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Effect of rain scavenging on altitudinal distribution of soluble gaseous pollutants in the atmosphere

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ABSTRACT

We suggest a one-dimensional model of rain scavenging of moderately soluble gaseous pollutants in the atmosphere. It is shown that below-cloud gas scavenging is determined by non-stationary convective diffusion equation with the effective Peclet number. The obtained equation was analyzed numerically in the case of log-normal droplet size distribution. Calculations of scavenging coefficient and the rates of precipitation scavenging are performed for wet removal of ammonia (NH_3) and sulfur dioxide (SO_2) from the atmosphere. It is shown that scavenging coefficient is non-stationary and height-dependent. It is found also that the scavenging coefficient strongly depends on initial concentration distribution of soluble gaseous pollutants in the atmosphere. It is demonstrated that in the case of linear distribution of the initial concentration of gaseous pollutants whereby the initial concentration of gaseous pollutants decreases with altitude, the scavenging coefficient increases with height in the beginning of rainfall. At the later stage of the rain scavenging coefficient decreases with height in the upper below-cloud layers of the atmosphere.

1. Introduction

Predicting chemical composition of the atmosphere and elucidating processes which affect atmospheric chemistry is important for addressing problems related to air quality, climate and ecosystem health. Wet deposition is very important in the removal of gaseous pollutants from the atmosphere, and thus strongly affects global concentration of gaseous pollutants in the atmosphere of Earth. Atmospheric composition is controlled by natural and anthropogenic emissions of gases, their subsequent transport and removal processes. Wet deposition, including below-cloud scavenging by rain, is one of the most important removal mechanisms that control the distribution, concentration and life-time of many gaseous species in the atmosphere. Rain, through the below-cloud scavenging and aqueous-phase processes, alter the chemical composition of the atmosphere on a global scale (see, e.g. Zhang et al., 2006). Inorganic nitrogen in wet deposition is a significant source of nutrients for phytoplankton and has a direct impact on the health of estuaries and coastal water bodies (see, e.g. Mizak et al., 2005). Negative impact of SO_2 on visibility was indicated, e.g. by Watson (2002), Green et al. (2005) and by Tsai et al. (2007). Mixed with water or reacting with other chemicals in the air SO_2 has negative health effect.

Gas scavenging by rain includes absorption of SO_2, NH_3 and other gases. Concentration measurements of SO_2, NH_3 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). Concentration of gases which are not associated with photosynthesis, e.g. SO_2 and NH_3, has a maximum at the Earth surface and decreases with height over the continents. The concentration of NH_3 over the continents decreases rapidly with altitude, reaching a constant background concentration at the altitudes of about 1500 m above the ground in winter and at the altitudes of about 3000 m above the ground on warm days (see Georgii and Müller, 1974; Georgii, 1978). On warm days the ground concentration of NH_3 is considerably higher than that on the cold days. Sulfur dioxide concentration in the ABL (atmospheric boundary layer) is higher during winter than during summer because of the higher anthropogenic SO_2 production.

In contrast to the concentrations of SO_2 and NH_3 over the continents, the profiles of concentration of these gases over the ocean have minimum at the ocean surface. This phenomenon is explained by a high solubility of SO_2 and NH_3 in a sea water whereby the ocean acts as a sink of soluble gases (see Georgii and Müller, 1974; Georgii, 1978). Information about the evolution of the vertical profile of soluble gases with time allows calculating fluxes

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Nomenclature

a	raindrop radius, m
c	total concentration of soluble trace gas in gas and liquid phases, mol m^{-3}
$c^{(G)}$	concentration of a soluble trace gas in a gaseous phase, mol m^{-3}
$c_c^{(G)}$	concentration of a soluble gas at a lower boundary of a cloud, mol m^{-3}
$c_{gr}^{(G)}$	concentration of a soluble gas at a ground level, mol m^{-3}
$C^{(G)} = c^{(G)}/c_{c,0}^{(G)}$	dimensionless concentration of trace gas in an atmosphere
$c^{(L)}$	concentration of dissolved gas in a droplet, mol m^{-3}
d	raindrop diameter, m
D_G	coefficient of diffusion in a gaseous phase, m^2 s^{-1}
D	effective coefficient of diffusion, m^2 s^{-1}
H_A	Henry's law constant, mol L^{-1} atm^{-1}
$m = H_A R_g \Theta$	dimensionless Henry's law coefficient
R	rainfall rate, m s^{-1}
R_g	universal gas constant, atm L mol^{-1} K^{-1}
L	distance between ground and lower boundary of a cloud, m
q_c	flux of dissolved gas, transferred by rain droplets, mol m^{-2} s^{-1}
$\mathrm{Pe} = UL/D$	Peclet number
$Re = u\, d/\nu_G$	external flow Reynolds number for a moving droplet
$\mathrm{Sc} = \nu_G/D_G$	Schmidt number
$\mathrm{Sh} = \beta\, d/D_G$	Sherwood number
t	time, s
$T = tU/L$	dimensionless time
u	terminal velocity of a droplet, m s^{-1}
U	"wash-down" front velocity, m s^{-1}
z	coordinate in a vertical direction, m

Greek symbols

β	coefficient of mass transfer m s^{-1}
$\eta = z/L$	dimensionless coordinate
Θ	temperature, K
ϕ	volume fraction of droplets in the air
μ	dynamic viscosity of a fluid, kg m^{-1} s^{-1}
ν	kinematic viscosity of a fluid, m^2 s^{-1}
τ_{ch}	characteristic time of concentration change in a gaseous phase, s
τ_D	characteristic time of diffusion process, s
Λ	scavenging coefficient, s^{-1}

Subscripts

0	initial value
c	value at a lower boundary of a cloud
gr	value at a ground
G	gaseous phase
L	liquid phase

of these gases in an the ABL. Vertical transport of 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 rain 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 contributes to the evolution of vertical distribution of these gases. At the same time the existence of vertical gradients of the soluble gases in the atmosphere affects the rate of gas absorption by rain droplets (see Elperin et al., 2009, 2010).

In spite of a large number of publications devoted to soluble gases scavenging by clouds (see, e.g. Elperin et al., 2007, 2008 and references therein) there are only a few studies on scavenging of these gases by rains. Hales (1972, 2002), Hales et al. (1973) and Slinn (1974) considered removal of soluble pollutant gases from gas plumes. Hales (2002) showed that if a drop falls through a plume and emerges into a clean air before reaching the ground, it may release most of the soluble gaseous pollutants that has been removed from more polluted regions. The significance of this effect is lowering the altitude of the regions with increased concentration of soluble gaseous pollutants under the influence of rain. Hales (2002) considered a set of equations that correspond to five kinds of Gaussian plume formulation. However such approach allows represent the equations for concentration of scavenged pollutants in falling raindrop but not evolution of concentration of trace gas in the atmosphere.

Slinn (1974) showed that plume's "wash-down" velocity can be calculated as $w = I_0 \cdot H'$, where I_0 is a rainfall rate and H' is a dimensionless Henry's constant. The latter approach is valid for uniform droplet size distribution in the rain. Zhang et al. (2006) investigated numerically gas scavenging by drizzle developed from low-level, warm stratiform clouds using the approach of Ackerman et al. (1995), developed for modeling condensation nuclei and water droplets size distributions, and considered precipitation rates in the range from 0.01 mm h^{-1} up to 0.06 mm h^{-1}. The conclusion of this study was that total droplet surface area is more appropriate than the precipitation rate for parameterizing scavenging coefficients, especially when precipitation has a large fraction of small drops. Zhang et al. (2006) concluded that the Henry's law equilibrium approach is able to simulate the gas removal by cloud droplets, but is likely to cause large errors for the soluble gases scavenged by rain drops. The extent of the errors from using the equilibrium approach depends on the size of droplets and the species' gas- and aqueous-phase concentrations.

Different aspects of soluble gaseous pollutants scavenging by rain droplets were discussed by Pruppacher and Klett (1997), Wurzler (1998), Stefan and Mircea (2003), Slinn (1977), Calderon et al. (2008), Asman (1995), Mircea et al. (2000, 2004), Kumar (1985), Levine and Schwartz (1982), Dana et al. (1975), Elperin and Fominykh (2005). Asman (1995) investigated absorption of highly soluble gases by rain using the approximation of infinite solubility of absorbate in the absorbent and assuming that distribution of soluble gas in the atmosphere during the rain is time-dependent and uniform. The latter assumption allowed calculating numerically the dependence of the scavenging coefficient on the rainfall rate in the atmosphere. Power law dependence of the scavenging coefficient on the rainfall rate for ammonia absorption by rain, which was predicted by Asman (1995) theoretically, was confirmed experimentally by Mizak et al. (2005). All the above studies did not account for the dependence of scavenging coefficient on height, time and initial profile of soluble gas in the atmosphere.

In this study we investigate the influence of the altitude absorbate inhomogeneity in a gaseous phase on the rate of soluble gas scavenging by falling rain droplets. The problem is reduced to the equation of non-stationary convective diffusion with the effective Peclet number that depends on droplets size distribution (DSD). The obtained equation was solved numerically for log-