

Scavenging of Soluble Gases by Slowly Evaporating Droplets in Inhomogeneous Atmosphere

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We present a one-dimensional model of scavenging of soluble gaseous pollutants by evaporating droplets which is valid for arbitrary initial vertical distribution of soluble trace gases in the atmosphere. It is shown that for low gradients of soluble trace gases in the atmosphere gas scavenging is determined by a linear wave equation that describes propagation of a wave in one direction. The derived equation is solved by method of characteristics. Calculations of scavenging coefficient are performed for wet removal of sulfur dioxide (SO_2) from the atmosphere for available in the literature initial distribution of trace gases and for different values of humidity in air. It is shown that for arbitrary initial vertical distribution of soluble trace gases in the atmosphere scavenging coefficient is non-stationary and height-dependent. For exponential initial distribution of soluble trace gases in the atmosphere scavenging coefficient in the region between the ground and the location of a scavenging front is proportional to rainfall rate at a bottom of a cloud, solubility parameter and the growth constant in the formula for the initial profile of a soluble trace gas in the atmosphere. This expression yields the same estimate of scavenging coefficient for sulfur dioxide as field estimates presented in McMahon and Denison (1979). It is demonstrated that the smaller the slope of the concentration profile the higher is the value of a scavenging coefficient.

1. Introduction

Rains play an important role in self-cleansing process of the atmosphere. Scavenging of atmospheric gaseous pollutants by rain droplets is the result of gas absorption mechanism (Pruppacher and Klett, 1997). Concentration measurements of trace gases in the atmosphere revealed vertical (altitudinal) dependence of the concentrations (Georgii, 1978). Concentration of gases which are not involved in photosynthesis, e.g. SO_2 and NH_3 , has a maximum at the Earth surface and decreases with height over the continents. Vertical distribution of soluble trace gases affects their residence time in the atmospheric boundary layer, and hence governs the long-range transport of these gases. Rain can change vertical distribution of radioactivity in the atmosphere by scavenging radioactive gases. Rain also influences the visibility in the atmosphere by changing altitudinal distribution of soluble trace gases. Most of the investigations on soluble gas scavenging by precipitation consider gas absorption by single droplets falling in the atmosphere with a uniform distribution of soluble trace gases. Typical examples are theoretical and experimental studies by Walcek and Pruppacher (1984) and Heusel-Waltrop et al. (2003) of sulfur dioxide absorption by falling rain droplets. Soluble trace gas absorption by a single droplet falling in the atmosphere with low gradient of concentration of soluble trace gas was analysed by Hales (1972). Hales (1972) assumed that initial distribution of a soluble trace gas in the atmosphere is linear and showed that if concentration gradient of soluble trace gas in the atmosphere is sufficiently low so that

$$\frac{a m u \left| \frac{dc^{(G)}}{dz} \right|}{\beta c_{gr}^{(G)}} \ll 1, \quad (1)$$

it is possible to assume that the instantaneous concentration of the dissolved gas in a droplet is equal to the concentration of saturation in liquid corresponding to the concentration of a soluble trace gas in an

atmosphere at a given height. Here a is raindrop radius, m is dimensionless Henry's law coefficient, u is droplet terminal velocity, $c^{(G)}$ is concentration of a soluble trace gas in a gaseous phase, $c_{gr}^{(G)}$ is concentration of a soluble gas at a ground level, β is gaseous-phase controlled mass transfer coefficient and z is vertical coordinate. Effects of atmospheric inhomogeneity on scavenging of soluble gases by single rain droplets were studied also by Elperin et al. (2009). Various aspects of soluble gaseous pollutants scavenging by precipitation were studied by Zhang et al. (2006), Banzhaf et al. (2012), Elperin et al. (2011). It must be emphasized that these studies did not account for the dependence of the scavenging coefficient on air humidity, height and on the initial profile of soluble gas in the atmosphere. In the present study we investigate effects of altitudinal absorbate inhomogeneity in a gaseous phase and droplets evaporation on the rate of soluble gas scavenging in the atmosphere by precipitation.

2. Description of the model

We consider absorption of a moderately soluble gas from a mixture containing inert gas by falling rain droplets. At time $t=0$ rain droplets begin to fall and simultaneously evaporate and absorb gaseous pollutants (trace gases) from the atmosphere. It is assumed that initial concentration of the dissolved trace gas in rain droplets is equal to the concentration of saturation in liquid corresponding to the concentration of a trace soluble gas in a cloud, and that the initial distribution (at time $t=0$) of a soluble trace gas in the atmosphere is known. We investigate gas absorption by slowly evaporating droplets when a condition $(a_0 - a_{gr})/a_0 \ll 1$ is satisfied, where a_0 is the initial radius of a rain droplet at the bottom of a cloud and a_{gr} is radius of evaporating droplet at the ground. It must be noted that only a small fraction of moderately soluble gas dissolves in cloud water. Therefore, concentration of moderately soluble gas in the interstitial air in cloud is close to the concentration of the soluble gas in the below-cloud atmosphere immediately adjacent to the cloud. Since the residence time of droplets in the cloud is large, equilibrium is established between concentration of a moderately soluble gas in the interstitial air and concentration of the dissolved gas in cloud droplets (Asman, 1995). The goal of this study is to determine evolution of concentration distribution of soluble trace gases in the atmosphere below the cloud under the influence of gas scavenging by falling rain droplets. Time dependence of radius of evaporating droplet is determined by a well-known formula (Pruppacher and Klett (1997) and Fuchs (1959)):

$$a^2 = a_0^2 - k_1 t, \quad (2)$$

where $k_1 = D_v Sh P_{v,sat} M (1 - RH\%/100) / (RT\rho_L)$, R is universal gas constant, M – molar mass of water, D_v – coefficient of diffusion of water vapour in air, $P_{v,sat}$ – pressure of saturated water vapour in the atmosphere, Sh – Sherwood number, T – temperature, ρ_L – liquid density. For 1.1 mm diameter water droplet falling in air with 90% relative humidity, $Sh = 13$ and $k_1 = 2.2 \cdot 10^{-10} m^2 s^{-1}$. Note that Eq. (2) is valid if conditions of equilibrium evaporation are fulfilled (see Fuchs, 1959). Hereafter for simplicity we can assume that Sherwood number for evaporating droplet during entire falling time remains constant. Dependence of fall velocity of droplet on droplet radius can be approximated by the following correlation:

$$u = c_1 [a(z)]^\alpha, \quad (3)$$

where values of constants c_1 and α in Eq. (3) can be found in Pruppacher and Klett (1997). Formula for volume fraction of evaporating droplets in the atmosphere vs. droplet diameter reads:

$$\phi(z) = [a(z)]^3 \phi_0 / a_0^3. \quad (4)$$

When condition (1) is met the instantaneous concentration of the dissolved gas in evaporating droplet can be assumed to be equal to the concentration of saturation in liquid corresponding to the concentration of a trace soluble gas in an atmosphere at a given height. Since SO_2 absorption by water is accompanied by chemical dissociation, we account for chemical dissociation in liquid by using an effective solubility parameter m^* in the Henry's law coefficient (Seinfeld and Pandis, 2006, Chapter 7):

$$c^{(L)}(z) = m^* c^{(G)}(z), \quad (5)$$

where $c^{(L)}$ is concentration of the dissolved gas in a droplet, [mole · litre⁻¹]. Clearly, the total flux of the dissolved gas transferred by rain droplets is $q_c = m \cdot \phi \cdot u \cdot c^{(G)}$. Using equation of mass balance for the soluble trace gas in the gaseous and liquid phases and applying approach described in Elperin et al. (2011) we arrive at the following equation for soluble trace gas distribution in the atmosphere:

$$\frac{\partial x^{(G)}}{\partial t} + U(z) \frac{\partial x^{(G)}}{\partial z} = 0, \quad (6)$$

where $U = U_0 \left(1 - \frac{(\alpha + 2) k_1 z}{2 c_1 a_0^{\alpha+2}} \right)^{(\alpha+3)/(\alpha+2)}$, U is a “wash-down” front velocity [m] and $U_0 = m \cdot \phi_0 c_1 a_0^\alpha$ is a

“wash-down” front velocity for a case of non-evaporating droplets. Dependence of scavenging velocity U on coordinate for various values of humidity for absorption of sulfur dioxide for 1.1 mm diameter droplets is showed in Fig. 1.

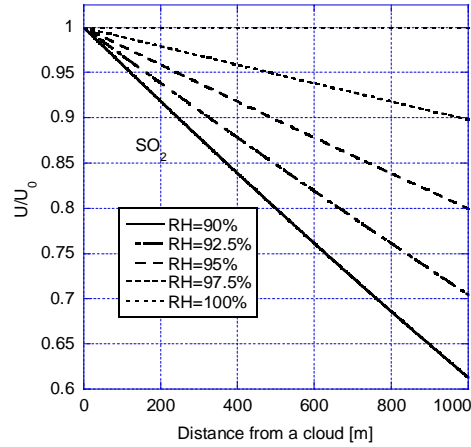


Figure 1: Dependence of scavenging velocity for gas absorption by evaporating droplets vs. distance from the bottom of a cloud for various values of humidity

The initial and boundary conditions for Eq. (6) are as follows:

$$t = 0, \quad x^{(G)} = f(z); \quad z = 0, \quad x^{(G)} = x_c^{(G)}, \quad (7)$$

where $x_c^{(G)}$ is mole fraction of a soluble gas at a lower boundary of a cloud. Equation (6) describes propagation of a wave in the positive direction of z axis. Equations (6) - (7) can be solved by the method of characteristics (see e.g. DuChateau and Zachmann, 2002), and the solution is given by the following formula:

$$x^{(G)} = \begin{cases} f(\eta - t) & \eta > t \\ x_c^{(G)} & \eta < t \end{cases}, \quad (8)$$

where $\eta = \frac{2a_0^2}{m\phi_0 k_1} \left[\left(1 - \frac{(\alpha + 2) k_1 z}{2c_1 a_0^{\alpha+2}} \right)^{-1/(\alpha+2)} - 1 \right]$. Coordinate of a scavenging front is determined by the

equation $\eta = t$. If the initial distribution of a soluble gas in the atmosphere is exponential, i.e.

$$t = 0, \quad x^{(G)} = x_c^{(G)} \cdot \exp(k_2 \cdot z), \quad (9)$$

where z is measured from the bottom of a cloud to the ground, the solution of Eq. (6) with the initial and boundary conditions (7) reads:

$$x^{(G)}(z) = \begin{cases} x_c^{(G)} \cdot \exp\left(\frac{2c_1 k_2 a_0^{\alpha+2}}{(\alpha+2)k_1} \left[1 - \left(1 + \frac{k_1 m \phi_0 (\eta - t)}{2a_0^2}\right)^{-(2+\alpha)}\right]\right) & \eta > t \\ x_c^{(G)} & \eta < t \end{cases} \quad (10)$$

When coefficient k_1 equals to zero, Eq. (10) recovers formula for soluble gas scavenging by non-evaporating droplets. The obtained solution allows us to calculate scavenging coefficient A for soluble trace gas absorption in the atmosphere (Seinfeld and Pandis, 2006):

$$A = -\frac{1}{x^{(G)}} \frac{\partial x^{(G)}}{\partial t} \quad (11)$$

In case of exponential initial vertical distribution of soluble trace gas in the atmosphere Eqs. (10) – (11) yield:

$$A = \begin{cases} k_2 \cdot m \phi_0 c_1 a_0^\alpha \left(\left(1 - \frac{(\alpha+2)k_1 z}{2c_1 a_0^{\alpha+2}}\right)^{-\frac{1}{(2+\alpha)}} - \frac{k_1 m \phi_0 t}{2a_0^2} \right)^{-(3+\alpha)} & \eta > t \\ 0 & \eta < t \end{cases} \quad (12)$$

Expression (12) yields the same estimate of scavenging coefficient for sulfur dioxide scavenging by rain as the field estimates presented in McMahon and Denison (1979). When coefficient k_1 in Eq. (12) is equal to zero, Eq. (12) yields $A = k_2 \cdot m \phi_0 c_1 a_0^\alpha$.

3. Results

Described above model of atmospheric trace gases scavenging by rain was applied to study evolution of trace soluble gas concentration in the atmosphere during rain fall. To the best of our knowledge there are no studies that report results of measurements of the evolution of concentration profiles during rain. In order to illustrate the suggested approach in the calculations we used available in the literature distributions of trace gas in the atmosphere. Calculations are performed for scavenging of SO_2 by rain. Results of calculations based on Eq.(10) are showed in Fig. 2. Vertical distribution of concentration of sulfur dioxide which was measured by Jost (1974) at heights between 0 and 1 km (see solid curve in Fig. 2) was approximated by the exponential function. Concentration of sulfur dioxide in the atmosphere varies in the range from 3.98 ppb at height 1 km to 7.53 ppb on the ground. The dependence of soluble trace gas concentration in the atmosphere vs. coordinate z can be approximated by Eq. (9), where the growth constant $k_2 = \frac{1}{L} \ln(x_{gr}^{(G)} / x_c^{(G)})$, $x_{gr}^{(G)}$ is mole fraction of soluble gas at the ground, L is the distance between the bottom of a cloud and ground in meters. When $x_c^{(G)} = 3.98$ ppb and $x_{gr}^{(G)} = 7.53$ ppb, $k_2 = 6.36 \cdot 10^{-4} m^{-1}$. Results shown in Fig. 2 were obtained for SO_2 absorption by 1.1 mm droplets and $\phi_L = 10^{-6}$. Inspection of Fig. 2 shows that sulfur dioxide is scavenged by rain until concentration in the interstitial air in a cloud is attained. The dependence of the scavenging coefficient vs. altitude in the case of sulfur dioxide wash out is shown in Fig. 3. For the exponential initial profile of soluble gas in the atmosphere, the scavenging coefficient increases with height. At the ground level the value of the scavenging coefficient increases with time because the concentration at the ground decreases faster than the rate of concentration change.

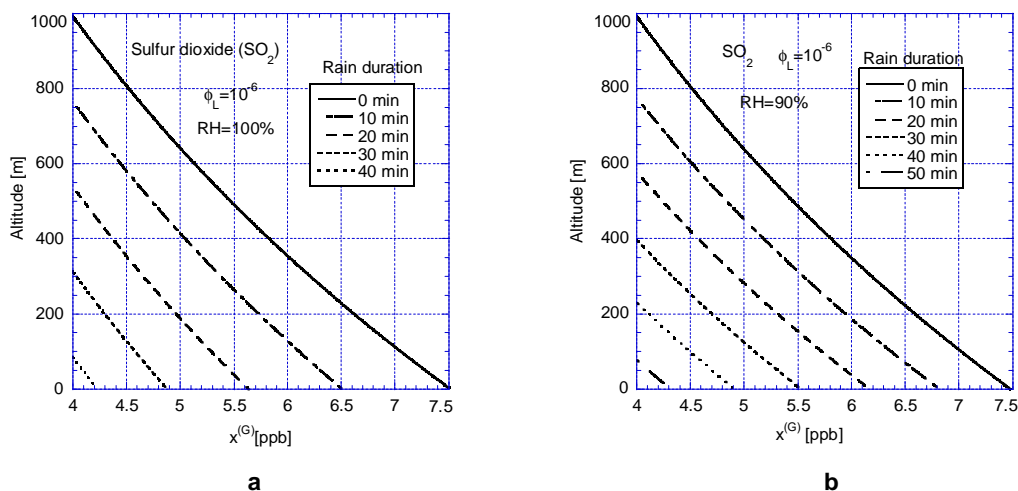


Figure 2: Evolution of sulfur dioxide distribution in the atmosphere caused by rain scavenging. The initial distribution of soluble trace gas in the atmosphere is exponential and is taken from Jost (1974), $\phi_L = 10^{-6}$. a - air humidity is 100%, b - air humidity is 90%.

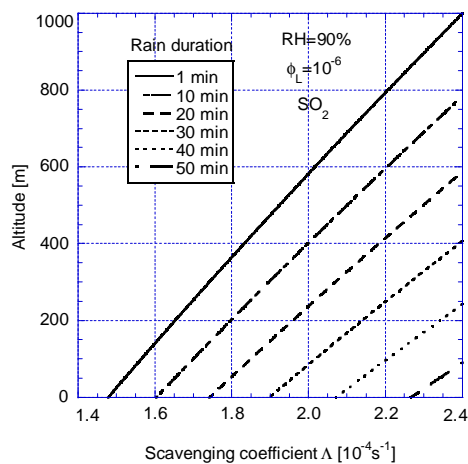


Figure 3: Dependence of scavenging coefficient vs. altitude for sulfur dioxide wash out by evaporating rain droplets. The initial distribution of soluble trace gas in the atmosphere is exponential and is taken from Jost (1974), $\phi_L = 10^{-6}$. Air humidity is 90%.

4. Conclusion

In this study we developed a model for scavenging of soluble trace gases by evaporating rain droplets which is applicable for low gradients of concentrations of soluble trace gas in the atmosphere. This model is valid for the arbitrary initial vertical distribution of soluble trace gas in the atmosphere. It is shown that gas scavenging for a case of low gradients of concentrations in the atmosphere is determined by linear wave equation that describes propagation of a wave in one direction without changing shape. The obtained equation was solved by the method of characteristics. Simple form of the obtained solution allows analysing the dependence of the rate of soluble gas scavenging on different parameters, e.g. rain intensity, gas solubility, gradient of the soluble gas concentration in a gaseous phase, humidity etc. Using the developed model we calculated scavenging coefficient and the rates of scavenging of SO_2 for different values of humidity in the atmosphere. The obtained results can be summarized as follows:

1. For arbitrary initial distribution of soluble trace gas in the atmosphere scavenging coefficient for wash out of soluble gases by precipitation is time-dependent and height-dependent. Scavenging of soluble gas begins in the upper atmosphere and scavenging front propagates downwards with the "wash down" velocity. Scavenging coefficient in a region between the bottom of a cloud and location of a scavenging front is always equals to zero.
2. In case of the exponential initial distribution of soluble trace gases in the atmosphere scavenging coefficient in the region between the ground and location of a scavenging front is proportional to rain intensity, solubility parameter and the growth constant k_2 in the initial trace gas profile. It is shown that the smaller is the slope of the concentration profile, the higher is the value of a scavenging coefficient.
3. Scavenging velocity for soluble gas scavenging by evaporating droplets depends upon humidity and decreases with the distance from the bottom of a cloud.
4. Neglecting the influence of rain droplet evaporation during soluble gas scavenging results in overestimating the rate of gas scavenging by precipitation.

The developed model can be used for the analysis of precipitation scavenging of hazardous gases in the atmosphere and for validating the advanced models for predicting scavenging of soluble gases by rain.

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