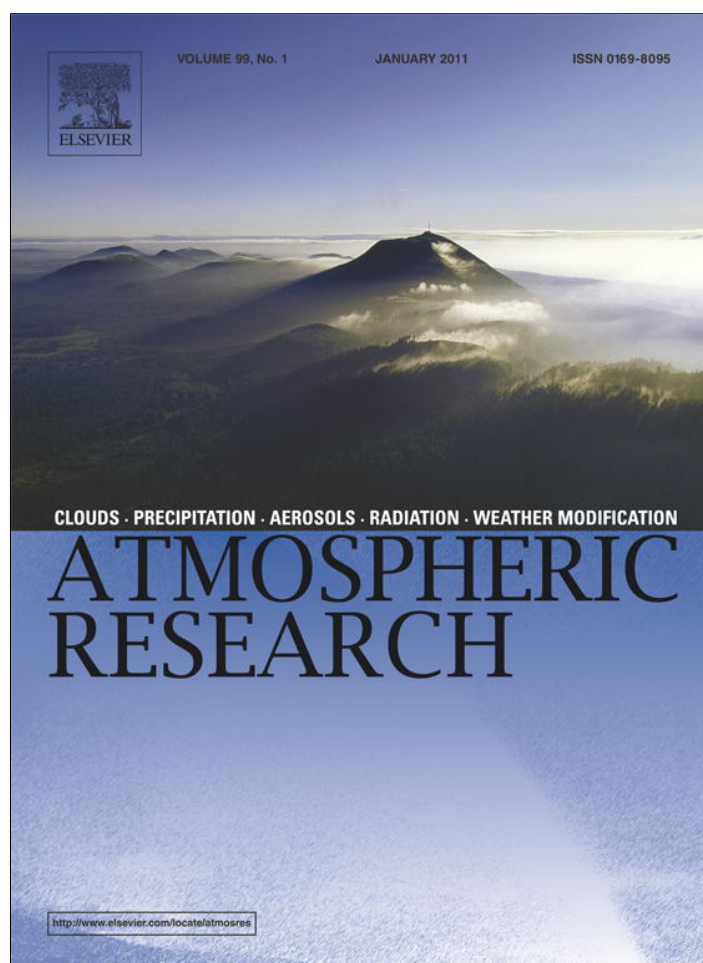




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Atmospheric Research

journal homepage: www.elsevier.com/locate/atmos

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

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ARTICLE INFO

Article history:

Received 7 March 2010

Received in revised form 16 September 2010

Accepted 17 September 2010

Keywords:

Atmosphere

Gaseous pollutants

Rain droplets

Gas scavenging

Nocturnal temperature profile

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 that 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%.

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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 $6.5 \text{ K} \cdot \text{km}^{-1}$ 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.

Due to the differences in solubility of gases in liquids, mass transfer during absorption of a soluble gas by droplets in the presence of an inert admixture can be continuous-phase controlled, liquid-phase controlled or conjugate. Continuous-phase controlled mass transfer by falling droplets was discussed by Kaji et al. (1985), Altwicker and Lindhjem (1988), Waltrop et al. (1991) and Wurzler (1998). Liquid-phase controlled mass transfer was studied, e.g., by Amokrane and Caussade (1999) and Chen (2001). Mass transfer controlled by both phases was analyzed by Walcek and Pruppacher (1984), Chen (2004), Elperin and Fominykh (2005), Elperin et al. (2007, 2008, 2009).

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-

ity transformation to a system of transient equations of convective diffusion and Duhamel's theorem. Then the problem reduces to the numerical solution of a linear-convolution Volterra integral equation of the second kind. Note that in our previous study (Elperin et al., 2009) it was assumed that the atmospheric temperature distribution is uniform.

In the present study we investigate the effect of the nocturnal temperature profile in the atmosphere on the rate of gas absorption by falling droplets. In the case of the uniform vertical distribution of the trace gas and temperature in the atmosphere the solution obtained in the present study recovers the expressions obtained in our previous study (Elperin and Fominykh, 2005). The latter approach was validated by comparing the numerical solution with available experimental data for CO_2 and SO_2 absorption by a falling droplet (see Altwicker and Lindhjem, 1988; Amokrane and Caussade, 1999).

2. Description of the model

Consider absorption of a soluble gas from a mixture containing an inert gas by a moving droplet. At time $t = 0$ the droplet begins to absorb gas from the atmosphere. Distribution of the concentration of the absorbate and temperature in the gaseous phase in the vertical direction is assumed to be known. Schematic view of a falling droplet with the attached frame of coordinates is shown in Fig. 1.

In the analysis we account for the resistance to heat and mass transfer in both phases and use the following simplifying assumptions: 1) we employ the approximation of the infinite dilution of the absorbate in the absorbent; 2) thicknesses of the diffusion and temperature boundary layers in both phases are assumed small compared with the droplet's size; 3) tangential molecular heat and mass transfer rates along the surface of a spherical droplet are assumed small compared with the molecular heat and mass transfer rates in the normal direction;

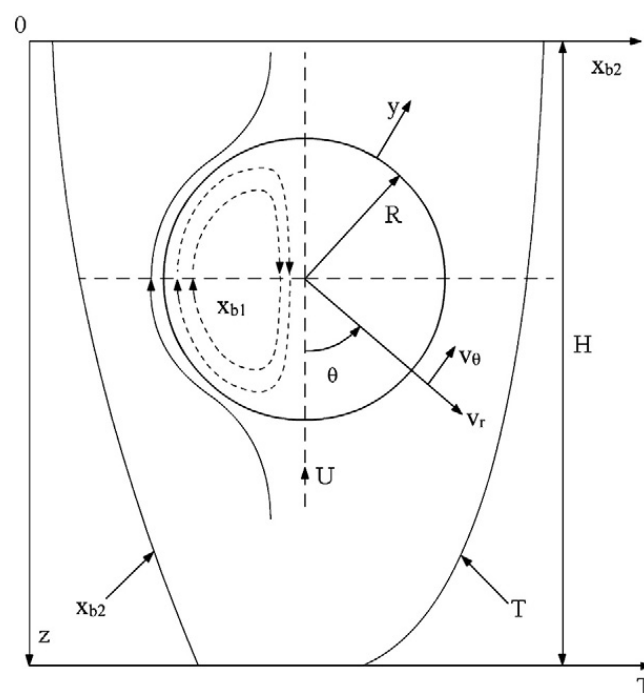


Fig. 1. Schematic view of a falling droplet.

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^{-1} 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 $\ell \sim D_T/U$, where D_T is the coefficient of turbulent diffusion. In a stably stratified boundary layer $\ell \sim 1 \div 10$ m (see, e.g. Sofiev et al., 2009). Clearly, $\ell \ll L_0$, where $L_0 = 1$ 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: $0.1 \text{ mm} \leq R \leq 0.6 \text{ mm}$, $10 \leq \text{Re} \leq 370$ and $0.7 \leq U \leq 4.6 \text{ (m s}^{-1}\text{)}$ (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 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 Korchinsky, 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):

$$v_\vartheta = -kU \sin \vartheta, \quad (1)$$

where the coefficient k is equal to 0.04 in the range of the external flow Reynolds numbers ($\text{Re} = 2UR\rho_2/\mu_2$) from 10 to 10^3 (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:

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

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

where $i = 1, 2$. The radial fluid velocity component in Eqs. (2) and (3) is determined by Eq. (1) and the continuity equation: $v_r = 2k \cos \vartheta U y/R$. 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:

$$x_i = x_{i0}, \quad \text{at } t = 0 \quad (4)$$

$$x_2 = x_{b2}(t) \quad \text{as } y \rightarrow \infty, \quad (5)$$

$$x_1 = x_{b1}(t) \quad \text{as } y \rightarrow -\infty, \quad (6)$$

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

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

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

$$T_i = T_{i0}, \quad \text{at } t = 0 \quad (9)$$

$$T_2 = T_{b2}(t) \quad \text{as } y \rightarrow \infty, \quad (10)$$

$$T_1 = T_{b1}(t) \quad \text{as } y \rightarrow -\infty, \quad (11)$$

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

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

where $N_{D_i} = -D_i C_i \frac{\partial x_i}{\partial y}$, $N_{T_i} = -\lambda_i \frac{\partial T_i}{\partial y}$, $y = r - R$, $y \ll R$, coefficient $m = H_A R_g T C_2 / C_1$ 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_g 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 10^6 and 10^2 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):

$$\eta_{Ti} = \frac{y}{\delta_{Ti}(t, \vartheta)} = \frac{Y}{\Delta_{Ti}} \cdot \eta_{Di} = \frac{y}{\delta_{Di}(t, \vartheta)} = \frac{Y}{\Delta_{Di}}. \quad (14)$$

Since gas absorption (desorption) does not affect 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 η_{Ti} allow us to obtain the solution of a system of partial differential Eq. (3) in the following form:

$$\Theta_i(Y, \vartheta, \tau) = \frac{\partial}{\partial \tau} \int_0^{\tau} \left[\Theta_{bi}(\xi) + \frac{(-1)^{i-1} \cdot (\gamma_T a)^{i-1} \cdot [\Theta_{b2}(\xi) - \Theta_{b1}(\xi)]}{1 + \gamma_T a} \operatorname{erfc} \left(\frac{Y}{\Delta_{Ti}(\vartheta, \tau - \xi)} \right) \right] d\xi. \quad (15)$$

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

$$X_i(Y, \vartheta, \tau) = \frac{\partial}{\partial \tau} \int_0^{\tau} \left[X_{bi}(\xi) + \frac{(-1)^i (X_{b1}(\xi) - m(\Theta_s) X_{b2}(\xi)) \cdot (\gamma D)^{i-1}}{1 + m(\Theta_s) \gamma D} \operatorname{erfc} \left(\frac{Y}{\Delta_{Di}(\vartheta, \tau - \xi)} \right) \right] d\xi, \quad (16)$$

where $\gamma_T = c_{p1} C_1 / c_{p2} C_2$, $a = \sqrt{a_1 / a_2}$, $\Theta_s = T_s / T_{10}$,

$$\Delta_{Di}^2 = \frac{4}{Pe_{Di} \sin^4(\vartheta)} \left\{ \cos(\vartheta) - \frac{1}{3} \cos^3(\vartheta) - \left[\frac{1 - f(\vartheta, \tau)}{1 + f(\vartheta, \tau)} - \frac{1}{3} \left(\frac{1 - f(\vartheta, \tau)}{1 + f(\vartheta, \tau)} \right)^3 \right] \right\}, \quad \Delta_{Ti}^2 = \Delta_{Di}^2 \cdot \frac{a_i}{D_i}, \quad (17)$$

$f(\vartheta, \tau) = \operatorname{tg}^2 \left(\frac{\vartheta}{2} \right) \exp(2\tau)$, $Pe_{Di} = \frac{RkU}{D_i}$, $Pe_{Ti} = \frac{RkU}{a_i}$, $\tau = tUk/R$ is dimensionless time, $Y = y/R$. The expression for the temperature at the surface of a droplet reads:

$$\Theta_s(\tau) = \Theta_{b1}(\tau) + \frac{\Theta_{b2}(\tau) - \Theta_{b1}(\tau)}{1 + \gamma_T a}. \quad (18)$$

The variables $\Theta_{b1}(\tau)$ and $X_{b1}(\tau)$ are the unknown functions of time which can be determined by means of an integral energy and material balances for the droplet (see, e.g. Elperin et al., 2009):

$$\frac{d\Theta_{b1}}{d\tau} = \frac{3}{2 \cdot Pe_{Ti}} \int_0^{\pi} \frac{\partial \Theta_1}{\partial Y} \bigg|_{Y=0} \sin \vartheta \, d\vartheta, \quad (19)$$

$$\frac{dX_{b1}}{d\tau} = \frac{3}{2 \cdot Pe_{D1}} \int_0^{\pi} \frac{\partial X_1}{\partial Y} \bigg|_{Y=0} \sin \vartheta \, d\vartheta. \quad (20)$$

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

$$\Theta_{b1}(t) = 1 + \frac{3}{\sqrt{\pi} \cdot Pe_{Ti} (1 + \gamma_T a)} \int_0^{\tau} [\Theta_{b2}(\xi) - \Theta_{b1}(\xi)] \int_0^{\pi} \frac{\sin \vartheta \, d\vartheta \, d\xi}{\Delta_{T1}(\vartheta, \tau - \xi)}, \quad (21)$$

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

$$X_{b1}(\tau) = \frac{X_{b10}}{m_0 X_{b20}} + \frac{3}{\sqrt{\pi} \cdot Pe_{D1}} \int_0^{\tau} \left[\frac{X_{b1}(\xi) - m(\Theta_s(\tau)) X_{b2}(\xi)}{1 + m(\Theta_s(\tau)) \cdot \gamma D} \right] \int_0^{\pi} \frac{\sin \vartheta \, d\vartheta \, d\xi}{\Delta_{D1}(\vartheta, \tau - \xi)}. \quad (22)$$

Note that Henry's constant in Eq. (22) is a function of the temperature. The magnitude of the temperature at a droplet interface is determined by Eqs. (18) and (21). The functional dependence of Henry's law constant vs. temperature reads (see, e.g. Seinfeld and Pandis, 2006):

$$\ln \frac{H_A(T_0)}{H_A(T)} = \frac{\Delta H^*}{R_g} \left(\frac{1}{T} - \frac{1}{T_0} \right), \quad (23)$$

where ΔH^* is the enthalpy change due to transfer of the absorbate from the gaseous phase to liquid, R_g is the universal gas constant. Time dependence of solute concentration in the bulk of falling droplets is determined via solving Eqs. (18), (21)–(23).

If temperature distribution in the atmosphere is homogeneous, the problem reduces to solving Eq. (22) with a constant parameter of solubility m_0 .

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

$$f(t) = \int_0^t f(\xi) K(t, \xi) d\xi + g(t). \quad (24)$$

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

$$\int_a^b F(\zeta) d\zeta = \sum_{i=1}^N \alpha_i F(\zeta_i) + R_N[F],$$

where $\zeta_i \in [a, b]$, $i = 1, 2, \dots, N$; α_i – coefficients which are independent of the function F ; $R_N[F]$ – remainder of the series after the N -th term. Using a uniform mesh with an increment $h (T_i = T_0 + ih, h = \frac{T_N - T_0}{N})$ and applying the trapezoidal integration rule yield:

$$f(0) = g(0), \quad \left(1 - \frac{1}{2} h \cdot K_{ii} \right) \cdot f_i = h \left(\frac{1}{2} K_{i0} f_0 + \sum_{j=1}^{i-1} K_{ij} \cdot f_j \right) + g_i, \quad (25)$$

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

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 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 presented 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 simultaneously. 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 parameter causes only the quantitative changes in the solution we prescribed a fixed value to this parameter while other parameters vary. The nocturnal vertical profile of the atmospheric 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 temperature 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 dependence 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 temperature 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 inversion. In this region gas desorption is replaced by absorption. This complicated behavior can be explained by the dependence 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 1
Thermophysical properties.

Gas	H_A $10^{-2} \text{ mol m}^{-3} \text{ Pa}^{-1}$	m	D_1 $10^{-9} \text{ m}^2 \text{ s}^{-1}$	D_2 $10^{-5} \text{ m}^2 \text{ s}^{-1}$	ΔH^* 10^5 J mol^{-1}
SO_2	1.21	$2.35 \cdot 10^{-2}$	1.67	1.22	−2.615
NH_3	61.2	1.184	1.7	2.1	−3.421

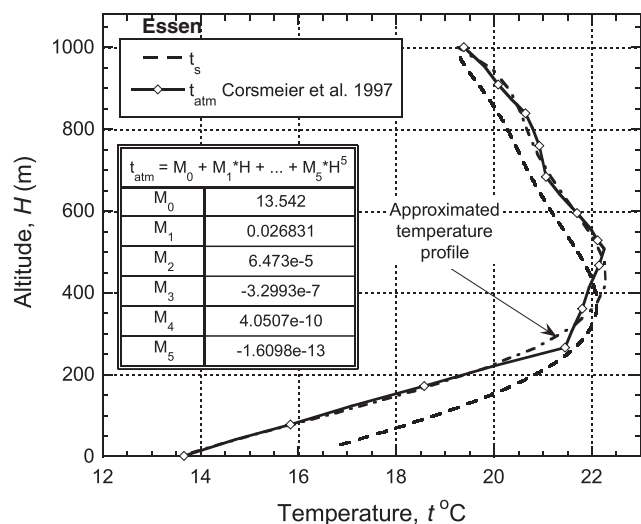


Fig. 2. Dependence of the atmospheric temperature t_{atm} and droplet surface temperature t_s vs. altitude (atmospheric temperature profile measured by Corsmeier et al. (1997) in Essen).

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

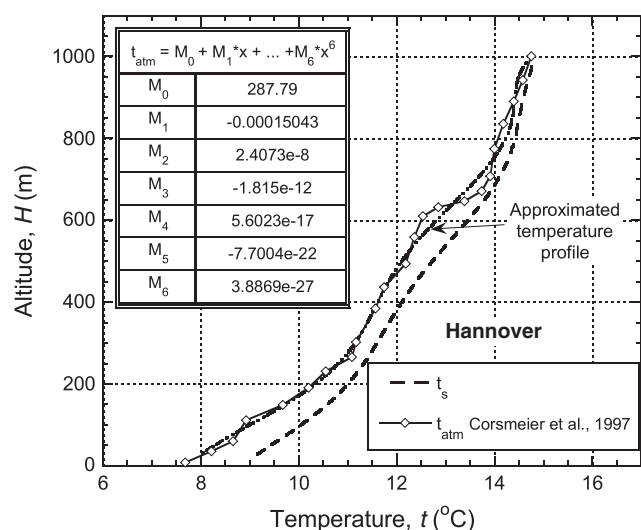


Fig. 3. Dependence of the atmospheric temperature t_{atm} and droplet surface temperature t_s vs. altitude (atmospheric temperature profile measured by Corsmeier et al. (1997) in Hannover).

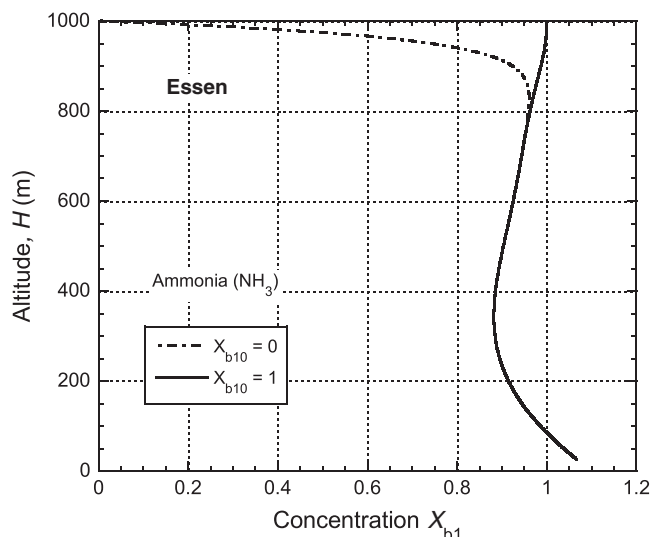


Fig. 4. Dependence of the concentration of the dissolved NH_3 gas in the bulk of a falling rain droplet vs. altitude (calculations are performed for the atmospheric temperature profile measured by Corsmeier et al. (1997) in Essen).

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%.

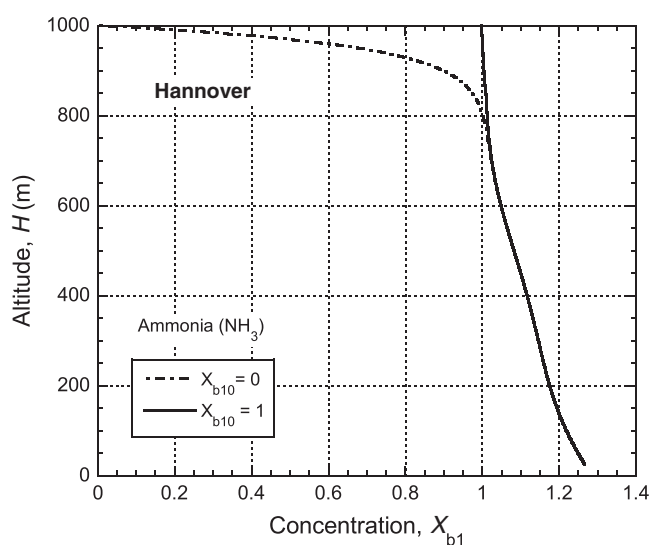


Fig. 5. Dependence of the concentration of the dissolved NH_3 gas in the bulk of a falling rain droplet vs. altitude (calculations are performed for the atmospheric temperature profile measured by Corsmeier et al. (1997) in Hannover).

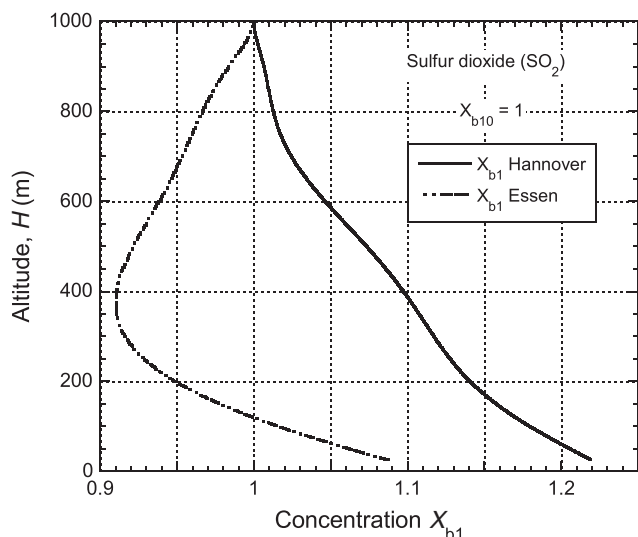


Fig. 6. Dependence of the concentration of the dissolved SO_2 gas in the bulk of a falling rain droplet vs. altitude (calculations are performed for the atmospheric temperature profiles measured by Corsmeier et al. (1997) in Hannover and Essen).

Inspection of Figs. 4–6 shows that in the case of homogeneous temperature distribution in the atmosphere the dimensionless concentration of the absorbate in rain droplets X_{b1} at the ground is equal to 1.

5. Conclusions

In this study we considered coupled heat and mass transfer during soluble gas absorption by a falling droplet with the internal circulation. The system of transient partial parabolic differential equations of convective diffusion and energy conservation in liquid and gaseous phases with time-dependent boundary conditions has been solved by combining the similarity transformation method with Duhamel's theorem. The simple form of the obtained solutions allows using them in the analysis of the dependence of the rate of heat and mass transfer on different parameters, e.g., upon the radius of the rain droplet, diffusion coefficient, concentration gradient of the soluble gaseous pollutants and temperature gradient in the atmosphere, etc.

The suggested model was applied for the analysis of the effect of the nocturnal temperature profile in the atmosphere on the rate of gas absorption by falling rain droplets.

The results obtained in this study can be summarized as follows:

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.

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, $\sqrt{a_1/a_2}$
c_p	specific heat, $\text{J mol}^{-1} \text{K}^{-1}$
C_i	molar density at the bulk of fluid, mol m^{-3}
D_i	molecular diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
D	square root of the diffusivities ratio, $\sqrt{D_1/D_2}$
H_A	Henry's law constant, $\text{mol l}^{-1} \text{atm}^{-1}$
k	coefficient in Eq. (1)
N_{D_i}	$-D_i C_i \frac{\partial x_i}{\partial y}$ molar flux density, $\text{mol m}^{-2} \text{s}^{-1}$
N_{T_i}	$-\lambda_i \frac{\partial T_i}{\partial y}$ heat flux density, W m^{-2}
m	distribution coefficient
m_0	distribution coefficient at temperature T_{20}
Pe_{D_i}	kRU/D_i Peclet number for a moving droplet
Pe_{T_i}	kRU/a_i Peclet number for a moving droplet
r	radial coordinate, m
R	droplet radius, m
R_g	universal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
t	time, s
T	temperature, K

U	translational velocity of a droplet, m s^{-1}
v_r, v_θ	velocity components, m s^{-1}
x	molar fraction of an absorbate
x_{b10}	initial value of molar fraction of an absorbate in a droplet
x_{b20}	value of molar fraction of an absorbate in a gas phase at height H
$x_{b1}(t)$	molar fraction of an absorbate in a bulk of a droplet
$x_{b2}(t)$	molar fraction of an absorbate in a bulk of a gas phase
$X_1(t) = x_1(t)/m_0x_{20}$	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

$\Theta_i = T_i/T_{10}$	dimensionless temperature
$\gamma = C_1/C_2$	molar densities ratio
δ_{D_i}	thickness of a diffusion boundary layer, m
δ_{T_i}	thickness of a thermal boundary layer, m
$\Delta_i = \delta_i/R$	dimensionless thickness of a boundary layer
ΔH^*	enthalpy change, J mol^{-1}
λ	thermal conductivity, $\text{W m}^{-1}\text{K}^{-1}$
ξ	variable
η_i	similarity variable
ϑ	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
θ	tangential direction
s	value at the gas–liquid interface

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