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The effect of random precipitation times on the scavenging rate for tropospheric nitric acid

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ABSTRACT

Studies of the effect of averaging the continuity equation for soluble species over wet and dry periods of a precipitation cycle have shown that the effective scavenging rate which must be used in such averaged models is less than the classical value obtained by a simple average of the scavenging rate over a cycle. This is a consequence of the fact that for an intermittent loss process such as precipitation wet periods correspond to depressed and dry periods to enhanced soluble species concentration. There is thus an inherent negative correlation between departures from the mean of the scavenging rate and soluble species concentration which is not accounted for in the averaging process. This study shows that if the source of the soluble species is time dependent, then periods of positive correlation between scavenging rate and species concentration may also result from temporal averaging. This can result when the end of a precipitation period is coincident with the diminution or termination of the source. A specific example considered is the late afternoon rainout of nitric acid occurring just prior to the night time cessation of its chemical production. Under some assumed precipitation scenarios, the positive correlation may dominate, leading to an effective scavenging rate exceeding the classical value. A model is developed to take account of the effect of random precipitation times on the nitric acid scavenging rate. These calculations give effective scavenging rates about a factor of 2 to 3 greater than those of some other published models. For small wet fractional periods, typically less than 0.1, the effective scavenging rate may exceed the classical value slightly, although the details of this calculation depend on the mean precipitation period and on some of the model's statistical assumptions.

1. Introduction

A general problem encountered in modeling the concentrations of atmospheric species results from the necessity of averaging the continuity equations describing such species over various spatial and temporal domains. Time independent box models represent an extreme, being averaged over all time and space scales, but three dimensional, time dependent models must also deal with processes which occur on scales smaller than the model resolution. The continuity equations contain products of species concentrations and various rate coefficients and the average of these product terms over some domain is not equal in general to the product of the individual averages. The problem may be illustrated by expressing the variables involved in the continuity equations as a mean value over some spatial or temporal scales of interest plus a term representing departures from the mean over those scales. Thus, if $c(x)$ is some variable of interest with x representing the set of independent variables which are not averaged over, we have

$$c(x) = \overline{c(x)} + c'(x) \tag{1}$$

and the continuity equations will generally contain expressions of the form

$$\overline{c_1(x)\,c_2(x)} = \overline{c_1(x)}\,\overline{c_2(x)} + \overline{c_1'(x)\,c_2'(x)}. \tag{2}$$

The overbar denotes a mean value. In later sections of this paper, where some quantities are treated as random variables, the corresponding means will be enclosed in brackets to indicate that they are expected values of random variables.

There are at least three methods for dealing with the primed terms on the right-hand side of eq. (2).

(1) Ignore them. This is a fairly common practice when the terms represent products of species concentrations. It is hoped that these terms may be neglected. This is valid if the product represents species which are uncorrelated over the domains of averaging. Chameides et al. (1987) have used real time data to investigate the effect of this approximation on limited aspects of tropospheric chemistry, finding that it was usually satisfactory for the conditions of their study. This is consistent with the general success of simplified models in describing many aspects of atmospheric chemistry.

(2) Evaluate the terms numerically using a model which is not averaged over the domains on which the c's of eq. (2) are averaged. This will provide a set of correction terms which may then be applied to averaged models. These correction terms will normally be incorporated into the rate coefficients, not explicitly shown in (2), to give an "effective" rate coefficient. This procedure has been carried out, for example, by Turco and Whitten (1978) to evaluate effective diurnally averaged photodissociation rates.

(3) Assume functional forms for the behavior of the factors in the product terms in (2) over the domains of averaging. The second term on the right-hand side of (2) may then be evaluated analytically and the result incorporated in a correction to various rate coefficients. This is the procedure used, for example, by Giorgi and Chameides (1985) in parameterizing the tropospheric scavenging rate for soluble species.

In this paper, errors involved in the temporal averaging of the tropospheric scavenging rate will be considered. The well known fact that a simple average of this rate over wet and dry periods gives poor results (Rodhe and Grandell, 1972, 1981; Thompson and Cicerone, 1982; Stewart et al., 1983; Giorgi and Chameides, 1985, 1986) is a manifestation of the importance of the second term on the right-hand side of (2) in this context.

It seems intuitively obvious when considering eq. (2) that the term representing the product of departures from the mean of the scavenging rate coefficient and the soluble species concentration will be negative as a consequence of a strong anti- or negative correlation between these terms. During precipitation periods, for example, the value of the scavenging rate coefficient will be higher than average while the soluble species concentration will be lower. The reverse is true during dry periods. This negative correlation results in a value for the effective scavenging coefficient less than that of the simple average and consequently in a longer residence time for the soluble species than would be inferred from the latter value. This underestimate of the residence time resulting from use of a simple average scavenging rate coefficient in model calculations is the problem considered by Rodhe and Grandell (1972), and Giorgi and Chameides (1985).

There are conditions, however, in which the correlation term in eq. (2) may be positive. Physically such a positive correlation can arise from circumstances in which the source of the soluble species, as well as the sink, is variable in time. For example, consider the case of a soluble species which is chemically produced during the day, but not at night. Scavenging, if it occurs in the late afternoon, will depress the concentration of the soluble species which will then remain at a low value during the night when the value of the scavenging rate is also, by assumption, low. There is thus a positive correlation between scavenging rate and soluble species concentration resulting from the occurrence of scavenging just prior to the cessation of the species source and this may in fact dominate the negative correlation arising from the scavenging process itself. These circumstances were present in the numerical model studies of Stewart et al. (1983). The "accidental" correlation between scavenging rate coefficient and nitric acid concentration resulting from these authors' assumption of a late afternoon rain resulted in a need to use a larger rate coefficient, averaged over wet and dry periods, than given by the simple average or "classical" value.

In Section 2 below, the method of developing an effective scavenging rate by assuming functional forms for the variations of scavenging rate and concentration during wet and dry periods will be described. A basic assumption in most realizations of this method is that precipitation events are periodic. It will be noted that the wet period decrease in concentration is not strongly dependent on meteorological details such as the time at which precipitation occurs or the length of the precipitation cycle, and that a simple exponential function adequately describes this decrease. It will be argued, however, that the dry period recovery is dependent on such factors and that no simple function can describe the range of possible dry period recovery scenarios. A recovery function will be suggested in this section which depends on a single parameter that may be varied to approximate a range of time dependent models results. A value for this parameter must be chosen, however, to obtain an effective scavenging rate. A weakness of the method described in this section is thus its inability to incorporate a range of possible dry period behaviors into a single expression for the effective scavenging rate.

This problem will be addressed in section 3 where a method for averaging the effective scavenging rate over a range of possible post precipitation recovery scenarios will be suggested. The effective scavenging rate derived in this section will thus depend on an assumed range of dry period behaviors rather than a single recovery function.

2. Scavenging rate parameterization

The effective scavenging rate will be defined as follows:

$$\lambda_e \bar{c} = \overline{\lambda c} \tag{3}$$

where c is the soluble species concentration, λ the scavenging rate, and λ_e the effective scavenging rate. The averages are over a precipitation period. Use of this definition replaces the product term $\overline{\lambda c}$ in the continuity equation for soluble species c by a term containing $\bar{c}$, thus facilitating its solution. With reference to eq. (2), the definition (3) may also be written as

$$\lambda_e = \bar{\lambda} + \overline{\lambda' c'}/\bar{c}. \tag{4}$$

As noted in the introduction, if functional forms are assumed for the variation of λ and c through the domains over which the continuity equation is to be averaged, in this case wet and dry periods, the right-hand side of (4) may be evaluated. If w and d are the fractional wet and dry periods, and subscripts w and d refer to the functional forms of variables during such periods, then

$$\overline{\lambda' c'} = w\overline{\lambda'_w c'_w} + d\overline{\lambda'_d c'_d}. \tag{5}$$

The fractional wet and dry periods are denoted by f and $1 - f$ in Giorgi and Chameides (1985). The change in notation is motivated by the use of f for probability density functions later in this paper. Using the definition (1) of the primed quantities on the right-hand side (hereafter r.h.s.) of (5) and using the fact that

$$\bar{\lambda} = w\overline{\lambda_w} + d\overline{\lambda_d}, \quad \bar{c} = w\overline{c_w} + d\overline{c_d}, \tag{6}$$

it follows that

$$\lambda_e \bar{c} = \bar{\lambda}\bar{c} + \overline{\lambda' c'} = w\overline{\lambda_w c_w} + d\overline{\lambda_d c_d}. \tag{7}$$

The r.h.s. of (7) is the equation actually used in the development of expressions for λ_e.

The assumption of functional forms for the variation of the soluble species concentration during wet and dry periods will typically involve parameters which must be eliminated from the expression for λ_e since their values are not known. There are three constraints which may be utilized in the development of λ_e, in addition to eq. (7). These express the continuity of the species concentration across the temporal boundaries between wet and dry periods and define the average concentration. They may be written as

$$c_d(0) = c_w(T), \tag{8}$$

$$c_d(t_d) = c_w(t_d), \tag{9}$$

$$\bar{c} = (1/T)\int_0^{t_d} c_d(t)\,dt + (1/T)\int_{t_d}^{T} c_w(t)\,dt, \tag{10}$$

where T, t_d, and t_w are the precipitation period and the length of the dry and wet periods. It is assumed in writing the above equations and in what follows that a dry period begins at time $t = 0$, lasts until t_d, and is followed by precipitation from t_d to T. The first of these constraints, eq. (8), states that the concentration at the end of a precipitation cycle returns to the value it had at the onset of that cycle. It is this equation, necessary in general for the elimination of unknown parameters in the equations for the effective scavenging rate, which imposes the assumption of periodicity on the model.

Once functional forms are assumed for λ and c through wet and dry periods, the prescription embodied in eqs. (7)–(10) permits a straightforward development of an expression for λ_e. For the scavenging coefficient it will be assumed that λ_w is constant and λ_d is zero as in Stewart et al. (1983) and Giorgi and Chameides (1985). It is also reasonable to assume that during wet periods scavenging dominates all other production and loss processes and the variation of $c(t)$ may be written as an exponential loss

$$c_w(t) = c_0\,e^{-\lambda_w(t - t_d)}, \tag{11}$$

where c_0 is the concentration at the onset of precipitation. Differences in parameterizations of the scavenging rate are thus to be expected as a result of different assumptions regarding the behavior of the soluble species concentration during the dry period. Such differences in assumptions may be used to reflect different circumstances in which scavenging takes place.

Giorgi and Chameides (1985) considered two scenarios for dry period recovery of the soluble species, an instantaneous recovery to the pre-precipitation values and a linear recovery over some specified time period. In the model study of Stewart et al. (1983), the post-precipitation recovery of nitric acid was relatively slow due to the assumption of a late afternoon rain. To model this, as well as a wide range of possible recovery scenarios, a power law dependence of concentration on time was assumed. As pointed out by Giorgi and Chameides (1985) the constraint given by eq. (7) was not utilized in the subsequent development. This however affects only the discussion given in that paper and does not account for the difference in results regarding the effective scavenging rate between Giorgi and Chameides (1985) and Stewart et al. (1983) since the model results given in Stewart et al. (1983) were all results of numerical integration of the continuity equations. A revised form of the power law recovery assumed for a dry period is

$$c_d(t) = c_1 + c_2(t/t_d)^n. \tag{12}$$

In (12) c_1 is the concentration of the scavenged species at the end of the wet period and c_2 is the amount needed for full recovery to pre-precipitation values. These unknown parameters are eliminated in the solution of eqs. (7) to (10) for λ_e. For example, the constraint given by eq. (8) combined with the assumed wet period behavior given by (11) shows that c_1 is given by (11) with $t = t_w + t_d$.

One advantage of assumption (12) is that a wide range of post-precipitation recovery scenarios may be modeled depending on the value assumed for n. Later developments will require a choice of the range of n values which represent feasible post-precipitation recovery scenarios. The philosophy guiding this choice is that comparison of the recovery function (12) with the results of numerical studies suggest, but do not delimit this range. If n is assumed to be large, the initial recovery proceeds slowly and increases more rapidly in the later stages until the pre-precipitation value of concentration is attained. The deferred recovery implied by larger n values means that such values result in a larger effective loss from scavenging since the positive correlation between departures from the mean of concentration and scavenging rate is enhanced. Similarly, smaller n values which give rapid initial and slower subsequent recovery imply less effective loss from scavenging. The latter behavior is typical, for example, of the model of Thompson and Cicerone (1982) in which an early morning precipitation was assumed with subsequent recovery over a one week cycle. Fig. 1 shows a comparison of the concentrations given by eqs. (11) and (12) with the model results of Stewart et al. (1983) and Thompson and Cicerone (1982). The former are represented fairly well with an assumed power law of $n = 4.0$. Lower n values give a better fit towards the end of the dry period but a poor fit through the central portion of the curve. High values give a poor fit towards the end of the dry period and not much improvement over $n = 4$ in the central part of the curve. The assumptions on which the Stewart et al. (1983) model were based resulted in very effective scavenging loss, although that was not their objective and no attempt was made to maximize this effectiveness. The value of $n = 4$ results in somewhat more effective scavenging than that present in the Stewart et al. model and will be taken as a preferred value for the upper limit on the recovery index in later developments. The value of $n = 0.5$ was similarly chosen by inspection as a "best" fit to the Thompson and Cicerone (1982) model. This will be taken as a preferred lower limit on the recovery index.

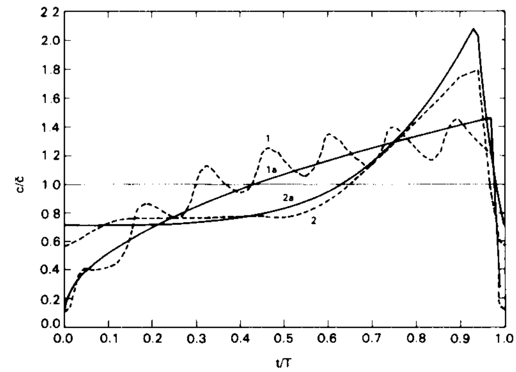

Fig. 1. Comparison of the Thompson and Cicerone (1982) (curve 1) and Stewart et al. (1983) (curve 2) model results with the analytic approximations given by eqs. (11) and (12). Concentration, normalized to its mean value over a precipitation cycle, is plotted as a function of time, normalized to the length of a precipitation cycle. The results from a typical precipitation cycle are shown for each model. The precipitation period is 168 h, with a wet period of 4 h, in the Thompson and Cicerone and 24 h, with a wet period of 1 h, in the Stewart et al. model. Curves 1a and 2a (solid lines) are the fits to these model results given by eqs. (11) and (12) with n in eq. (12) set to 0.5 and 4 for curves 1a and 2a, respectively.

Using the assumed functional behavior for wet and dry periods given by (11) and (12) and the prescription for developing a parameterization contained in eqs. (7)–(10) the effective scavenging rate is

$$\lambda_e = (1/QT)(1 - e^{-\lambda_0 T}), \tag{13}$$

where λ_0 is the simple average of the scavenging rate over wet and dry periods given by

$$\lambda_0 = w\lambda_w \tag{14}$$

and the factor Q is given by

$$Q = (1 - w)\frac{1 + n e^{-\lambda_0 T}}{1 + n} + (w/\lambda_0 T)(1 - e^{-\lambda_0 T}). \tag{15}$$

Q is the ratio of the mean species concentration over a precipitation cycle to the mean species concentration during a dry period (Giorgi and Chameides, 1985). The case $n = 0$ in eqs. (12) and (15) corresponds to instantaneous post-precipitation recovery as considered by Giorgi and Chameides (1985). The expressions for Q in eq. (15) and for λ_e in (13) reduce to those given by Giorgi and Chameides (1985) for this case. If $n = 1$ the expressions for Q and λ_e reduce to the case of linear recovery considered by Giorgi and Chameides (1985) if recovery proceeds throughout the entire dry period.

For comparison in what follows, note that Rodhe and Grandell (1972) developed an expression for the expected value of the lifetime of an aerosol particle based on exponential distributions of wet and dry periods. The effective value of the scavenging coefficient, based on their result is

$$\lambda_e = \lambda_0/(1 + d^2 \lambda_0 T). \tag{16}$$

Figs. 2a, b show values of the scavenging rate for the Giorgi and Chameides (1985) instantaneous recovery model, eq. 13 with $n = 0$, the Rodhe and Grandell (1972) model, eq. (16), and the Stewart et al. (1983) model. In Fig. 2a the precipitation period is taken as 24 h, with a dry period recovery index of $n = 4$ in the Stewart et al. (1983) model for this case. In Fig. 2b the precipitation period is taken as 96 h with a dry period recovery index of $n = 0.5$ assumed appropriate for this case. All the rates have been normalized to a wet period rate assumed to be 2.0×10^{-4} s^{-1}. This is close to the value calculated by Levine and Schwartz (1982) for an assumed Best (1950) drop size distribution in a shower of 5 mm/h intensity and is the value adopted in the model study of Thompson and Cicerone (1982). The independent variable is the fractional wet period, w. In the limits of no rain ($w = 0$) and perpetual rain ($w = 1$) all parameterizations must converge to the values 0 and 1. For the more interesting cases of w between 0 and 1 it is seen that assumptions regarding the dry period behavior of the scavenged species result in substantially different values for the effective scavenging rate. Higher values of the dry period recovery index, corresponding to slower post precipitation recovery, are more appropriate for relatively short precipitation periods. If the precipitation period extends over several days, as in the Thompson and Cicerone (1982) model study, then the time over which departures from the mean of scavenging rate and nitric acid concentration (λ' and c') are positively correlated is less, as a fraction of the precipitation period, than for shorter periods. In Fig. 1, for example, the nitric acid concentration reaches its mean

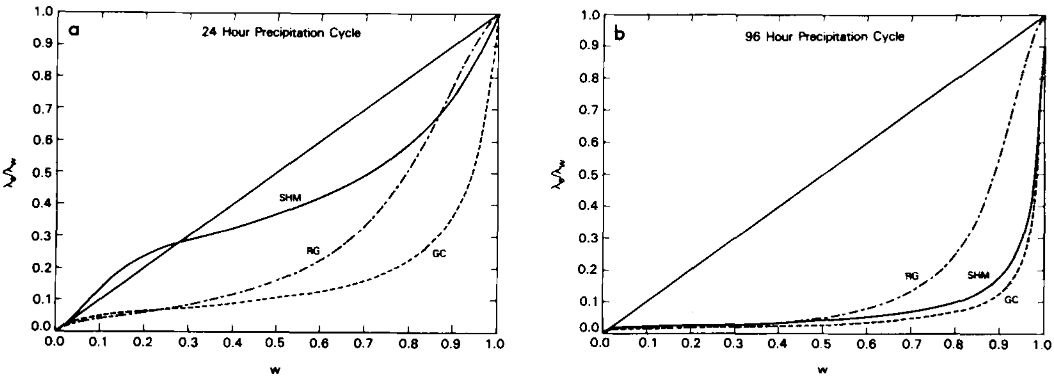

Fig. 2. (a) Comparison of parameterized scavenging rates calculated from the Rodhe and Grandell (1972) (curve RG), Stewart et al. (1983) (curve SHM), and Giorgi and Chameides (1985) instantaneous recovery (curve GC) models. Scavenging rate, normalized to a wet period value of 2.0×10^{-4}, is plotted as a function of wet fraction. A dry period recovery index of $n = 4$ is assumed for the SHM curve and a precipitation period of 24 h is used in all calculations. The diagonal line is the simple average or "classical" value. (b) The same models as (a) but with a dry period recovery index of $n = 0.5$ for the SHM curve and an assumed precipitation period of 96 h in all calculations.

value, recovering from its depressed post precipitation value, in about 0.3 to 0.4 of a precipitation period in the Thompson and Cicerone (1982) model, but requires about 0.65 period in the Stewart et al. (1983) model. A later assumed rainfall on the first day of the Thompson and Cicerone (1982) precipitation period would not be likely to modify these results significantly since the recovery of the nitric acid concentration will proceed rapidly in the first daylight hours following precipitation. For purposes of this study the photochemistry of the Thompson and Cicerone (1982) and Stewart et al. (1983) models, which gives rise to the nitric acid behavior illustrated in Fig. 1, is assumed correct.

3. The effect of random precipitation events

3.1. The distribution of rain events and fractional wet periods

The parameterized scavenging rates discussed above are based on the assumption of periodic precipitation events. This is convenient for the specification of the constraint eqs. (8)–(10) on the functional forms of the soluble species concentration during wet and dry periods, but is unrealistic. A better assumption regarding precipitation events is that the wet and dry periods are independent and exponentially distributed. This assumption is used in the derivation of the Rodhe and Grandell (1972) model. Sperber and Hameed (1986) have determined least square fits to exponential distributions, for various precipitation types, based on 6 years data from Brookhaven National Laboratory. The parameters which are of direct interest in our discussion of effective scavenging rates are the total precipitation period and the fractional wet period. It is thus of interest to determine the statistics of these parameters based on assumed independent exponential distributions for wet and dry periods. The wet and dry periods, denoted by t_w and t_d, are assumed to be random variables with exponential probability density functions given by

$$f(t_w) = \alpha \, e^{-\alpha t}, \quad f(t_d) = \beta \, e^{-\beta t}. \tag{17}$$

Their expected values are

$$\langle t_w \rangle = 1/\alpha, \quad \langle t_d \rangle = 1/\beta. \tag{18}$$

The distributions and expected values of the random variables representing total precipitation period and wet fraction are required. These are defined in terms of the random variables t_w and t_d by

$$T = t_w + t_d, \quad w = t_w/(t_w + t_d). \tag{19}$$

The prescription for determining the density functions for T and w, given those for t_w and t_d is given in standard texts such as Papoulis (1984) and excessive detail will be avoided in the following. The joint density function for T and w is given by

$$f(T, w) = f(t_w, t_d)/|J(t_w, t_d)| \tag{20}$$

where $f(t_w, t_d)$ is the joint density functions for t_w and t_d and J is the Jacobian of the transformation eqs. (19). The arguments t_w and t_d on the r.h.s. of (20) must be understood as the solutions of the transformation eqs. (19) for t_w and t_d. The r.h.s. of (20) would generally contain a summation over all such solutions, but in our case there is just one real solution given by

$$t_w = wT, \quad t_d = (1 - w)T. \tag{21}$$

The Jacobian of (19) is

$$J = -1/(t_w + t_d), \tag{22}$$

and in view of the assumed independence of t_w and t_d their joint density function is just the product of the individual densities. The joint density function of eq. (20) is thus

$$f(T, w) = \alpha\beta T e^{-\beta T} e^{-(\alpha - \beta)Tw}, \tag{23}$$

where $0 \leqslant T \leqslant \infty$ and $0 \leqslant w \leqslant 1$.

The marginal densities may now be obtained by integration

$$f(T) = \int_0^1 f(T, w)\,\mathrm{d}w, \quad f(w) = \int_0^\infty f(T, w)\,\mathrm{d}t, \tag{24}$$

and are

$$f(T) = \frac{\alpha\beta}{\alpha - \beta} e^{-\beta T}(1 - e^{-(\alpha - \beta)T}), \tag{25}$$

$$f(w) = \frac{\alpha\beta}{[\beta + (\alpha - \beta)w]^2}. \tag{26}$$

In terms of expected values of wet and dry periods the expected values of T and w are:

$$\langle T \rangle = \langle t_w \rangle + \langle t_d \rangle, \tag{27}$$

$$\langle w \rangle = \frac{\langle t_w \rangle \langle t_d \rangle}{(\langle t_w \rangle - \langle t_d \rangle)^2} [\ln(\langle t_d \rangle / \langle t_w \rangle) + (\langle t_w \rangle / \langle t_d \rangle - 1)]. \tag{28}$$

The value for $\langle T \rangle$ is just the sum of the expected values of $\langle t_w \rangle$ and $\langle t_d \rangle$ and follows readily from the definition (19) without going through the above arguments. The expected value for the wet fraction differs from that which would be obtained from a simple ratio obtained by substituting expected values into the r.h.s. of (19). Eq. (28) is the expression that would be obtained for the expected value of the scavenging rate (normalized to a constant wet period value) from the classical definition if t_w and t_d were considered as random variables. Although not immediately obvious from eq. (28), it can be shown that

$$\langle w \rangle \to \tfrac{1}{2} \quad \text{when } \langle t_w \rangle \to \langle t_d \rangle.$$

Our main purpose in obtaining (28) is to get some idea of reasonable values for the expected wet fraction at which to compare various models of the scavenging rate since the differences in model values depend on the values of $\langle w \rangle$ at which they are compared. Table 1 gives a few values of $\langle T \rangle$ and $\langle w \rangle$ for some available estimates of $\langle t_w \rangle$ and $\langle t_d \rangle$. This table indicates that realistic values of w range from roughly 0.05 to 0.30.

3.2. *A quasi-random model for the scavenging rate*

In this section one method is suggested of accounting for the random times of precipitation events on the effective scavenging rate for species which have a variable source, such as nitric acid. The model to be developed will be described as a quasi-random model since it utilizes the functional form of the parameterized scavenging rate coefficient derived from assumed periodic precipitation events, eq. (13). The random part of the model is the dry period recovery function which, as has been argued above, exhibits a

Table 1. *Expected values of precipitation period (wet and dry periods) and wet fraction based on expected values of wet and dry periods from various sources; in the source column, SH refers to Sperber and Hameed (1987), RG to Rodhe and Grandell (1972), and SHM and TC to the model studies of Stewart et al. (1983), and Thompson and Cicerone (1982)*

Source		$\langle t_w \rangle$ h	$\langle t_d \rangle$ h	$\langle T \rangle$ h	$\langle w \rangle$
SH	rain	5.1	79.4	84.5	0.13
SH	snow	4.4	79.4	83.8	0.12
SH	rain showers	1.5	79.4	80.9	0.059
SH	thunder showers	1.1	79.4	80.5	0.047
RG	summer	4	92	96	0.10
RG	winter	9	40	49	0.27
RG	year	7	68	75	0.18
SHM	model	1.5	22.5	24	0.14
TC	model	4	164	168	0.07

behavior dependent on the time at which precipitation occurs. The power law recovery index n will be treated as a random variable. This will, in effect, average over the times of precipitation events, incorporating the range of dry period recovery functions into a single expression for the scavenging rate. This expression will depend on 3 quantities. The first two of these are the fractional wet period and the total precipitation period which may be derived from meteorological statistics for any region of interest. The third quantity is the probability distribution which must be assumed for the dry period recovery index n. It is essential that the effective scavenging rate be most strongly dependent on the first two parameters, which are observables, and less dependent on assumed model statistics. The discussion of the previous sections has prepared the way for what are offered as reasonable assumptions regarding the range of values of the recovery index, n. The sensitivity of the model to substantial extensions of this range will be investigated.

Both a range of n values and a probability distribution over this range must be assumed. The sensitivity of the results to two simple but distinctly different distribution functions will be considered. The first of these will be a uniform distribution over n values which span the range from those giving rapid to slow post precipitation recovery. In light of the discussion given following Fig. 1, $n = 0.5$ to 4.0 are taken as standard values for this range. The second distribution to be considered will be a triangular distribution function peaked at the lower n value. This implies that relatively rapid post precipitation recovery scenarios are more probable than slow recovery. If there were no reason to prefer any particular values of the recovery index the uniform distribution would be the more reasonable working choice. However, as noted earlier, higher values of n such as 4 are appropriate to relatively short precipitation periods of about a day. Although the data in Table 1 are not exhaustive, they do imply that typical precipitation periods are of several days duration. Relatively rapid post precipitation recovery of nitric acid is therefore probably closer to the norm and higher n values, corresponding to slow recovery, should be given less weight in any assumed probability distribution. The triangular distribution function accomplishes this goal and is to be preferred over the uniform distribution. The uniform distribution, however, has the virtue of simplicity and its consideration permits a wider range of model sensitivity studies than would result from the assumption of a single distribution. To assess the sensitivity of results to the assumed range of n values, ranges of 0.5 to 4 (preferred) and 0 to 8 will be used in the uniform and triangular distributions. These distributions will be denoted by $U(0.5–4)$, $U(0–8)$, $T(0.5–4)$, and $T(0–8)$, with $T(0.5–4)$ resulting in the preferred model.

It is convenient for the following discussion to define several auxiliary variables in order to shorten the notation. The effective scavenging rate in eq. (13) will be written as a product of a factor involving the recovery index, n, and a factor independent of n:

$$\lambda_e = G(n)\,L, \tag{29}$$

and further define the following:

$$\varepsilon = e^{-\lambda_0 T}, \quad a = d + (w/\lambda_0)\,L, \quad b = d\varepsilon + (w/\lambda_0)\,L. \tag{30}$$

The factor $G(n)$ is $1/Q(n)$ where $Q(n)$ is given by (15) and, from (13) and (30)

$$L = \frac{(1-\varepsilon)}{T}. \tag{31}$$

As before, d and w are the fractional dry and wet periods, λ_0 is the classical scavenging rate, and T is the precipitation period. The relationships between scavenging rate, λ, and recovery index, n, may now be written as

$$\lambda = \frac{(1+n)\,L}{a+bn}, \quad n = -\frac{L-a\lambda}{L-b\lambda}. \tag{32}$$

With λ and n now assumed to be random variables, the relationship between their density functions is (see e.g. Papoulis, 1984),

$$f(\lambda) = f(n)/|g'(n)|, \tag{33}$$

where $g(n)$ is the transformation between λ and n given in (32) and $f(n) = 1/(n_2 - n_1)$ is the uniform distribution function over the range from n_1 to n_2. From (32) and (33)

$$f(\lambda) = \frac{d(1-\varepsilon)\,L}{(l-b\lambda)^2}\, f(n). \tag{34}$$

There is no need to substitute $f(n)$ from the

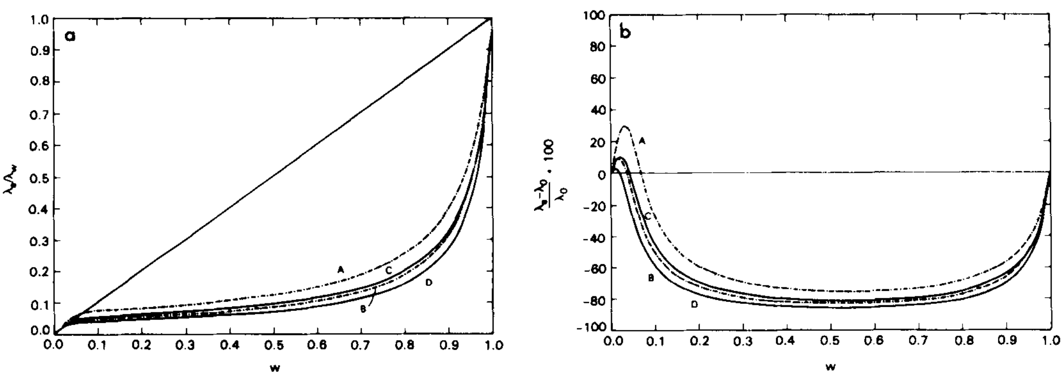

Fig. 3. (a) Comparison of scavenging rate values based on the present quasi-random parameterization, eqs. (36) and (40). Axes are the same as those of Figs. 2(a) and 2(b). The numerator of the ratio given on the ordinate is labelled λ_e, indicating an effective rate, in this and the following figures. For curves representing the quasi-random model this is the same as the expected values, $\langle\lambda\rangle$, in the text. This figure indicates the sensitivity of model values to the statistical assumptions regarding the distribution of dry period recovery index. Curvs A and B are based on the uniform distributions (dashed lines) U(0–8) and U(0.5–4), respectively. Curves C and D (solid lines) are based on the triangular distributions T(0–8) and T(0.5–4). The assumed precipitation period is 96 h for all cases. The axes are the same as those of Fig. 2. (b) The same models as (a), but plotted as a percent difference from the classical scavenging rate.

second equality in eq. (32) since $f(n)$ is constant in this case. The expected value of λ is

$$\langle\lambda\rangle = \int_{\lambda_1}^{\lambda_2} \lambda f(\lambda)\,\mathrm{d}\lambda, \tag{35}$$

where λ_1 and λ_2 are the limiting values of λ corresponding to the limits on n for the uniform distribution. For any choice of n's these are evaluated from (32). The result of the integration in (35) is

$$\langle\lambda\rangle = \frac{d(1-\varepsilon)L}{b^2} f(n)\left[\ln\left(\frac{L-b\lambda_2}{L-b\lambda_1}\right) + \frac{bL(\lambda_2-\lambda_1)}{(L-b\lambda_1)(L-b\lambda_2)}\right]. \tag{36}$$

Due to our assumption of a uniform distribution $f(n)$ is constant and not involved in the integration of (35). The triangular distribution, peaked at the smaller limit, n_1, of n values is given by

$$f(n) = C\frac{n_2-n}{n_2-n_1}, \tag{37}$$

where the constant C is derived from the requirement that the integral of $f(n)$ from n_1 to n_2 be 1 and is

$$C = \frac{2}{n_2-n_1}. \tag{38}$$

The transformation equations between n and λ are the same as before (eq. (32)) and $f(n)$ may be written as the sum of a constant and a function of λ.

$$f(n) = kn_2 + k\frac{L-\lambda a}{L-\lambda b}, \quad k = \frac{2}{(n_2-n_1)^2}. \tag{39}$$

The expected value of λ will thus consist of a term proportional to that found for the uniform distribution plus a contribution from the integral over the second term on the r.h.s. of (39). Omitting the details

$$\langle\lambda\rangle_T = \frac{2n_2}{n_2-n_1}\langle\lambda\rangle_U + \frac{kd(1-\varepsilon)La}{b^3}\left[\ln\frac{y_2}{y_1} + (1+m)\left(\frac{1}{y_2}-\frac{1}{y_1}\right) - \frac{mL^2}{2}\left(\frac{1}{y_2^2}-\frac{1}{y_1^2}\right)\right]. \tag{40}$$

The subscripts T and U refer to triangular and uniform distributions, m is $1-b/a$, and y is a variable defined for convenience in performing

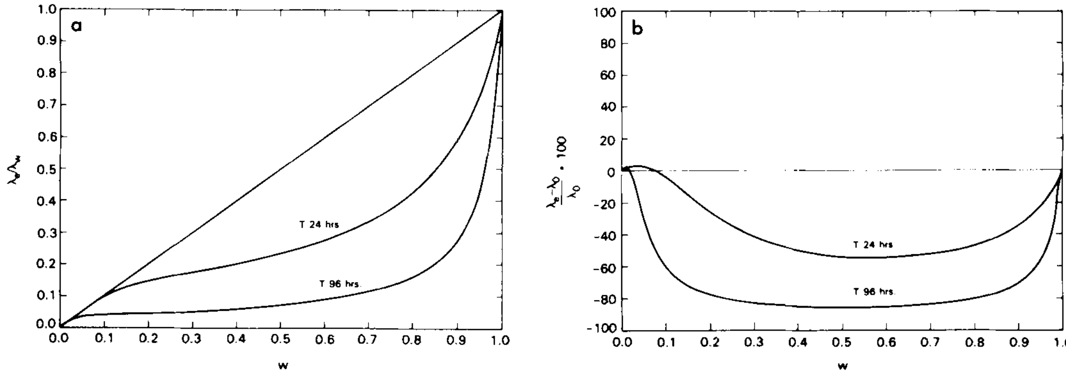

Fig. 4. (a) Comparison of quasi-random scavenging rate values based on the $T(0.5\text{–}4)$ distribution for assumed total precipitation periods of 24 and 96 h. Axes are the same as those of Figs. 2(a) and (b). (b) The same models as (a), but plotted as a percent difference from the classical scavenging rate.

the integral over the second term on the r.h.s. of (39).

$$y = L - b\lambda. \tag{41}$$

The values of y_1 and y_2 in (40) are the lower and upper limits on y derived from the assumed limits on n.

4. Results and discussion

Since the preceding development contains assumptions regarding the statistics of the dry period recovery index, n, it is necessary to examine the sensitivity of the expressions for the expected values of the scavenging rate, eqs. (36) and (40), to these assumptions. As noted previously, these expressions will be more useful if their dependence on precipitation statistics such as the expected values of the precipitation period and wet fraction is greater than their dependence on model assumptions. Fig. 3a shows values of $\langle\lambda\rangle$ based on eqs. (36) and (40) for assumes ranges of n from (0.5–4.0) and (0–8). Curves A, B, C, and D result from $U(0\text{–}8)$, $U(0.5\text{–}4)$, $T(0\text{–}8)$, and $T(0.5\text{–}4)$. The mean precipitation period is assumed to be 96 h in all cases. Expected scavenging rate values based on the uniform distribution are more sensitive to the upper limit assumed for n since all n values are given equal weight in this distribution whereas higher n values are lightly weighted in the triangular distribution. For a given wet fraction, the curves in Fig. 3a show larger $\langle\lambda\rangle$ values for larger assumed upper limits on the dry period recovery index. This is in accord with expectations since such n values correspond to the slow post precipitation recovery scenarios which give rise to positive correlation between λ' and c', eq. (4). The highest and lowest values of the scavenging rate given by the four models shown in Fig. 3a differ by a factor of about 1.8 over the middle range of wet fractions. Fig. 3b shows the same $\langle\lambda\rangle$ values plotted as a percent difference from the classical value. The assumed precipitation period for all the curves in Figs. 3a and b is 96 h.

Figs. 4a, b indicate the sensitivity of the results to the precipitation period. Curves A and B are based on $T(0.5\text{–}4)$ for periods of 24 and 96 h, respectively. The shorter precipitation periods give rise to higher $\langle\lambda\rangle$ values, all else being equal, since more precipitation necessarily occurs during periods of diminished source. For a given wet fraction the precipitation period determines the degree of correlation between λ' and c', and this is consistent with the sensitivity to period indicated by Figs. 4a, b.

Figs. 5a, b illustrate the differences between the quasi-random model developed above and the Giorgi and Chameides (1985) and Rodhe and Grandell (1972) models for assumed precipitation periods of 96 and 24 h. The Giorgi and Chameides (1985) curve plotted is for their

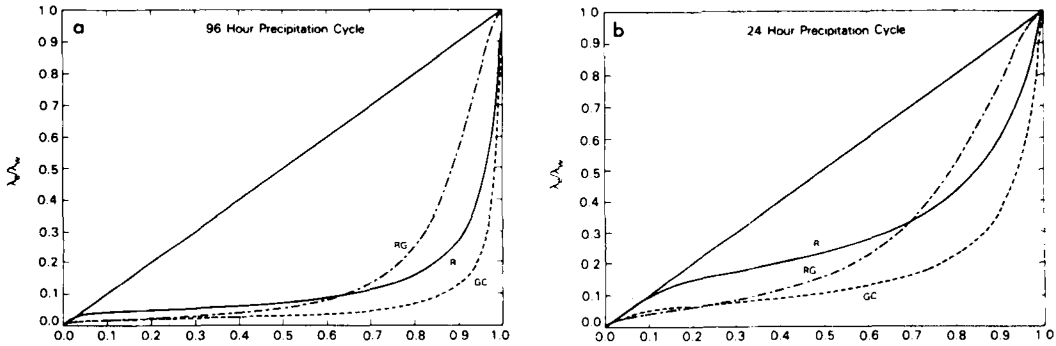

Fig. 5. (a) Comparison of the quasi-random scavenging rate values based on the $T(0.5\text{–}4)$ distribution (curve R—solid line) with the Rodhe and Grandell (1972) (long–short lines) and Giorgi and Chameides (even dashes) (1985, instantaneous recovery) models. Axes are the same as those of Figs. 2(a) and (b). The precipitation period is assumed to be 96 h. (b) The same models as (a) but with an assumed precipitation period of 24 h.

instantaneous recovery model. The Giorgi and Chameides and Rodhe and Grandell results are quite similar over most of the range of probable wet fractions and are likely to be good estimates of the effective scavenging rate for species whose sources do not undergo substantial variation on the scale of the precipitation cycle. The quasi-random model represented by curve R is based on $T(0.5\text{–}4)$. The difference between the present model and the Rodhe and Grandell (1972) and Giorgi and Chameides (1985) models shown in these figures is about a factor of 2.6 over the middle range of wet fractions.

5. Summary and conclusions

A model for the effective scavenging rate of a soluble species has been developed which takes into account the possibility of positive as well as negative correlations between departures from the mean of the scavenging rate and species concentration. Positive correlations arise from an accidental coincidence between the cessation of scavenging and the diminution or termination of the species source, not from the physical nature of the scavenging process. In light of this fact, the model described above should only be applied to soluble species, such as nitric acid, whose source shows substantial variation on time scales of the same order as or smaller than the time scale of scavenging events. It is also worth reiterating that this model deals with temporal averaging only and does not consider effects that may arise from spatial variations in rainfall and soluble species concentration. The latter have been considered, for example, in the study of Giorgi and Chameides (1986). The consequences of day–night variations in the chemical production of nitric acid have been noted, but other factors may also influence the scavenging rate–concentration correlation. In the marine troposphere, for example, the photolytic production of NO in surface waters may be an important source of lower tropospheric odd nitrogen. This obviously shows a diurnal variation and may be locally anti-correlated with precipitation so some effect on the effective scavenging rate would be expected. There are other factors, such as the variation of rain intensity during precipitation and the implications of various assumed drop size distributions, which may influence the effective scavenging loss, but have not been considered in this paper.

The present model results in effective scavenging rates roughly a factor of two to three larger than those of the models of Rodhe and Grandell (1972) and Giorgi and Chameides (1985) when compared for the same values of wet fractions over a range of about 0.05 to 0.3 and precipitation periods of about 1–8 days.

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