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Sensitivity of the Precipitation Scavenging Coefficient of Nitric Acid Vapour to Raindrop Size Distribution

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Abstract. The aim of this paper is to calculate the scavenging coefficient, Λ, for the removal of nitric acid vapour from the atmosphere by rain, and to evaluate the coefficient sensitivity to raindrop-size distribution.Due to the high dependence of calculated values on the selection of the distribution function and the lower limit over which the integration is performed (Levine and Schwartz, 1982) and because of the large variety of precipitation types and rates, the scavenging coefficient was computed using two distribution functions, Marshall-Palmer and Khrgian-Mazin.These functions are widely used in describing the rain droplet spectrum (Pruppacher and Klett, 1978) and their parameters were determined in order to describe a dimensional range of droplets, each droplet spectrum being associated with a class of rain (Mircea and Stefan, 1998). The values of the scavenging coefficient suggest that the classification of rain in classes could be a way of obtaining a better representation of the wet removal in the atmospheric models. The results also indicate the sensitivity of the precipitation scavenging coefficient to size-distribution functions, methods of integration and to the limits over which the integration is performed.

Key words: precipitation scavenging, nitric acid, rain size distribution

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1. Introduction

NO_2 and NO(NO_x*)* have a large indirect effect owing to their importance in troposphere chemistry and physical processes. There, the role of NO_x is that of a catalyst promoting the formation of O_3 and controlling the concentration of OH, the most important oxidising agent of the troposphere. Through OH, emissions of NO_x influence the adjustment times and thus the abundance of infrared absorbing gases. NO_x is emitted mainly as NO by a large variety of sources. Fossil fuel combustion in the stationary power and transport sectors is the largest source of NO_x .

Atmospheric oxidation of NO_2 to HNO_3 by OH in the day time and to NO_3 by O_3 at night is the most important removal processes of NO_x from the troposphere.

Except for the small fraction which is dry deposited as NO_2, all of the NO_x is converted to nitrate and deposited as such by dry or wet processes which allows an independent check of the removal of NO_x from the troposphere (IPCC Climate Change, 1994).

The elementary reactions that comprise these processes are now quite well understood (Levine and Schwartz, 1982).

The formation rate of HNO_3 vapour has been estimated in model calculations to be as great as 0.2 ppb min^{-1} for conditions associated with urban photochemical smog. Also, NO_x transformation rates (to HNO_3) have been reported as great as 0.14 - 0.24 h^{-1} in an urban plume (Spicer, 1980). The values of concentrations of HNO_3 reported for clear air (Kelly et al., 1980) are invariably less than NO_x concentrations.

Data about the concentrations of HNO_3 and NO_x in different locations are presented in Levine and Schwartz (1982) and in Climate Change (1994).

The formation of the nitric acid and its removal process are the very interesting subject for researchers of air pollution. The nitric acid is removed from the atmosphere either by dry deposition or by precipitation scavenging due to the high solubility of HNO_3 in water.

In this paper, the scavenging coefficient, Λ, of nitric acid vapour is calculated for three classes of rain, and the coefficient dependence on raindrop-size distribution and integration method is evaluated. The following calculations were made assuming that HNO_3 is an irreversible soluble gas. (Levine and Schwartz, 1982).

2. Precipitation Scavenging of gases

In the precipitation scavenging of gases, the rate of transfer of gas molecules to the surface of a stationary or falling drop can be very accurately predicted; difficulties in predicting gas scavenging rates arise when the scavenged gas has an appreciable vapour pressure over the surface of the drop and thus the composition, of the drop must be known in order to predict the net rate of transfer of material to the drop.

Gas flux to a cloud or rain drop can be expressed as $k_g(c - c_s)$, where k_g is the gas-phase mass transfer coefficient (cm sec^{-1}), c is the bulk gas-phase concentration in the air and c_s is the gas concentration in the drop.

The convective- diffusive mass transfer coefficient is given by Frossling (1938) equation:

$$k_g = \frac{D_g}{D_0}\left[2 + 0.6\left(\frac{D_0 u}{\upsilon}\right)^{1/2}\left(\frac{\upsilon}{D_g}\right)^{1/3}\right] \tag{1}$$

where D_g is the diffusivity coefficient of the gas in air ($\mathrm{cm}^2\ \mathrm{s}^{-1}$), υ is the cinematic viscosity ($\mathrm{cm}^2\ \mathrm{s}^{-1}$), u the drop falling terminal velocity (cm s^{-1}) and D_0, the drop equivalent diameter.

The local rate of removal of an irreversible soluble gas like HNO_3 for a given raindrop-size distribution of a rain event, $\frac{dN}{dD_0}$ is:

$$\int_0^\infty \boldsymbol{k_g (\pi D_0^2) c \frac{dN(D_0)}{dD_0} dD_0} \tag{2}$$

and the scavenging coefficient defined as the fractional rate of removal of the gas by dissolution is:

$$\Lambda = \pi \int k_g D_0^2 \frac{dN}{dD_0} dD_0 \tag{3}$$

The dependence of k_g upon D_0 is related to the terminal velocity of the raindrop, u, which in turn, is a function of the equivalent drop diameter (Pruppacher and Klett, 1978):

$$u = 958[1-\exp(-(D_0/0.1710)^{1.147})]\ (\mathrm{cm\ s}^{-1}) \tag{4}$$

The raindrop spectrum is considered to be described by Marshall-Palmer (MP) and Khrgian-Mazin (KM) distribution functions, given by:

$$\text{MP:} \quad \frac{dN}{dD_0} = Ae^{-\beta D_0}$$

$$\text{KM:} \quad \frac{dN}{dD_0} = AD_0^2 e^{-\beta D_0}$$

The complex dependence of k_g on the drop diameter does not allow an analytical expression for the scavenging coefficient. Two methods of integration (Press et al., 1992): trapezoidal and Romberg method were used to evaluate the right term of equation (3). Trapezoidal rule is the starting point for a variety of algorithms and it can be refined when we integrate a function until some specified degree of accuracy has been achieved. Romberg integration use the results from k successive refinements of the extended trapezoidal rule to remove all terms in the error series up to, but not including $O(1/N^{2k})$.

3. Results and Discussions

With two models for raindrop-size distribution and three classes of rain, the calculations have been carried out to determine the scavenging coefficients for the removal of acid nitric vapour by rain droplets, from the atmosphere.

The considered class of rain are: light rain (LR), moderate rain (MR) and heavy rain (HR), with intensities (1 - 5) mmh^{-1}, (5 - 50) mmh^{-1} and > 50mmh^{-1}.

Levine and Schwartz (1982) have shown that the choice of the lower limit employed in the integration strongly affects the computed values of the scavenging coefficient.

Because the choice of a lower limit to D_0 in the evaluation of Λ is rather arbitrary, we consider that the integration method is also very important to calculate Λ. In addition, we consider different dimensional ranges over which the integration is performed for the three rain classes.

We have used for the integration the trapezoidal rule and Romberg method (Press et al., 1992).

Trapezoidal rule is the starting point for a variety of algorithms and it can be refined when we integrate a function until some specified degree of accuracy has been achieved. Romberg integration use the results from k succesive refinements of the extended trapezoidal rule to remove all terms in the error series up to, but not including $O(1/N^{2k})$.

In the case of the trapezoidal rule, the lower limit of integration, cannot be 0. Therefore, we have chosen especially lower limits for each rain classes (Table 1). We have also chosen the different upper limits for each rain classes to test the sensitivity of precipitation coefficients to integration methods.

In the case of Khrgian-Mazin size-distribution function, the results have shown:

- for $D_{min.} \leq 10^{-5}$cm and for each class of precipitation the values of the scavenging coefficient are similar both the Romberg and the Trapezoidal methods of integration;

-the upper limits affect the values obtained with Romberg method for moderate and light rain: **MR** $D_0 \in [10^{-7} - 0.1]$ cm, $\Lambda = 1.88 \times 10^{-3}$ s^{-1}, $D_0 \in [0 - 1]$ cm, $\Lambda =$ 6,17x10^{-5} s^{-1}; **LR** $D_0 \in [10^{-7} - 10^{-2}]$ cm, $\Lambda = 1.94 \times 10^{-1}$ s^{-1}, $D_0 \in [0 - 10^{-3}]$ cm, $\Lambda =$

$4.73 \times 10^{-6}\ s^{-1}$.

In the case of the Marshall-Palmer size-distribution function, the results have shown:

-the method of integration don't influence the result s, for the $D_{min.} \leq 10^{-5}$cm and for each class of precipitation;

-the values of the Λ obtained by the trapezoidal rule are strongly affected of lower limit for moderate and light rain : **MR** $D_0 \in [10^{-7} - 1]$ cm, $\Lambda = 1.0 \times 10^{-3}\ s^{-1}$, $D_0 \in [0.002 - 1]$ cm, $\Lambda = 1.18 \times 10^{-4}\ s^{-1}$; **LR** $D_0 \in [10^{-7} - 10^{-2}]$ cm, $\Lambda = 9.30 \times 10^{-2}\ s^{-1}$, $D_0 \in [0.0002 - 10^{-1}]$ cm, $\Lambda = 2.93 \times 10^{-4}\ s^{-1}$.

The values of the scavenging coefficients computed for the two drop - size distribution functions and classes of rain show that both the choice of the method of the integration and the limit of integration affect in different manner, the values of these coefficients (Table 1).

Table 1. Precipitation scavenging coefficients

Integration methods	**Class of rain**	**D_0 (cm)**	**$\Lambda(s^{-1})$** **KM**	 **MP**
Romberg	LR	$0 - 10^{-3}$	4.73×10^{-6}	9.30×10^{-2}
	MR	0 - 1	6.17×10^{-5}	1.01×10^{-3}
	HR	0 - 10	3.85×10^{-4}	3.48×10^{-4}
Trapezoidal	LR	$2 \times 10^{-4} - 10^{-1}$	1.29×10^{-1}	2.93×10^{-4}
	MR	$2 \times 10^{-3} - 1$	1.40×10^{-3}	1.18×10^{-4}
	HR	$2 \times 10^{-3} - 10$	4.84×10^{-4}	2.47×10^{-4}

Consequently, the lower limit of the integration is unimportant when Romberg method is used but upper limit is important in the case of moderate and light rain. Contrary, the lower limit is very important for trapezoidal rule and strongly affects the values of the scavenging coefficients, for moderate and light rain.

In figures 1 to 3 we have presented the differential scavenging coefficient $\frac{d\Lambda}{dD_0}$, evaluated for each of the two drop - size distribution functions and for each class of rain.

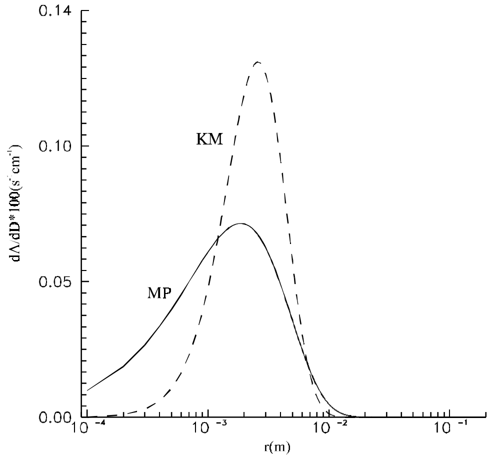

Fig.1 - Differential scavenging coefficient for the heavy - rain class and for the Marshall-Palmer and Khrgian-Mazin raindrop size distribution.

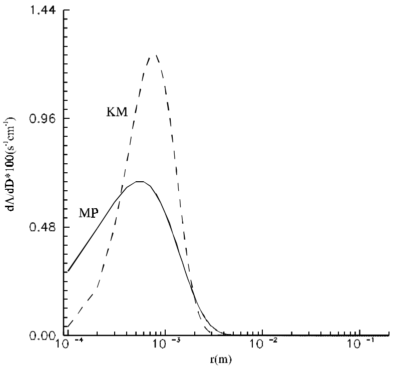

Fig.2 - Differential scavenging coefficient for the moderate - rain class and for the Marshall-Palmer and Khrgian-Mazin raindrop size distribution.

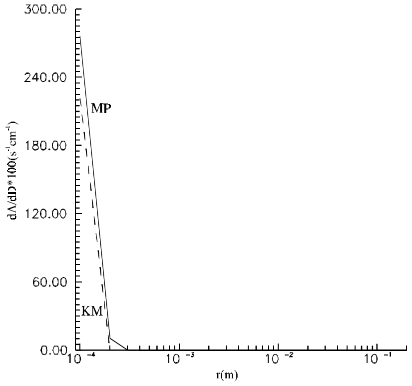

Fig.3 - Differential scavenging coefficient for the heavy - rain class and for the Marshall-Palmer and Khrgian-Mazin raindrop size distribution.

We note as rain intensity increases, $\Lambda(D_0)$ decreases (Figures 1,2,3), for each size distribution function, contrary to results of Levine and Schwartz (1982). Our results are explained by the choice of a very small lower limit for integration with Romberg method, because the smaller drops accumulating a greater concentration per fall distance because of their slower velocities, increased gas mass- transfer and increase surface to volume-ratio.

The larger values occurring at the smaller rainfall intensities emphasise that drops with smaller diameters make the greatest contribution to the washout scavenging coefficient.

The maximum value of differential scavenging coefficient can be observed closely to the radius of $2x10^{-1}$ cm, for heavy rain (Fig. 1) and closely to the $5x10^{-2}$ cm radius, for moderate rain (Fig. 2). This result emphasises the importance of the lower limit in integration.

The values of differential scavenging coefficient obtained for KM function are greater than the values for MP function and the maxim values of this coefficient are larger with one order of magnitude for moderate rain compared to the heavy rain and for moderate rain is with two order of magnitude less than the light rain.

The scavenging coefficient values calculated for light rain have maxim values in the range of very small particles (10^{-2}cm radius), both for Marshall-Palmer and Khrgian-Mazin raindrop-size distributions (Fig. 3).

These results show that the integration by Romberg method have not excluded from consideration the large number of small drops that could be responsible for an appreciable fraction of the overall scavenging of HNO_3 by precipitation.

4. Conclusions

We have performed examples of calculation to illustrate the effects of raindrop spectra on the interpretation of precipitation scavenging of irreversibly soluble gas, HNO_3. These calculations indicate that HNO_3 is rapidly scavenged by precipitation. The values of Λ are reasonably characteristic of the precipitation scavenging rates of nitric acid and they decrease as rain intensity increases.

These values reflect the important contribution of small drops to the precipitation scavenging rates of highly soluble gases as HNO_3.

The calculated values of scavenging coefficient show their dependence on the size distribution functions over which the integration is performed.

The Marshall-Palmer size distribution function underestimates the values of the scavenging coefficients compared to Khrgian-Mazin function in the moderate and heavy rain cases.

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