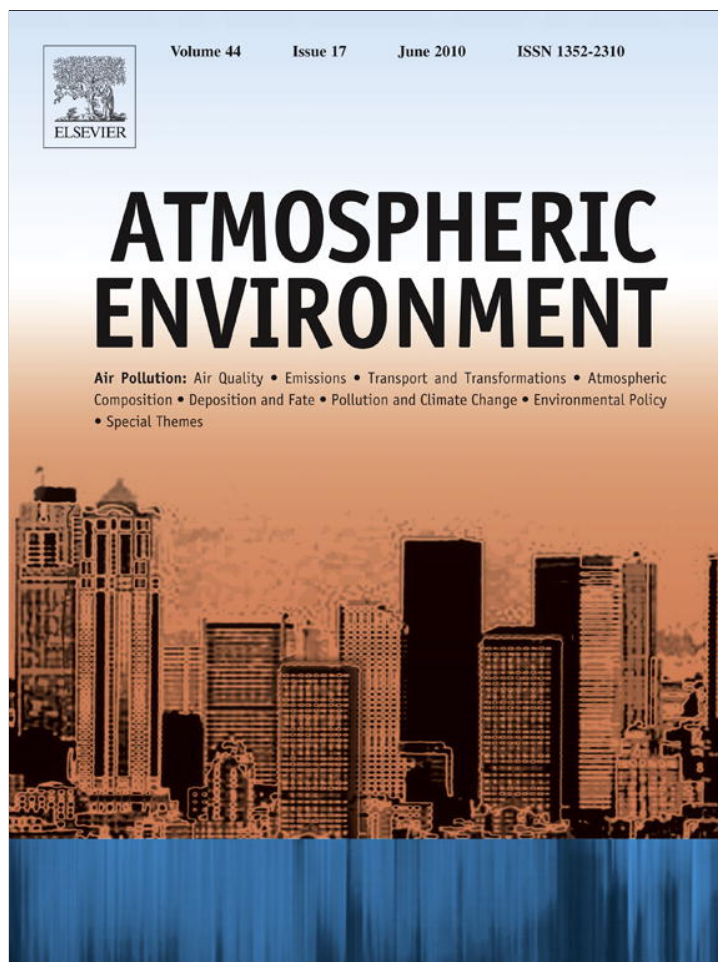




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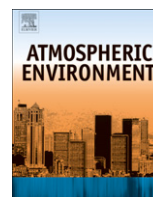
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Scavenging of soluble trace gases by falling rain droplets in inhomogeneous atmosphere

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ARTICLE INFO

Article history:

Received 8 May 2009

Received in revised form

21 February 2010

Accepted 24 February 2010

Keywords:

Precipitation scavenging

Trace gases

Rain droplets

Gas absorption

Heat transfer

Mass transfer

ABSTRACT

We analyze non-isothermal absorption of trace gases by the rain droplets with internal circulation which is caused by interfacial shear stresses. It is assumed that the concentration of soluble trace gases and temperature in the atmosphere varies in a vertical direction. The rate of scavenging of soluble trace gases by falling rain droplets is determined by solving heat and mass transfer equations. In the analysis we accounted for the accumulation of the absorbate 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 droplet and in the surrounding air. We assumed that the bulk of a droplet, beyond the diffusion boundary layer, is completely mixed and concentration of the absorbate and temperature are homogeneous and time-dependent in the bulk. By combining the generalized similarity transformation method with Duhamel's theorem, the system of transient conjugate equations of convective diffusion and energy conservation for absorbate transport in liquid and gaseous phases with time-dependent boundary conditions 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 concentration and temperature profiles in the atmosphere.

It is shown that if concentration of a trace gas in the atmosphere is homogeneous and temperature in the atmosphere decreases with height, beginning from some altitude gas absorption is replaced by gas desorption. Neglecting temperature inhomogeneity in the atmosphere described by adiabatic lapse rate leads to essential overestimation of the trace gas concentration in a droplet on the ground.

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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. Furthermore, scavenging of soluble hazardous gases by rains is an important part of self-cleansing process of the atmosphere (see, e.g. Flossmann, 1998; Pruppacher and Jaenicke, 1995).

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.

Concentration measurements of CO₂, SO₂, NH₃ and other trace gases in the atmospheric boundary layer revealed vertical

(altitudinal) dependence of the concentrations (see Georgii, 1978; Gravenhorst et al., 1978; Georgii and Müller, 1974; Denning et al., 1995). Concentration of gases which are not associated with photosynthesis, e.g. SO₂ and NH₃, has a maximum at the Earth surface and decreases with height over the continents. The concentration of NH₃ over the continents decreases rapidly with altitude, reaching a constant background concentration in winter and warm days at the altitudes of about 1500 m above the ground and 3000 m above the ground, respectively (see Georgii and Müller, 1974; Georgii, 1978). On warm days in summer the ground concentration of NH₃ is considerably higher than that on the cold days in winter. Sulfur dioxide concentration in the ABL (atmospheric boundary layer) is higher during winter than during summer because of the higher anthropogenic SO₂ production caused by enhanced combustion of fossil fuels in winter. Diurnal and seasonal variations of CO₂ distribution with altitude occur due to the competition between different phenomena, e.g. photosynthesis, respiration and thermally driven buoyant mixing (see Denning et al., 1995). Information about the evolution of the vertical profile of soluble gases with time allows calculating fluxes of these gases in the ABL. Vertical transport of

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Nomenclature

a	square root of the thermal diffusivities ratio, $\sqrt{a_1/a_2}$
c_p	specific heat, $\text{kJ kmole}^{-1} \text{K}^{-1}$
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, $\text{mole litre}^{-1} \text{atm}^{-1}$
k	coefficient in Eq. (1)
$N_{Di} = -D_i C_i (\partial x_i / \partial y)$	molar flux density, $\text{mol m}^{-2} \text{s}^{-1}$
$N_{Ti} = -\lambda_i \partial T_i / \partial y$	heat flux density, W m^{-2}
m	distribution coefficient
m_0	distribution coefficient at temperature T_{20}
$Pe_{Di} = kRU/D_i$	Peclet number for a moving droplet
$Pe_{Ti} = kRU/a_i$	Peclet number for a moving droplet
r	radial coordinate, m
R	droplet radius, m
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 absorbate in a droplet
x_{b20}	value of molar fraction of an absorbate in a gas phase at height H
x_{b200}	value of molar fraction of absorbate in a gas phase on the ground
$x_{b1}(t)$	molar fraction of absorbate in a bulk of a droplet
$x_{b2}(t)$	molar fraction of an absorbate in a bulk of a gas phase

$X_1(t) = x_1(t)/m_0 x_{20}$	normalized molar fraction of an absorbate in a liquid phase
$X_2(t) = x_2(t)/x_{20}$	normalized 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_{Di}	thickness of a diffusion boundary layer, m
δ_{Ti}	thickness of a thermal boundary layer, m
$\Delta_i = \delta_i/R$	dimensionless thickness of a boundary layer
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 the 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 gas–liquid interface

soluble gases in the 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 improved understanding of the cycle of soluble gases is also essential for the analysis of global climate change. Clouds and rains play essential role in vertical redistribution of SO_2 , NH_3 and other soluble gases in the atmosphere. Scavenging of soluble gases, e.g. SO_2 , NH_3 by rain affects the evolution of vertical distribution of these gases. At the same time the vertical gradients of the soluble gases concentration in the atmosphere affect the rate of gas absorption by rain droplets. Note that 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.

Existence of the 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 Strickler, 1964; Manabe and Wetherald, 1967) revealed 6.5 K km^{-1} lapse rate. Evolution of the lapse rate during the last decades is discussed by Trenberth and Smith (2006). Vertical temperature profiles in atmosphere during nocturnal inversions were investigated experimentally and theoretically, e.g. by Anfossi et al. (1976), Surridge (1986), Surridge and Swanepoel (1987), Anfossi (1989). Analytical expressions for nocturnal temperature distribution in the atmosphere and for decrease of temperature at a ground during the night were determined by Surridge (1986) and Anfossi (1989). Influence of vertical distribution of 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 temperature (see, e.g. Reid et al., 1987). Accounting for vertical distributions of absorbate and temperature in the gaseous phase requires solution of heat and mass

transfer equations which describe gas absorption by falling rain droplet.

Due to the differences in solubility of gases in liquids, mass transfer during absorption of soluble gas by droplets in the presence of 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 Saboni and Alexandrova (2001). 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), Alexandrova et al. (2004), Chen (2004), Elperin and Fominykh (2005), Elperin et al. (2007a,b, 2008, 2009), Kroll et al. (2008).

Accumulation of the dissolved atmospheric gases in a falling water droplet during absorption in the presence of vertical distribution of the absorbate concentration and temperature in a gaseous phase and circulation of fluid inside a droplet caused by shear stresses at the interface is determined by a system of unsteady convective diffusion and energy conservation equations with time-dependent boundary conditions. Analytical solution of these equations requires application of rather sophisticated methods (see, e.g. Bartels and Churchill, 1942; Ruckenstein, 1967).

The effect of altitudinal distribution of the absorbate in a gaseous phase on the rate of gas absorption by falling rain droplets was investigated by Elperin et al. (2009). The suggested approach includes applying the generalized similarity transformation to a system of transient equations of convective diffusion and a Duhamel's theorem. Then the problem reduces to a numerical solution of a linear convolution Volterra integral equation of the second kind.

In the present study we investigate simultaneous effect of the absorbate and temperature inhomogeneity in a vertical direction in a gaseous phase on the rate of gas absorption by falling droplets.

where $N_{D_i} = -D_i C_i (\partial x_i / \partial y)$, $N_{T_i} = -\lambda_i (\partial T_i / \partial y)$, $y = r - R$, $y \ll R$, coefficient $m = H_A R_g T_{C2} / C_1$ 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 universal gas constant ($R_g = 0.082$ atm litre mole⁻¹ K⁻¹). 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 diffusion Peclet number of the droplet in this study were of the order of 10^4 and 10^2 for the liquid and gaseous phases, respectively. The characteristic values of temperature Peclet number of the droplet in this study are of the order of 10^2 for both phases. Consequently, the use of the boundary

layer approximation is justified. The solution of Eqs. (2)–(3) can be obtained using the similarity transformation method which was suggested first by Ruckenstein (1967).

3. Method of solution

Since the boundary conditions (4)–(5) and (8)–(9) to Eqs. (2)–(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):

$$\eta_{T_i} = \frac{y}{\delta_{T_i}(t, \vartheta)} = \frac{Y}{\Delta_{T_i}}, \quad \eta_{D_i} = \frac{y}{\delta_{D_i}(t, \vartheta)} = \frac{Y}{\Delta_{D_i}}. \quad (12)$$

Since gas absorption (desorption) do not affect distribution of temperature in both phases, we can solve heat transfer equation (Eqs. (3) and (8)–(11)) independently from the mass transfer equation. Variables η_{T_i} allow us to obtain solution of a system of partial differential equations (3) in a following form:

$$\Theta_1(Y, \vartheta, \tau) = \frac{\partial}{\partial \tau} \int_0^\tau \left[\Theta_{b1}(\xi) + \frac{\Theta_{b2}(\xi) - \Theta_{b1}(\xi)}{1 + \gamma_T a} \operatorname{erfc} \left(\frac{Y}{\Delta_{T_1}(\vartheta, \tau - \xi)} \right) \right] d\xi, \quad (13)$$

$$\Theta_2(Y, \vartheta, \tau) = \frac{\partial}{\partial \tau} \int_0^\tau \left[\Theta_{b2}(\xi) - \frac{\gamma_T a \cdot [\Theta_{b2}(\xi) - \Theta_{b1}(\xi)]}{1 + \gamma_T a} \times \operatorname{erfc} \left(\frac{Y}{\Delta_{T_2}(\vartheta, \tau - \xi)} \right) \right] d\xi. \quad (14)$$

Solution of Eqs. (2) with boundary conditions (4)–(7) reads:

$$X_1(Y, \vartheta, \tau) = \frac{\partial}{\partial \tau} \int_0^\tau \left[X_{b1}(\xi) - \frac{X_{b1}(\xi) - (m(\Theta_s(\tau))/m_0) \cdot X_{b2}(\xi)}{1 + m(\Theta_s)\gamma D} \times \operatorname{erfc} \left(\frac{Y}{\Delta_{D_1}(\vartheta, \tau - \xi)} \right) \right] d\xi, \quad (15)$$

$$X_2(Y, \vartheta, \tau) = \frac{\partial}{\partial \tau} \int_0^\tau \left[X_{b2}(\xi) + \frac{[X_{b1}(\xi) - (m(\Theta_s(\tau))/m_0) \cdot X_{b2}(\xi)] \gamma D}{1 + m(\Theta_s)\gamma D} \times \operatorname{erfc} \left(\frac{Y}{\Delta_{D_2}(\vartheta, \tau - \xi)} \right) \right] d\xi \quad (16)$$

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

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

$$\Delta_{T_i}^2 = \frac{4}{Pe_{T_i} \sin^4(\vartheta)} \left\{ \cos(\vartheta) - \frac{1}{3} \cos^3(\vartheta) - \left[\frac{1-f(\vartheta, \tau)}{1+f(\vartheta, \tau)} - \frac{1}{3} \left(\frac{1-f(\vartheta, \tau)}{1+f(\vartheta, \tau)} \right)^3 \right] \right\}, \quad (18)$$

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

$$\Theta_s(\tau) = \Theta_{b1}(\tau) + \frac{\Theta_{b2}(\tau) - \Theta_{b1}(\tau)}{1 + \gamma_T a}. \quad (19)$$

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 balance for the droplet (see, e.g. Uribe-Ramirez and Korchinsky, 2000; Elperin et al., 2007b):

$$\frac{d\Theta_{b1}}{d\tau} = \frac{3}{2 \cdot Pe_{T_1}} \int_0^\pi \frac{\partial \Theta_1}{\partial Y} \Big|_{Y=0} \sin \vartheta d\vartheta, \quad (20)$$

$$\frac{dX_{b1}}{d\tau} = \frac{3}{2 \cdot Pe_{D_1}} \int_0^\pi \frac{\partial X_1}{\partial Y} \Big|_{Y=0} \sin \vartheta d\vartheta. \quad (21)$$

Substituting expression for the temperature in the droplet (Eq. (13)) into Eq. (20) yields:

$$\Theta_{b1}(t) = 1 + \frac{3}{\sqrt{\pi} \cdot Pe_{T_1} (1 + \gamma_T a)} \int_0^\tau [\Theta_{b2}(\xi) - \Theta_{b1}(\xi)] \times \int_0^\pi \frac{\sin \vartheta d\vartheta d\xi}{\Delta_{T_1}(\vartheta, \tau - \xi)}, \quad (22)$$

where $\Theta_{b1} = T_{b1}/T_{10}$. Substituting expression (15) for the absorbate concentration in the droplet into Eq. (21) yields:

$$X_{b1}(\tau) = \frac{x_{b10}}{m_0 x_{b20}} + \frac{3}{\sqrt{\pi} \cdot Pe_{D_1}} \int_0^\tau \left[\frac{X_{b1}(\xi) - (m(\Theta_s(\tau))/m_0) \cdot X_{b2}(\xi)}{1 + m(\Theta_s(\tau)) \cdot \gamma D} \right] \times \int_0^\pi \frac{\sin \vartheta d\vartheta d\xi}{\Delta_{D_1}(\vartheta, \tau - \xi)}. \quad (23)$$

Note that Henry's constant in Eq. (23) is a function of temperature. The magnitude of temperature at a droplet interface is determined by Eqs (19) and (22). The functional dependence of the Henry's law constant vs. temperature reads (see, e.g. Seinfeld and Pandis, 2006):

$$\ln \frac{H_A(T_0)}{H_A(T)} = \frac{\Delta H^*}{R_g} \left(\frac{1}{T} - \frac{1}{T_0} \right), \quad (24)$$

where ΔH^* is the enthalpy change due to transfer of absorbate from the gaseous phase to liquid, R_g is the gas constant. Time dependence of solute concentration in the bulk of falling droplets is determined via solving Eqs (19), (22)–(23).

If temperature distribution in the atmosphere is homogeneous, problem is reduced to solving Eq. (23) with constant parameter of solubility m_0 . For the linear vertical temperature distribution in the atmosphere:

$$T_{b2} = T_{b20} + \operatorname{grad} T_{b2} \cdot z, \quad (25)$$

where T_{b20} – temperature at the ground, T_{b20} – temperature at the height H from the ground, z is directed from the cloud to the ground, $\operatorname{grad} T_{b2} = (T_{b200} - T_{b20})/H$ and $z = U \cdot t$.

Eq. (23) is a linear convolution Volterra integral equation of the second kind (Apelblat, 2008; Chapter 3). Eq. (23) can be written in the following form:

$$f(t) = \int_0^t f(\xi) K(t, \xi) d\xi + g(t). \quad (26)$$

The method of solution of the integral equation (26) is based on approximating integral in Eq. (26) 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 ($T_i = T_0 + ih$, $h \equiv (T_N - T_0)/N$) and applying the trapezoidal integration rule yields:

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

$$\left(1 - \frac{1}{2}h \cdot K_{ii}\right) \cdot f_i = h \left(\frac{1}{2}K_{i0}f_0 + \sum_{j=1}^{i-1} K_{ij} \cdot f_j \right) + g_i, \quad (27)$$

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 equations (22)–(23) we can represent the equation (26) 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 equation (27) 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 a homogeneous and non homogeneous atmosphere containing a soluble trace gas. It should be noted that this value is equal to the average diameter of rain droplets of Feingold-Levin droplet size distribution (Feingold and Levin, 1986) corresponding to low rain intensity of 5–6 mm h⁻¹.

Influence of diurnal variations of CO₂ concentration and temperature distribution in the atmosphere with altitude on trace gas scavenging by a falling droplet is shown in Figs. 2–5. Vertical profiles of CO₂ concentration measured by Perez-Landa et al. (2007) at the heights between 25 m and 800 m at 06:23 (see curve 1 in

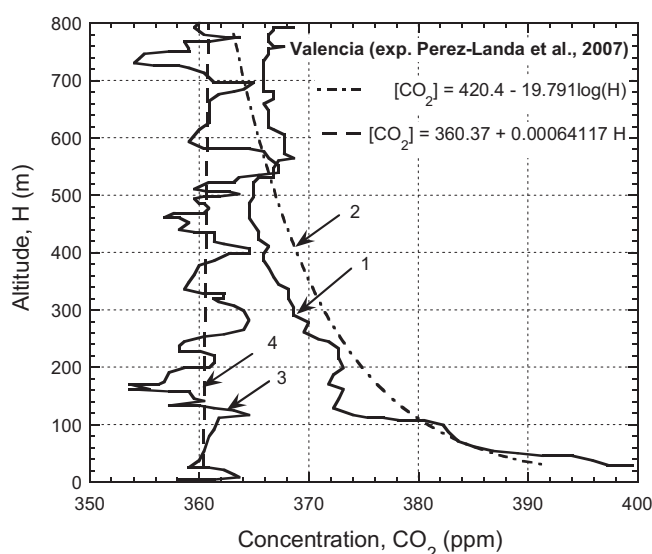


Fig. 2. Dependence of CO₂ concentration in the atmosphere vs. altitude (1) aircraft measurements Valencia 6:23 (by Perez-Landa et al., 2007); (2) and (4) approximation of the measured data; (3) aircraft measurements Valencia 13:03 (by Perez-Landa et al., 2007).

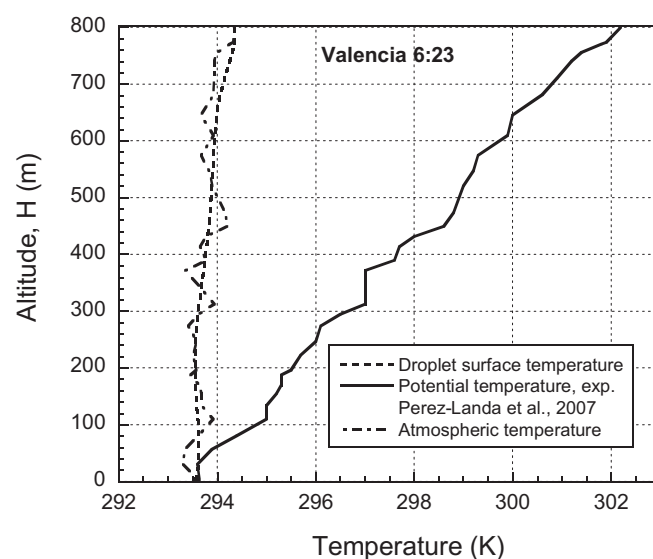


Fig. 3. Dependence of the potential, atmospheric and droplet surface temperature in the morning vs. altitude.

Fig. 2) and 13:03 (see curve 3 in Fig. 2) during the growing season over a rice paddy field in Valencia coastal region, Spain, were approximated by logarithmic and linear functions (see curves 2 and 4 in Fig. 2) using least-squares method. The vertical profiles of the potential temperature measured by Perez-Landa et al. (2007) and atmospheric and droplet surface temperature calculated using these data are showed in Figs. 3 and 4. The vertical profiles of the atmospheric temperature were approximated using polynomial functions of the fifth order. Droplet surface temperature was calculated using Eq. (19).

Numerical results for CO₂ concentration inside a falling droplet are showed in Fig. 5. In our calculations we used the soluble gas concentration and temperature profiles measured by Perez-Landa et al. (2007) at 06:23 and 13:03. We also compared the obtained results with our previous calculations (Fig. 5) performed for uniform temperature distribution in the atmosphere (see Elperin et al., 2009). The comparison of the results (see Fig. 5) shows that taking into account the vertical temperature distribution in the

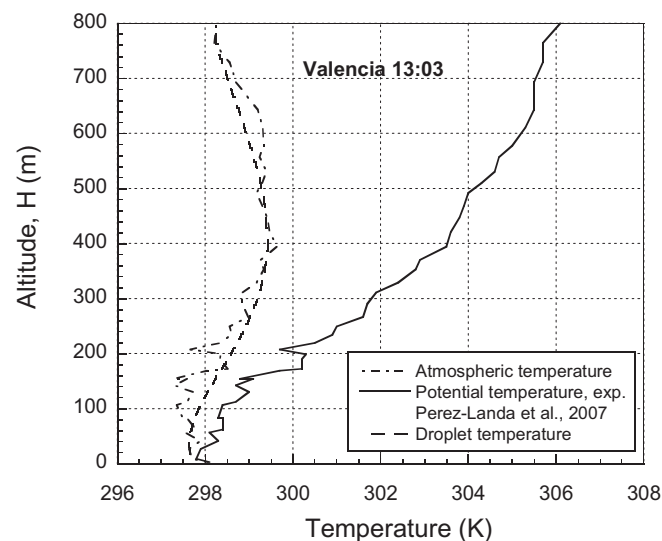


Fig. 4. Dependence of the potential, atmospheric and droplet surface temperature in the afternoon vs. altitude.

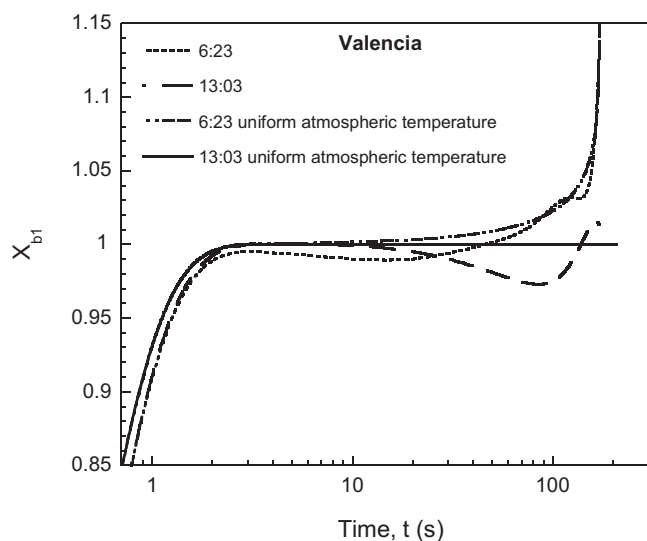


Fig. 5. Dependence of the concentration of the dissolved CO_2 gas in the bulk of a falling rain droplet vs. time, $x_{b10} = 0$.

atmosphere changes the rate of gas absorption by a droplet during its fall. Inspection of Fig. 5 shows that changing the vertical profiles of CO_2 from the logarithmic early in the morning to the uniform in the afternoon for uniform temperature distribution in the atmosphere alters the scenario of the trace gas absorption by a falling rain droplet. Early in the morning concentration of the absorbate in the gaseous phase has a pronounced maximum at the surface and decreases with altitude. Correspondingly, the droplet absorbs the soluble gas during all free fall period from a cloud to the ground.

In the afternoon, due to CO_2 vertical rectification in the atmosphere, absorbate concentration in the droplet attains saturation after a few seconds and at the final stage of their fall droplets do not absorb soluble trace gases (see Fig. 5).

Influence of temperature distribution in the atmosphere on soluble gas scavenging by falling rain droplet is analyzed via numerical solution of Eqs. (19) and (22)–(24). Dependence of the interfacial temperature of falling rain droplet vs. altitude in the atmosphere with temperature gradient equal to -6.5 K km^{-1} is shown at Fig. 6. Results of numerical calculations show that if a rain

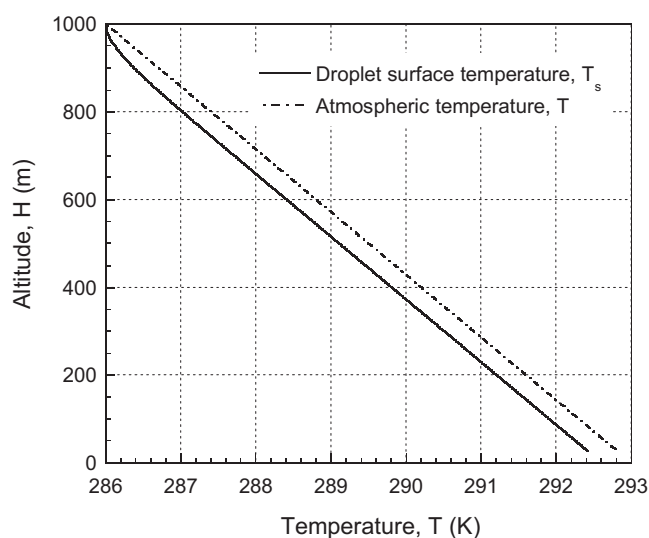


Fig. 6. Dependence of the interfacial temperature of a falling rain droplet vs. altitude.

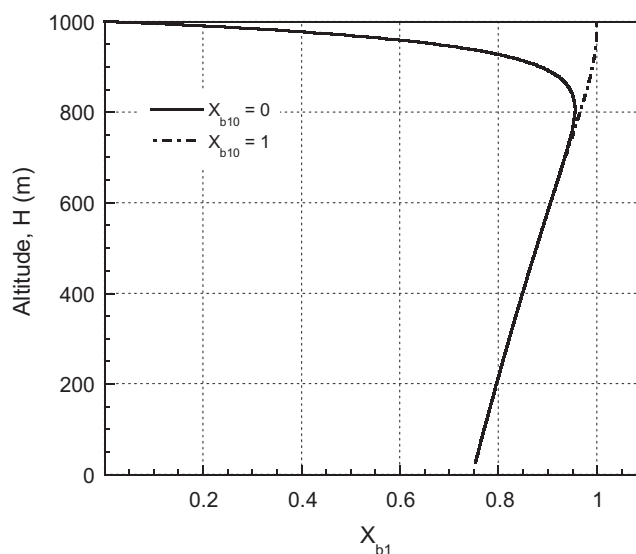


Fig. 7. Dependence of the normalized concentration of the dissolved gas in the bulk of a water droplet vs. time for absorption of ammonia by water in the atmosphere when temperature in the atmosphere decreases with height with the rate 6.5 K km^{-1} .

droplet arrives from a region with a lower ambient temperature to a region with a higher ambient temperature, droplet's surface temperature at a given height is always lower than atmospheric temperature at the same height. When concentration of soluble trace gases in the atmosphere is constant and temperature distribution is homogeneous, solute concentration in the droplet attains saturation after a certain time elapsed, and at the final stage of their fall droplets do not absorb soluble trace gases, see, e.g. Elperin and Fominykh (2005).

If temperature in the atmosphere decreases with height, beginning from some altitude gas absorption is replaced by gas desorption for a droplet with negligibly small initial concentration of soluble gas (see Fig. 7). This behavior can be explained by the dependence of Henry's constant and gas solubility in liquid on temperature. The higher is the temperature, the lower is the solubility of trace gas in liquid and the lower is the concentration of saturation of a trace gas in a droplet. If a rain droplet arrives from a region with lower temperature to a region with a higher temperature, after a while the droplet desorbs the dissolved gas. If the droplet falling from a cloud is initially saturated, it desorbs gas during all the fall period.

The suggested model of soluble gas scavenging by falling drops can be incorporated into the existing models of global transport in the atmosphere to take into account the influence of rains on biogeochemical cycles of different gases.

5. Conclusions

In this study we considered conjugate heat and mass transfer during soluble gas absorption by a falling droplet with the internal circulation from a mixture containing an inert gas using approximation of a thin concentration and temperature boundary layers in the liquid and gaseous phases and accounting for the absorbate accumulation in the bulk of the liquid. The bulk of the droplet, beyond the diffusion and temperature boundary layers, is completely mixed and concentration of absorbate and temperature is homogeneous and time-dependent in the bulk. 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 droplet, diffusion coefficient, gradient of the absorbate concentration and gradient of temperature in a gaseous phase etc. The obtained solution can be also used for validating modeling procedures for solving more involved problems of gas absorption by falling liquid 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 accumulation inside a droplet and effect of the absorbate and temperature distributions in a gaseous phase on the rate of heat and mass transfer.
2. It is shown that the dependence of the radius-averaged concentration and temperature vs. time in a falling droplet is determined by 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 if concentration of a trace gas in the atmosphere is homogeneous and temperature in the atmosphere decreases with height, beginning from some altitude gas absorption is replaced by gas desorption. Neglecting temperature inhomogeneity in the atmosphere described by the adiabatic lapse rate leads to overestimating the trace gas concentration in a droplet at the ground by tens of percents. If concentration of soluble trace gas is homogeneous and temperature increases with height e.g. during the nocturnal inversion, droplet absorbs gas during all the time of its fall. This behavior can be qualitatively explained by the increase of trace gas solubility in a droplet with temperature decrease. 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 numerical solution of a system of integral equations (22)–(23).

The developed model can be used for the analysis of scavenging of hazardous gases in the atmosphere by rain droplets and can be incorporated into the appropriated computer codes.

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