Uptake of soluble gaseous pollutants by rain droplets in the atmosphere with nocturnal temperature profile

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Abstract

We analyze the uptake of gaseous pollutants by the rain droplets falling in the atmosphere with nocturnal temperature inversion. The rate of uptake of soluble trace gases by falling rain droplets is determined by solving energy and mass conservation equations. In the analysis we accounted for the accumulation of the soluble gas and energy in the bulk of the falling rain droplet. The problem is solved in the approximation of a thin concentration and temperature boundary layers in the vicinity of the droplet surface. It is assumed that the bulk of a droplet, beyond the diffusion boundary layer, is completely mixed and distributions of concentration of the absorbate and temperature are homogeneous and time-dependent in the bulk. The problem is reduced to a system of linear-convolution Volterra integral equations of the second kind which is solved numerically. Calculations are performed using available experimental data on nocturnal temperature profiles in the atmosphere. It is shown than if the concentration of gaseous pollutants in the atmosphere is homogeneous and the absolute temperature in the atmosphere increases with altitude, a droplet absorbs gas during all the period of its fall. In the case when the temperature–altitude curve comprises the nocturnal inversion and temperature fall segments, gas absorption by a falling rain droplet can be replaced by desorption and vice versa. Neglecting temperature inhomogeneity in the atmosphere caused by nocturnal temperature profile leads to significant underestimation of the concentration of gaseous pollutants inside a droplet on the ground. The calculations performed using temperature profiles measured by Corsmeier et al. (1997) showed that the underestimation of the concentration of gaseous pollutants in rain droplets at the ground can exceed 20%.

1. Introduction

Gas absorption by the falling rain droplets is of relevance in meteorology and environmental engineering. Rains play an important role in wet removal of gaseous pollutants from the atmosphere. Scavenging of atmospheric gaseous pollutants by rain droplets is a result of a gas absorption mechanism (Pruppacher and Klett, 1997). Comprehensive study of mass transfer during gas absorption by falling rain droplets is also required for predicting transport of hazardous gases in the atmosphere. Vertical transport of soluble gases in the atmospheric boundary layer (ABL) is an integral part of the atmospheric transport of gases and is important for understanding the global distribution pattern of soluble trace gases. An enhanced understanding of the cycle of soluble gases is also important for the analysis of global climate change (see e.g., Aalto et al., 2006). Clouds and rains play a significant role in vertical redistribution of SO₂, NH₃ and other soluble gases in the atmosphere (see, e.g. Zhang et al., 2006). Scavenging of soluble gases, e.g., SO₂, and NH₃ by rain affects the evolution of vertical distribution of these gases. At the same time the vertical gradients of the soluble gas concentration in the atmosphere affect the rate of gas absorption by rain droplets. Notably, the existing models of global transport in the atmosphere (see, e.g., de Arellano et al., 2004) do not take into account the influence of rains on biogeochemical cycles of different gases.

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Vertical temperature distribution in the atmosphere was discovered in 1749 by A. Wilson (see Wilson, 1826). Inspired by Wilson, numerous measurements and modeling of vertical temperature distribution in the atmosphere (see, e.g. Dines, 1911; Taylor, 1960; Manabe and Wetherald, 1967) revealed the existence of a $6.5 K \cdot km^{-1}$ lapse rate. Evolution of the lapse rate during the last decades is discussed by Trenberth and Smith (2006).

Enhanced interest to a problem of nocturnal temperature inversion during the last decades can be explained by the importance of these meteorological conditions for the dispersion of air pollutants and for fog and frost formation. In his pioneering theoretical study Brunt (1934) showed that infrared radiative transfer behaves like a diffusive process leading to the exponential type temperature profile with a strong negative curvature. Brunt (1934) assumed that the heat flux at the ground is constant throughout the night. Later studies were devoted to forecasting of temperature profile evolution in the lower layers of the atmosphere, the height of the inversion layer and inversion strength (see, e.g. Anfossi et al., 1976; Surridge and Swanepoel, 1987; Anfossi, 1989; Gassmann and Mazzeo, 2001). Two latter parameters are related to the radiation heat flux from the ground to the night sky and the rate at which heat propagates through the atmosphere to the ground. It was demonstrated (see, e.g. Anfossi, 1989) that the height of the inversion layer can expand to hundreds of meters.

Influence of vertical distribution of the temperature in the atmosphere on the rate of gas scavenging by falling rain droplets is explained by a strong nonlinear dependence of the solubility parameter (Henry’s constant) for aqueous solutions of different gases on the temperature (see, e.g. Reid et al., 1987). Accounting for vertical distributions of soluble gaseous pollutants and temperature in the atmosphere requires solution of energy and mass conservation equations which describe gas absorption by falling rain droplets.


Accumulation of the dissolved atmospheric gases in a falling water droplet during gas absorption is determined by a system of unsteady convective diffusion and energy conservation equations. An analytical solution of these equations requires application of rather sophisticated methods (see, e.g. Ruckenstein, 1967). Moreover, in the Earth atmosphere the problem is complicated by the vertical gradients of the absorbate concentration and temperature in the gaseous phase.

The effect of altitudinal distribution of the soluble gases in the atmosphere on the rate of gas absorption by falling rain droplets was investigated by Elperin et al. (2009). The suggested approach includes applying the generalized similar-
4) the bulk of a droplet, beyond the diffusion and temperature boundary layers, is assumed to be completely mixed and the concentration of the absorbate and the temperature are homogeneous in the bulk; 5) the droplet has a spherical shape; 6) internal circulation inside the droplet and the gas velocity in the vicinity of the droplet have axial symmetry; and 7) the solubility parameter (Henry’s constant) depends upon the temperature.

It must be emphasized that the timescale of gas absorption by falling rain droplets is small in comparison with the timescales of the macro processes occurring in the atmosphere. For example, the timescale of rain droplet saturation by the absorbate for a given temperature varies in the range from $10^{-3}$ to 1 s (depending on droplet radii) and the time of a rain droplet fall is of the order of $10^2$ s while a timescale for the effects of turbulence on the whole Stable Boundary Layer (SBL) is of the order of 7 to 30 h (see e.g. Stull, 1988). The characteristic vertical length scale of spatial stratification of falling droplets by turbulence is of the order of $\varepsilon \sim D_f/U$, where $D_f$ is the coefficient of turbulent diffusion. In a stably stratified boundary layer $\varepsilon \sim 1 \sim 10$ m (see, e.g. Soheev et al., 2009). Clearly, $\varepsilon \ll \ell_B$, where $\ell_B = 1$ km is the initial height of the droplet. Consequently, the effects of large-scale turbulent motion on spatial distribution of droplets can be neglected.

The assumptions about the circulation inside a droplet and that the droplet has a spherical shape are valid in the following ranges of the falling in air water droplet radii, Reynolds numbers and velocities: 0.1 mm $\leq R \leq 0.6$ mm, 10 $\leq U \leq 370$ and 0.7 $\leq U \leq 4.6$ (m s$^{-1}$) (see, e.g. Pruppacher and Klett, 1997, Chapter 10). Circulations inside a falling droplet are caused by shear stresses at the droplet–gas interface. The existence of internal circulations allows us to assume that the liquid inside a droplet is a fully mixed and distinguish between the two regions in the droplet, adjacent to the droplet’s surface diffusion or temperature boundary layers and a bulk. A similar approach was applied for the analysis of liquid extraction by the dispersed phase (see Uribe-Ramirez and Korchkinsy, 2000). The analysis of fluid flow around a moving droplet showed that at different Reynolds numbers the tangential fluid velocity component in the vicinity of a gas–liquid interface can be approximated by the following equation (see, e.g. Pruppacher and Klett, 1997, p. 392):

$$v_\theta = -k U \sin \vartheta.$$  \hspace{1cm} (1)

where the coefficient $k$ is equal to 0.04 in the range of the external flow Reynolds numbers ($Re = 2URp_d/\mu_2$) from 10 to $10^2$ (see, e.g. Pruppacher and Klett, 1997, p. 386). The dependence of the terminal fall velocity of liquid droplets on their diameter was analyzed by Pruppacher and Klett (see Pruppacher and Klett, 1997, Chapter 10). In this study we assume that gas absorption does not disturb temperature distribution in gaseous and liquid phases. At the same time heat transfer between the atmosphere and a falling droplet affects the rate of gas absorption/desorption by a falling droplet. This dependence is explained by a very strong variation of the solubility parameter (Henry’s constant) with the temperature (see, e.g. Reid et al., 1987). Since the dependence of other thermodynamic parameters on the temperature is by the order of magnitude weaker, we assume them to be constant. Following the approach suggested by Ruckenstein (1967) we arrive at the following system of transient equations of convective diffusion and energy conservation for the liquid and gaseous phases which account for convection in radial and tangential directions:

$$\frac{\partial x_i}{\partial t} + U \cdot k \left( -\sin \vartheta \frac{\partial x_i}{\partial R} + 2y \cos \vartheta \frac{\partial x_i}{\partial y} \right) = D_i \frac{\partial^2 x_i}{\partial y^2}. \hspace{1cm} (2)$$

$$\frac{\partial T_i}{\partial t} + U \cdot k \left( -\sin \vartheta \frac{\partial T_i}{\partial R} + 2y \cos \vartheta \frac{\partial T_i}{\partial y} \right) = a_i \frac{\partial^2 T_i}{\partial y^2}. \hspace{1cm} (3)$$

where $i = 1, 2$. The radial fluid velocity component in Eqs. (2) and (3) is determined by Eq. (1) and the continuity equation: $v_r = 2k \cos \vartheta \frac{U y}{R}$. Eqs. (2) and (3) are written in a frame attached to the falling droplet and valid for $y \ll R$. Since the velocity of the droplet fall is known and $z = U \cdot t$, the vertical coordinate-dependent boundary conditions can be transformed into the time-dependent boundary conditions. The vertical coordinate $z$ is aligned with the direction of the droplet fall. The initial and boundary conditions to Eqs. (2) read:

$$x_1 = x_0, \quad \text{at} \quad t = 0 \hspace{1cm} (4)$$

$$x_2 = x_{b_2}(t) \quad \text{as} \quad y \to \infty, \hspace{1cm} (5)$$

$$x_1 = x_{b_1}(t) \quad \text{as} \quad y \to -\infty, \hspace{1cm} (6)$$

$$x_1 = m x_2 \quad \text{at} \quad y = 0, \hspace{1cm} (7)$$

$$N_{D_1} = N_{D_2} \quad \text{at} \quad y = 0. \hspace{1cm} (8)$$

The initial and boundary conditions to Eqs. (3) can be written as follows:

$$T_1 = T_{b_1}, \quad \text{at} \quad t = 0 \hspace{1cm} (9)$$

$$T_2 = T_{b_2}(t) \quad \text{as} \quad y \to \infty, \hspace{1cm} (10)$$

$$T_1 = T_{b_1}(t) \quad \text{as} \quad y \to -\infty, \hspace{1cm} (11)$$

$$T_1 = T_2 \quad \text{at} \quad y = 0, \hspace{1cm} (12)$$

$$N_{T_1} = N_{T_2} \quad \text{at} \quad y = 0, \hspace{1cm} (13)$$

where $N_{b_1} = -D_i \frac{\partial x_i}{\partial y}, N_{T_1} = -\lambda_i \frac{\partial T_i}{\partial y}, y = r - R, y \ll R$, coefficient $m = H_A R_e T_{C_2}/C_1$ is a distribution coefficient that characterizes the solubility of gases in liquids, $H_A$ is Henry’s constant (see Seinfeld and Pandis, 2006, p. 288) and $R_e$ is the universal gas constant. The equations of convective diffusion and energy conservation (2) and (3) describe variations of concentration and temperature near the gas–droplet interface inside and outside the droplet in a boundary-layer approximation. The characteristic values of the diffusion Peclet number of the droplet in this study are of the order of $10^2$ and $10^3$ for the liquid and gaseous phases, respectively, and the characteristic values of the temperature Peclet number of the droplet are of the order of $10^4$ for the liquid phase and $10^2$ for the gaseous phase. Consequently, the use of the boundary-layer approximation is justified. The solution of Eqs. (2) and (3) can be obtained using the similarity transformation method which was suggested first by Ruckenstein (1967).
3. Method of solution

Since the boundary conditions (5)–(8) and (10)–(13) to Eqs. (2) and (3) are time-dependent, the solution can be found by combining the similarity transformation method with Duhamel’s theorem. Let us introduce the following self-similar variables (for details see Ruckenstein, 1967):

$$\eta_j = \frac{y}{\partial_j(T, \Theta)} = \frac{Y}{\Delta_i}, \eta_0 = \frac{y}{\partial_0(T, \Theta)} = \frac{Y}{\Delta_0}. \quad (14)$$

Since gas absorption (desorption) does not affect the distribution of the temperature in both phases, heat transfer equation (Eqs. (3) and (9)–(13)) can be solved independently from the mass transfer equation. Variables $\eta_j$ allow us to obtain the solution of a system of partial differential Eq. (3) in the following form:

$$\Theta_i(Y, \Theta, \tau) = \frac{\partial}{\partial \tau} \int_{\eta_i}^{\eta_i(\Theta, \tau - \Delta \eta_i)} \left[ \Theta_{b1}(\xi) + \frac{(-1)^{i-1}(\gamma_1 \alpha_{b2}(\xi) - \Theta_{b1}(\xi))}{1 + \gamma_1 \alpha_{b1}(\xi)} \right] d\xi. \quad (15)$$

The solution of Eq. (2) with boundary conditions (5)–(10) reads:

$$X_i(Y, \Theta, \tau) = \frac{\partial}{\partial \tau} \int_{\eta_i}^{\eta_i(\Theta, \tau - \Delta \eta_i)} Y X_{b1}(\xi) + \frac{(-1)^{i-1}(X_{b1}(\xi) - m(\Theta, X_{b2}(\xi)) \cdot (\gamma D)^{-1}}{1 + m(\Theta, \gamma D)} d\xi. \quad (16)$$

where $\gamma_1 = c_{p1} c_{1}/c_{p2} c_{2}$, $a = \sqrt{a_1/a_2}$, $\Theta_1 = T_1/T_2$.

$$\Delta_0^2 = \frac{4}{\rho_{f0} \sin^2(\Theta)} \left( \cos(\Theta) - \frac{1}{3} \cos^3(\Theta) - \frac{1-f(0, \tau)}{1+f(0, \tau)} \right), \Delta_i^2 = \frac{4}{\rho_{f0} \sin^2(\Theta)} \frac{a_i}{D_i}. \quad (17)$$

where $f(\Theta, \tau) = t g^2(0) \exp(2\tau)$, $P_{f0} = \frac{R Q_{f0}}{D_i}$, $P_{f1} = \frac{R K Q_{f0}}{D_i}$, $\tau = t \Delta k / R$.

The variables $\Theta_{b1}(\tau)$ and $X_{b1}(\tau)$ are the unknown functions of the temperature at the surface of a droplet:

$$\Theta(\tau) = \Theta_{b1}(\tau) + \frac{\Theta_{b2}(\tau) - \Theta_{b1}(\tau)}{1 + \gamma_1 \alpha_{b1}(\Theta, \tau)}. \quad (18)$$

Substituting expression for the temperature in the droplet (Eq. 15) into Eq. (19) yields:

$$\Theta_{b1}(t) = \frac{3}{\sqrt{\pi} \rho_{f0}(1 + \gamma_1 \alpha_{b1})} \int_{0}^{\tau} \sin \delta \ d\delta. \quad (21)$$

where $\Theta_{b1} = T_0 / T_{10}$. Substituting expression (16) for the absorbate concentration in the droplet into Eq. (20) yields:

$$X_{b1}(\tau) = \frac{X_{b1}(0) m_{b0}}{m_{b0} D_i} + \frac{3}{\sqrt{\pi} \rho_{f0} \gamma_1} \int_{0}^{\tau} \left[ X_{b2}(\xi) - m(\Theta, \xi) \Theta_{b1}(\xi) \right] d\xi. \quad (22)$$

Note that Henry’s constant in Eq. (22) is a function of the temperature.

If temperature distribution in the atmosphere is homogeneous, the problem reduces to solving Eq. (22) with a constant parameter of solubility $m_{b0}$.

Eqs. (21) and (22) are linear–convolution Volterra integral equations of the second kind and can be written in the following form:

$$f(t) = \frac{1}{\theta} \int_{0}^{t} f(\xi) K(t, \xi) d\xi + g(t). \quad (24)$$

The method of the solution of the integral Eq. (24) is based on approximating the integral in Eq. (24) using some quadrature formula:

$$\int_{0}^{b} f(\xi) d\xi = \sum_{i=1}^{N} \alpha_i F(\xi_i) + R_{M}[F],$$

where $\xi_i \in [a, b]$, $i = 1, 2, ..., N; \alpha_i$ – coefficients which are independent of the function $F$; $R_{M}[F]$ – remainder of the series after the N-th term. Using a uniform mesh with an increment $h \left( T_i = T_0 + i \Delta k, h \equiv \frac{T_{10} - T_0}{N} \right)$ and applying the trapezoidal integration rule yield:

$$f(0) = g(0),$$

$$\left( 1 - \frac{1}{2} h K_{ii} \right) f_i = h \left( \frac{1}{2} K_{i0} f_0 + \sum_{j=1}^{i-1} K_{ij} f_j \right) + g_i. \quad (25)$$

where $i = 1, ..., N, f_i = f(i \cdot h)$, $g_i = g(i \cdot h)$, $K_{ij} = K(i \cdot h, j \cdot h)$.

In order to solve the system of Eqs. (21) and (22) we can represent Eq. (24) as a vector equation for the vector of $M$ ($M = 1, 2$) functions $f(t)$. In this case the kernel $K(t, \xi)$ is a $M \times M$ matrix.
matrix and Eq. (24) can be viewed as a vector equation. For each 

\( i \) we solved the \( M \times M \) set of linear algebraic equations using the 

Gaussian elimination method.

4. Results and discussion

Calculations of temperatures and concentrations of the 
dissolved gas inside water droplets were performed for the 

rain droplets with diameter 1.2 mm falling in the non-

homogeneous atmosphere containing a soluble gaseous 
pollutant. This diameter of rain droplets is equal to the 

average diameter of rain droplets of Feingold–Levin droplet 

size distribution (Feingold and Levin, 1986) corresponding to 

a low rain intensity of 5–6 mm/h.

The suggested model was applied for the numerical analysis 
of uptake of soluble ammonia (NH\(_3\)) and sulfur dioxide (SO\(_2\)) by 

rain droplets falling in the atmosphere with the nocturnal 
temperature profile. The thermophysical properties of the 
ammonia–water and sulfur dioxide–water systems are pre-

sented in Table 1. In numerical calculations we used the 
temperature profiles measured during the night from 23 to 24 
September 1994 by Corsmeier et al. (1997) in Essen and 

Hannover, Germany while the concentration of soluble gaseous 
pollutants in the atmosphere was assumed to be uniform. The 

known concentration profile as well as the temperature profile in the 

external gaseous mixture appears explicitly in the 

obtained analytical solution (see Eqs. (18), (21) and (22)). 

Therefore numerical calculations require the knowledge of the 
temperature and concentration profiles measured or calculated 
using a certain mathematical model of heat and mass transfer in 

the Atmospheric Boundary Layer (ABL). However, to the best of 

our knowledge, there are no publications where nocturnal 
temperature and concentration profiles were measured simul-

taneously. Moreover, gas absorption by falling rain droplets is 
governed by various physical and chemical phenomena, e.g. 

droplet evaporation, internal circulation, effect of external 

concentration and temperature profiles, chemical reactions in 

the atmosphere, dissociation of the dissolved molecules into 
ions, etc. Taking into account all these effects renders the 

problem quite involved. Consequently, when a certain param-

eters vary. The nocturnal vertical profile of the atmo-

spheric temperature measured by Corsmeier et al. (1997) 

shows an increase of the atmospheric temperature with height 

from a ground up to approximately 500 m and a further 
temperature decrease with height for heights larger than 500 m 

(see Fig. 2). At the same time the nocturnal profile in Hannover 

reveals a strong temperature increase up to 1000 m altitude 

(see Fig. 3). The vertical profiles of the atmospheric tempera-
ture were approximated using polynomial functions (the 
coefficients of the polynomial function are showed in Figs. 2 

and 3). The droplet surface temperature was calculated using 

Eqs. (18) and (21).

In our previous study we showed that when distributions of 
soluble trace gas and temperature in the atmosphere are 

uniform, the concentration of the dissolved gas in the droplet 
attains saturation after a certain time interval; at the final 

stage of their fall, droplets do not absorb soluble trace gases 
(see Elperin et al., 2009). The presence of temperature and 
concentration gradients in the atmosphere changes the 
scenario of gas absorption by falling rain droplets.

The effect of nocturnal temperature distribution in the 

atmosphere on soluble gas scavenging by falling rain droplet 
(see Figs. 4 and 5) is analyzed via the numerical solution of 

the system of Eqs. (21) and (22). The temperature of the 
droplet surface is calculated using Eq. (18) and the depend-

ence of Henry’s constant on the temperature is taken into 
account using Eq. (23). The initial temperature of a droplet 
was assumed to be equal to an air temperature in the below-
cloud atmosphere immediately adjacent to the cloud. 

Dependence of the interfacial temperature of falling rain 

droplet vs. altitude in the atmosphere is shown in Figs. 2 and 

3. The concentration of the trace soluble gas in the 
atmosphere was assumed to be uniform. Calculations of the 

dissolved average gas concentration were performed (see 

Figs. 4 and 5) for rain droplets initially saturated with soluble 

gas (solid curves) and for the rain droplet with a negligibly 

small initial concentration of the dissolved gas (dashed 

curves). In the case when the soluble gas is distributed 
uniformly in the atmosphere and the atmospheric tempera-

ture depends on the altitude (see Fig. 2) gas absorption by 
the falling rain droplet is replaced by desorption and vice versa 
(see Fig. 4). In particular, in a region where the temperature 

in the atmosphere decreases with height (as it is shown in 
Fig. 2), the initially saturated falling droplet desorbs gas into 
the atmosphere (see Fig. 4). In contrast, the droplet with an 
initial negligibly small concentration of the dissolved gas 

absorbs gas from the atmosphere in this region. Inspection of 

Fig. 4 shows that eventually absorption is replaced by 

desorption. Up to the altitude of approximately 500 m the 
temperature increases with height due to nocturnal inver-

sion. In this region gas desorption is replaced by absorption. 

This complicated behavior can be explained by the depen-
dence of Henry’s constant and gas solubility in the liquid on 

the temperature. The lower the temperature the higher the 
solubility of the trace gas in the liquid and the higher the 

concentration of saturation of a soluble gas in a droplet. In the 

case of the inversed nocturnal atmospheric temperature 
profile the rain droplet absorbs the soluble gas during all the 
period of its fall (Fig. 5). The latter behavior does not depend 
on the initial concentration of the dissolved gas in a droplet.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Thermophysical properties.</th>
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<tbody>
<tr>
<td>Gas</td>
<td>( h_s ) ( 10^{-2} ) mol m(^{-3} ) Pa(^{-1} )</td>
</tr>
<tr>
<td>SO(_2)</td>
<td>1.21</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>61.2</td>
</tr>
</tbody>
</table>
The results of numerical calculations of gas absorption of SO$_2$ by initially saturated rain droplets falling in the atmosphere with temperature profiles measured by Corsmeier et al. (1997) in Hannover and Essen are shown in Fig. 6. The comparison of Figs. 4–6 demonstrates that the dependencies of the concentrations of the dissolved ammonia and sulfur dioxide in the bulk of a falling rain droplet on the altitude are similar, and the difference is only quantitative as can be readily seen in Figs. 4–6.

In this study the numerical calculations were conducted for homogeneous vertical distribution of soluble gases. Clearly, this assumption can be violated in some cases. The concentration of the soluble gases in the immediate vicinity of the ground or ocean surface decreases due to dry deposition or due to soluble gas absorption by water. This situation was discussed in our previous study (see Elperin et al., 2009). The distribution of sulfur dioxide in the atmosphere is rarely uniform since high stacks of power plants often emit it into the troposphere. Consequently, feasibility of desorption of SO$_2$ which is indicated in this study, can be of relevance in the analysis of gaseous pollutant scavenging by rain.

Neglecting temperature inhomogeneity in the atmosphere caused by the nocturnal temperature profile causes considerable underestimation of the concentration of gaseous pollutants in a droplet on the ground. As it can be seen from Figs. 4–6 for the temperature profiles measured by Corsmeier et al. (1997) underestimation of the concentration of gaseous pollutants in rain droplets at the ground can exceed 20%.
The developed model can be used for the analysis of scavenging of hazardous gases in the atmosphere by rain droplets and can be used for the creation of various parameterization and look-up tables that can be incorporated into the existing computer codes.

Appendix A

Nomenclature

- $a$ square root of the temperature diffusivities ratio, \( \sqrt{\alpha_1 / \alpha_2} \)
- $c_p$ specific heat, J mol\(^{-1}\) K\(^{-1}\)
- $C_i$ molar density at the bulk of fluid, mol m\(^{-3}\)
- $D_i$ molecular diffusion coefficient, m\(^2\) s\(^{-1}\)
- $D$ square root of the diffusivities ratio, $\sqrt{D_1 / D_2}$
- $H_A$ Henry’s law constant, mol l\(^{-1}\) atm\(^{-1}\)
- $k$ coefficient in Eq. (1)
- $N_{D_0}$ molar flux density, mol m\(^{-2}\) s\(^{-1}\)
- $N_f$ heat flux density, W m\(^{-2}\)
- $m$ distribution coefficient
- $m_0$ distribution coefficient at temperature $T_{50}$
- $Pe_D = kRU / D_i$ Peclet number for a moving droplet
- $Pe_f = kRU / a_i$ Peclet number for a moving droplet
- $r$ radial coordinate, m
- $R_g$ universal gas constant, J mol\(^{-1}\) K\(^{-1}\)
- $t$ time, s
- $T$ temperature, K

1. The suggested model of gas absorption by a falling liquid droplet in the presence of inert admixtures takes into account a number of effects that were neglected in the previous studies, such as the effect of dissolved gas and energy accumulation inside a rain droplet and the effect of temperature distribution in the atmosphere on the rate of soluble gas uptake.

2. It is shown that the dependence of the radius-averaged concentration and temperature vs. time in a falling droplet is determined by a system of linear-convolution Volterra integral equations of the second kind which is easier to solve numerically than the original system of partial differential equations.

3. It is shown that in a region where the concentration of the soluble species in the atmosphere is uniform and the temperature increases with height, due to nocturnal inversion, the rain droplet absorbs gas from the atmosphere during all the period of its fall. This behavior is explained by the increase of trace gas solubility in a droplet with a decrease of the temperature. At the same time in our model the average temperature in a droplet at a given altitude is not equal to the atmospheric gas temperature at the same altitude. Consequently, the instantaneous concentration of the dissolved gas in a droplet is not equal to the concentration of saturation in a liquid corresponding to the concentration of a trace soluble gas in an atmosphere at a given height. Therefore, the exact quantitative analysis of the soluble trace gas concentration evolution in a droplet can be performed only through the numerical solution of a system of integral equations.

4. Neglecting temperature inhomogeneity in the atmosphere caused by the nocturnal temperature profile leads to considerable underestimation of the concentration of gaseous pollutants in a droplet at the ground. Calculations performed using the available experimental data on nocturnal temperature profiles in the atmosphere showed that the underestimation of the concentration of gaseous pollutants in a droplet at the ground can exceed 20%.

5. In the case when the soluble gas is distributed uniformly in the atmosphere and the temperature-altitude curve comprises nocturnal inversion and temperature fall segments, gas absorption by the falling rain droplet can be replaced by desorption and vice versa.
$U$ translational velocity of a droplet, m s$^{-1}$
$v_{u}$, $v_{b}$ velocity components, m s$^{-1}$
$x$ molar fraction of an absorbate
$x_{010}$ initial value of molar fraction of an absorbate in a droplet
$x_{20}$ value of molar fraction of an absorbate in a gas phase at height $H$
$x_{21}(t)$ molar fraction of an absorbate in a bulk of a droplet
$x_{22}(t)$ molar fraction of an absorbate in a bulk of a gas phase
$X_{1}(t) = x_{1}(t)/x_{020}$ relative molar fraction of an absorbate in a liquid phase
$X_{2}(t) = x_{2}(t)/x_{20}$ relative molar fraction of an absorbate in a gaseous phase
$y$ distance from the surface of a droplet, m
$Y = y/R$ dimensionless distance from the surface of a droplet
$z$ coordinate in a vertical direction, m

Greek symbols
$\Theta = T_{i}/T_{g0}$ dimensionless temperature
$\gamma = C_{i}/C_{g}$ molar densities ratio
$\delta_{d0}$ thickness of a diffusion boundary layer, m
$\delta_{T}$ thickness of a thermal boundary layer, m
$\Delta T = \delta_{T}/R$ dimensionless thickness of a boundary layer
$\Delta H^e$ enthalpy change, J mol$^{-1}$
$\lambda$ thermal conductivity, W m$^{-1}$K$^{-1}$
$\xi$ variable
$\eta_{i}$ similarity variable
$\vartheta$ angle
$\tau = tUk/R$ dimensionless time

Subscripts
$0$ value at height $H$ in the atmosphere
$1$ liquid phase
$2$ gaseous phase
$b$ value in the bulk
$r$ radial direction
$\theta$ tangential direction
$s$ value at the gas–liquid interface

References