_{eff}) relative to the real uptake coefficient (γ) versus γ, for three cases with different ratio of the coating thickness to tube radius (ε_{max}/R_0). The choices of ε_{max}/R_0 cover the general ratio range in previous studies. The curves cannot be further extended due to reaching the limits of diffusion correction methods (see Appendix A.3).

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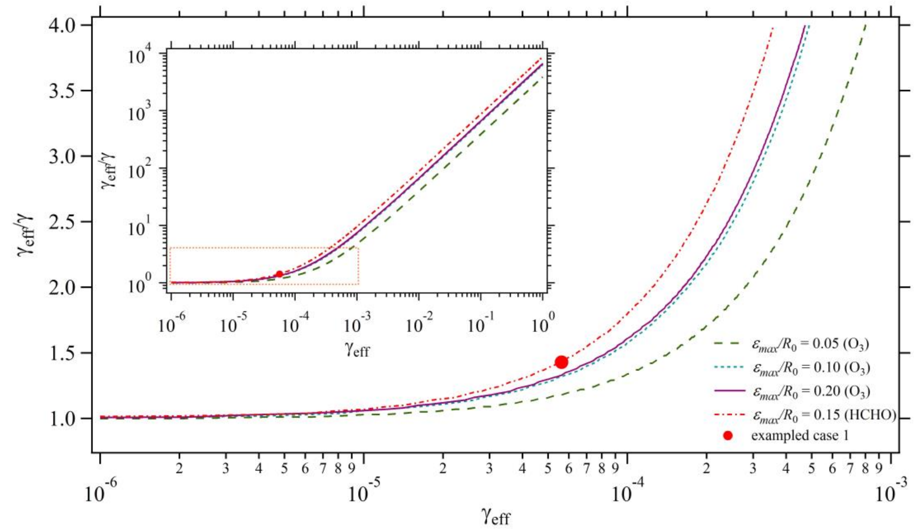

Figure 7. Estimated maximum relative error of the effective uptake coefficient (γ_{eff}), γ_{eff}/γ, versus changing γ_{eff}, for three different cases of relative ratio of the roughness thickness to tube radius (ε_{max}/R_0). The red solid circle represents an example of a soil coating experiment (case 1 in Fig. 5B). The inset shows the complete range of values applicable within the limits of diffusion correction methods (see Appendix A.3), while the main diagram shows a more detailed representative range (orange dotted area in the inset).

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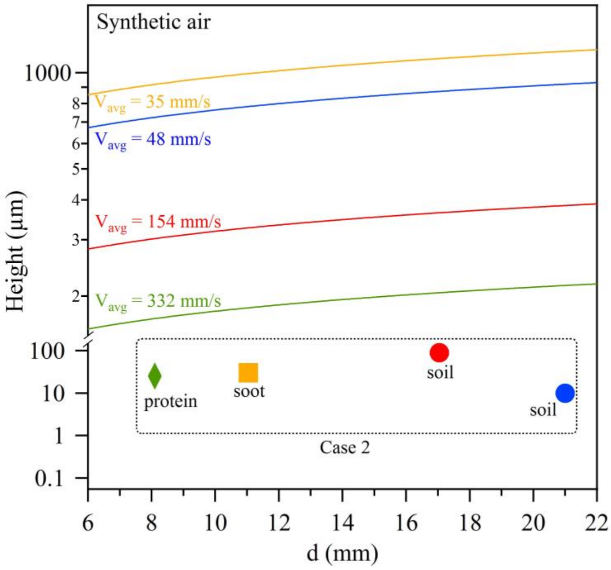
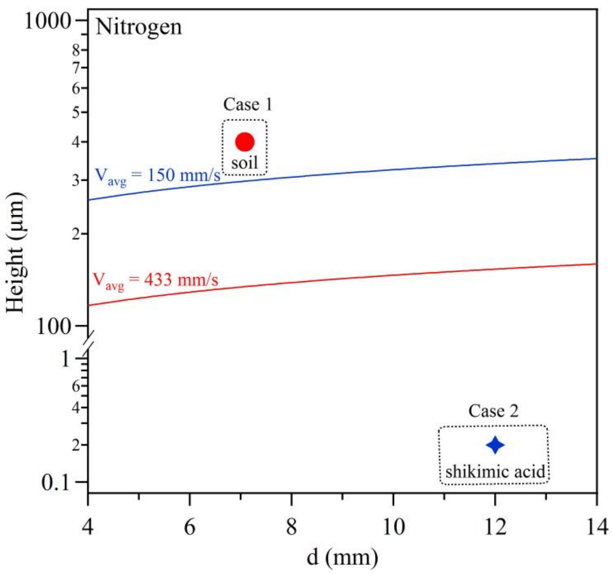


(A)



(B)

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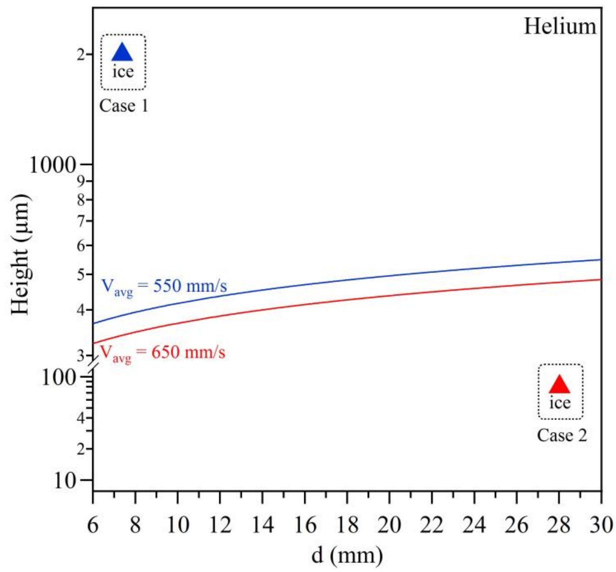

(C)

Figure A.1. Calculated δ_c (solid lines) and exampled coating thicknesses ε_{max} (symbols) versus tube diameter d and flow velocity V_{avg} in flow tube experiments with carrier gases of synthetic air (A), nitrogen (B) and helium (C), respectively. In each plot, the vertical location of symbols relative to solid lines shows which cases their coating roughness may potentially have. The exampled coating material and thickness information are from the same sources as shown in Fig. 5.

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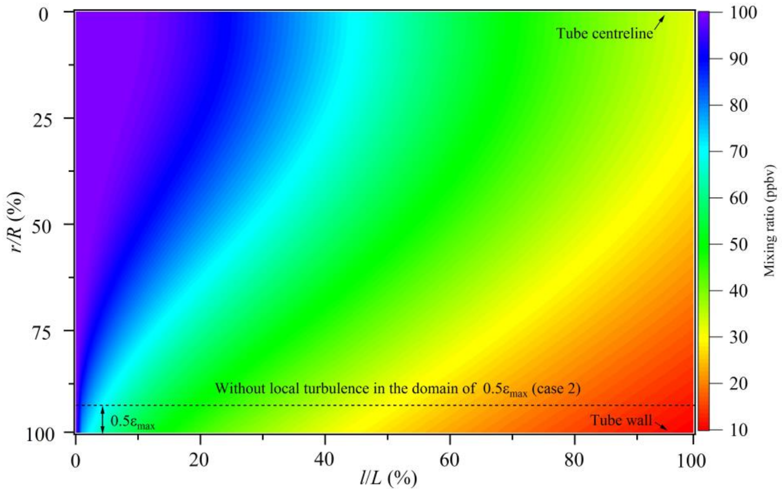
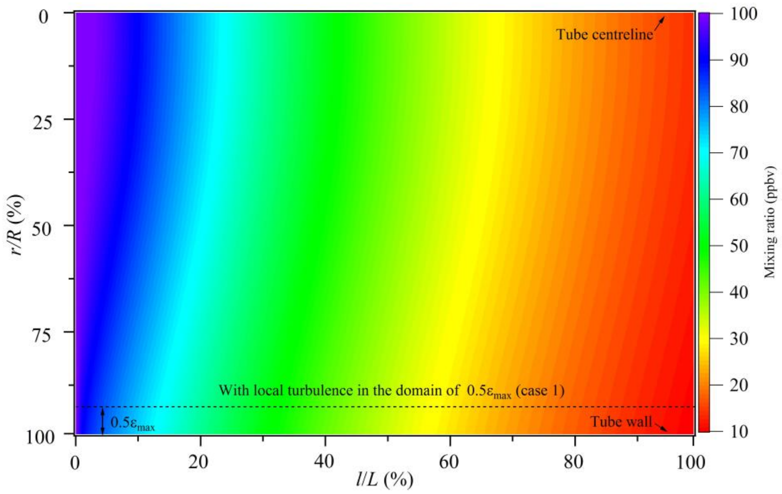


(A)



(B)

Figure A.2. Simulated HCHO concentration profile in a soil-coated flow tube: (A) without local turbulence and (B) with local turbulence in the domain of $0.5\varepsilon_{max}$. r/R denotes the relative radial location and l/L means the relative axial location within the flow tube. The HCHO mixing ratio at tube inlet ($l/L = 0$) is set as 100 ppbv (see color code).

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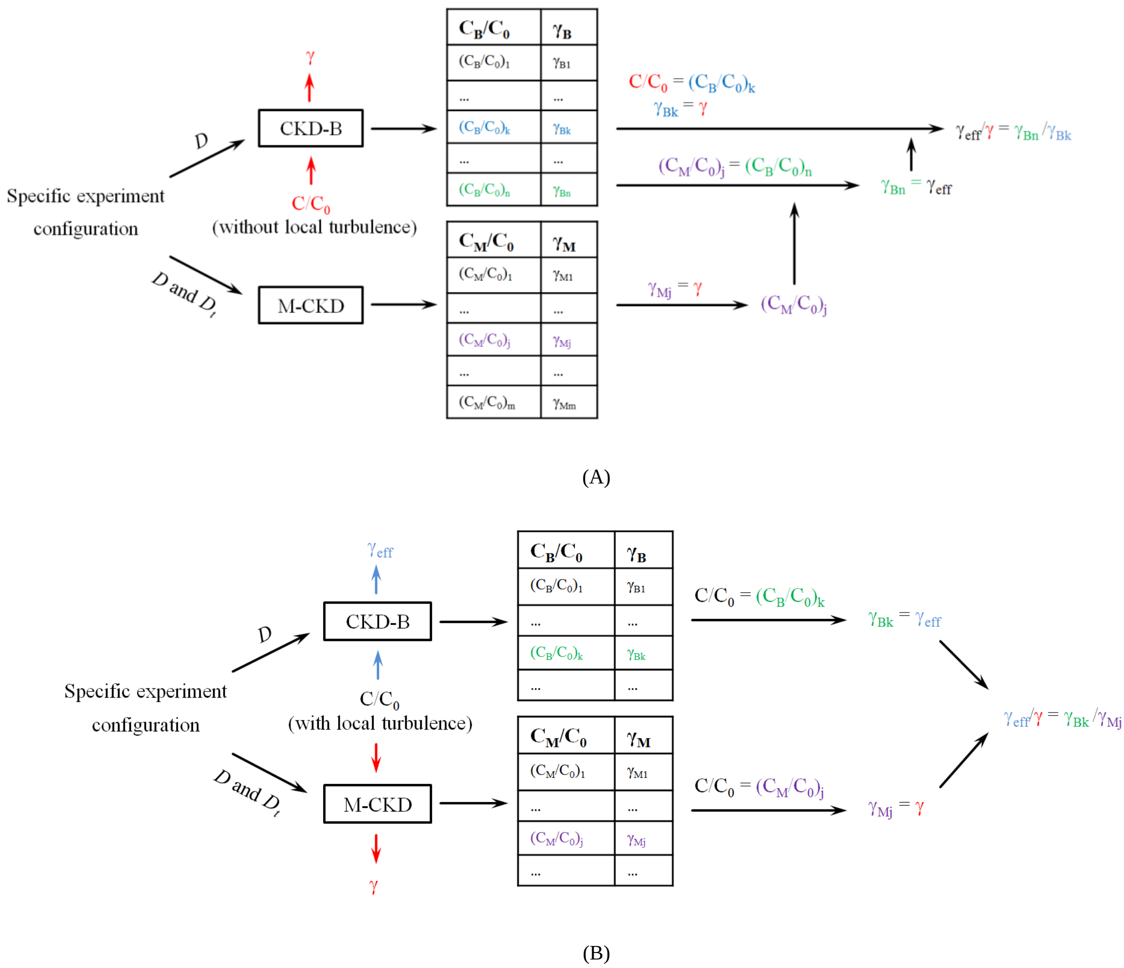

Figure A.3. Schematic of the derivation procedure for γ_{eff}/γ versus γ (A) and γ_{eff} (B), respectively. The subscripts of *B* and *M* in C/C_0 or γ denote the concentration transmittance or uptake coefficient derived from the CKD-B method and the M-CKD method, respectively.

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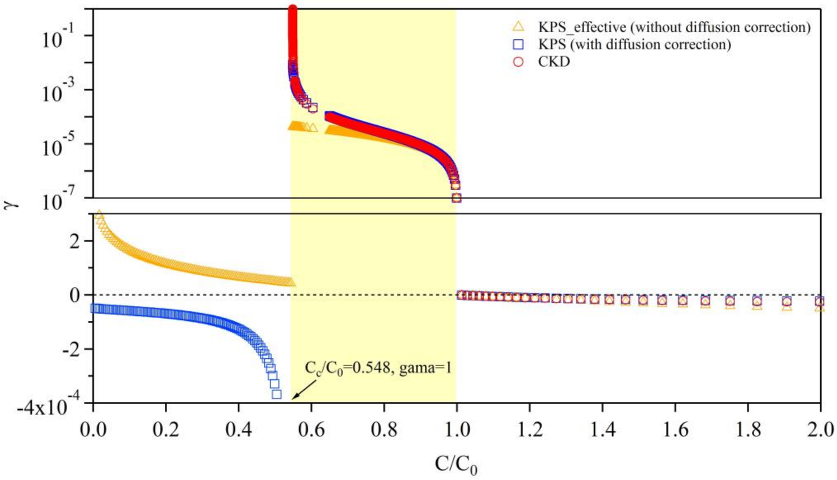

Figure A.4. Comparison between γ (derived from KPS and CKD methods, respectively) versus concentration transmittance C/C_0, based on a specific flow tube experiment configuration (see SO_2 in Table A.1).

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