

# Residence times in reservoirs under non-steady-state conditions: application to atmospheric SO<sub>2</sub> and aerosol sulfate<sup>1</sup>

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## ABSTRACT

The definitions of the residence times describing the rate of removal of materials from natural reservoirs, i.e., the mean age, the mean transit time, and the turn-over time, have been extended to encompass time-dependent rates of introduction and removal. This treatment leads to two sets of such residence times, pertinent either to material present in the reservoir at a given observation time or to material that entered the reservoir at a given time of introduction. Whereas the former quantities reflect the time dependence of both the rates of introduction and removal processes, the latter quantities are properties only of the rates of removal processes. Relationships are examined among the several residence times, as well as to the burden of material in the reservoir attributable to a given rate of introduction. Additionally the several definitions are extended to encompass secondary materials, i.e., materials formed *in situ* as a consequence of reactions of materials directly introduced.

The above framework is applied to a consideration of the residence times and burdens of atmospheric SO<sub>2</sub> and sulfate aerosol, for assumed time-dependent rates of SO<sub>2</sub>-to-sulfate conversion and dry deposition. It is found that even for such rates exhibiting strong diurnal modulation, as expected from considerations of photochemical reaction rates and atmospheric stability, the turn-over times and atmospheric burdens of SO<sub>2</sub> and sulfate exhibit relatively little diurnal modulation, unless the fraction of SO<sub>2</sub> removed per day substantially exceeds 50%, a circumstance that is at variance with the present understanding of the fate of this material in the atmosphere. These considerations suggest that it may be adequate for many purposes to model the evolution of atmospheric sulfur compounds according to diurnal average rate coefficients.

Regarding secondary materials one further useful quantity is the relative burden, or the ratio of the amounts of secondary to primary materials present in the reservoir. This quantity is directly comparable to ratio of the observed concentrations of these materials and thus serves as an additional condition that must be satisfied by models describing their transformation and removal.

## 1. Introduction

In consideration of the budgets of materials introduced into natural reservoirs, it is useful to describe the rates of removal processes in terms of the characteristic times associated with these processes. For a material which is removed from a reservoir by a first-order process with constant coefficient the characteristic time is equal to the

inverse of the rate coefficient and may be interpreted variously as the mean age of material in the reservoir, as the mean transit time through the reservoir, or as the "turn-over time", the ratio of the amount of material in the reservoir to the flux through the reservoir. However, as has been pointed out by several authors (Eriksson, 1971; Bolin and Rodhe, 1973; Nir and Lewis, 1975) these quantities no longer coincide if the rate of the removal process is other than first order with constant coefficient. The precise definition of these

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several residence times in terms of distribution functions describing the probability of the persistence of matter in the reservoir has been treated by Bolin and Rodhe (1973). That discussion was motivated by the utility of these quantities in consideration of such concepts as material budgets (Rodhe, 1978), transport within reservoirs (Rodhe, 1972), and spatial variability within reservoirs (Junge, 1974).

A common feature of the above discussions is that they are restricted to steady-state conditions, i.e., conditions in which the rates of neither introduction nor removal exhibit time dependence, although it is evident that such a time dependence may be exhibited by many processes (Nir and Lewis, 1975). For example, source strengths may exhibit a diurnal or annual cycle as may transformation and removal rates. Thus the seasonal variation in concentrations of atmospheric  $\text{CO}_2$  at various locations has been attributed to variation in the rate of removal of  $\text{CO}_2$  by photosynthesis (Ekdahl and Keeling, 1973; Woodwell et al., 1978). Similarly a diurnal dependence has recently been inferred for the chemical evolution of atmospheric sulfur compounds (Husar et al., 1978); the latter authors have, in fact, suggested the application of Bolin and Rodhe's treatment to such time-dependent processes. In this context it now seems useful to extend the treatment previously given to encompass such non-steady-state conditions. This will permit an examination of the dependence of such quantities as the turn-over time of a pollutant upon the time of introduction into the atmosphere, or as a function of the time of observation. By examination of such dependencies for a given model of time-dependent removal and/or introduction processes we may discern the extent to which these quantities depart from the values given by a steady-state model. In turn it will be possible to infer the extent to which such time dependence will be reflected in measurable quantities, e.g., species concentrations. Additionally, if there is revealed a strong dependence upon the time of introduction, then this may serve to guide formulation of strategies for air quality management. A second purpose of the present article is to extend the definitions given to material that is not itself directly introduced to the reservoir, but that is formed *in situ* as a consequence of reaction of materials that are so introduced. An example of interest is the formation of so-called secondary

pollutants, e.g., aerosol sulfate formed by the atmospheric reaction of sulfur dioxide. The extension to secondary pollutants follows naturally from the present approach. These concepts will then be applied to the specific example of  $\text{SO}_2$  and aerosol sulfate.

## 2. Residence times

Bolin and Rodhe (1973) introduce in their discussion three time quantities characterizing the duration of residence of materials in reservoirs into which they are admitted:

- (a) *Turn-over time* ( $\tau_0$ ): the ratio of the amount of material present in the reservoir to the amount of material passing through the reservoir per unit time.
- (b) *Mean age* ( $\tau_a$ ): the average age subsequent to introduction into the reservoir of material present in the reservoir.
- (c) *Mean transit time* ( $\tau_t$ ): the average age subsequent to introduction into the reservoir of material leaving the reservoir.

These authors (cf. also Eriksson, 1971, and Nir and Lewis, 1975) establish, under steady-state conditions, the equivalence of the turn-over time and the mean transit time. They further suggest, as we shall see in detail below, that in consideration of material budgets, as well as consideration of the scale of transport of materials within a reservoir, the mean transit time, rather than the mean age, is the more relevant measure of the rate of sink processes. On the other hand, for consideration of the chemical evolution of these materials, the mean age is more useful.

To aid in gaining an appreciation of the several residence times, an analogy to human populations may be helpful. The mean age is simply the average age of the population living at any time. The mean transit time is the average age at the time of death. The turn-over time is ratio of the population to the birth rate (or to the death rate, since, at steady state this equals the birth rate).

We turn now to the evaluation of these several time quantities for non-steady-state conditions. Initially this discussion will be restricted to materials directly admitted into the reservoir, i.e., primary materials. Let  $A(t, t_0)$  be the amount of

material per unit time introduced into the reservoir at time  $t_0$  remaining at time  $t$ . It may be seen that  $A(t_0, t_0)$  is the rate at which material is introduced into the reservoir at time  $t_0$ . The ratio  $A(t, t_0)/A(t_0, t_0)$  may be considered to represent either the fraction of material introduced at time  $t_0$  that will survive at least to time  $t$ ,  $t \geq t_0$ , or, alternatively, the probability that a molecule introduced at time  $t_0$  will survive at least to time  $t$ . Since we have explicitly restricted our discussion thus far to a primary material, it is evident that  $A(t, t_0)$  is a non-increasing function of time  $t$ , any decrease representing the removal of material by a physical or chemical process, e.g., for an atmospheric pollutant, deposition or chemical reaction. We further assume that we are dealing with a non-conservative material, so that at large time,  $t \rightarrow \infty$ , all material that entered the reservoir at a given time  $t_0$  has been removed from the reservoir. In order to guarantee convergence of integrals to be introduced below we introduce the condition

$$\lim_{t \rightarrow \infty} t^n A(t, t_0) = 0, \quad n \leq 2 \quad (1)$$

This condition is minimally restrictive and would not appear to exclude any cases of practical interest.

The persistence function  $A(t, t_0)$ , serves as the basis of the subsequent discussion. This discussion may take two different courses, and we shall explore them both, basing our definitions either upon material that is present in the reservoir at a particular time of observation  $t$  (a given "population") or upon material that has entered the reservoir at a given time of introduction  $t_0$  (a given "cohort"). In the steady state, of course, average quantities computed for both distributions must be the same.

### 2.1. Population-based residence times

The several population-based residence times are pertinent to material that is present in the reservoir at a given time of observation  $t$ , resulting from introduction at times  $t_0$  prior to  $t$ . For this set of material we proceed to define and develop mathematical expressions for evaluating the three residence times analogous to those given by Bolin and Rodhe (1973) for steady-state conditions.

(a) *Turn-over time.* The turn-over time is defined as the ratio of the amount of material present in the reservoir to the amount of material

passing through the reservoir per unit time. The amount of material present in the reservoir at time  $t$ , or burden, may be computed as the time integral of the persistence function,

$$M_A(t) = \int_{-\infty}^t A(t, t_0) dt \quad (2)$$

In order to compare integrals such as (2) with those to be developed later it is convenient to introduce the time variable  $u \equiv t - t_0$ , the age subsequent to introduction; the burden of material present in the reservoir at time  $t$  may now be expressed as

$$M_A(t) = \int_0^\infty A(t, t - u) du \quad (3)$$

In addition to serving as the basis for evaluating the turn-over time, this burden is of intrinsic interest since, under the condition of a well-mixed reservoir, the burden will be proportional to the concentration measurable at time  $t$ .

Under steady-state conditions the amount of matter passing through the reservoir per unit time, or flux, as this quantity is generally denoted (Eriksson, 1971), is unambiguously defined as the rate at which matter enters or leaves the reservoir. However, under non-steady-state conditions this quantity is not uniquely defined, since the flux into the reservoir is not generally equal to the flux out of the reservoir. This leads to two possible definitions of the turn-over time. Noting that the flux into the reservoir at time  $t$  is  $A(t, t)$ , then this choice of flux leads to the definition

$$\tau'_0(t) = \frac{1}{A(t, t)} \int_{-\infty}^t A(t, t_0) dt_0 \quad (4)$$

Alternatively, we might utilize the flux out of the reservoir at time  $t$ ,

$$F''(t) = \int_{-\infty}^t \left( -\frac{dA(t, t_0)}{dt} \right) dt_0 \quad (5)$$

to define the turn-over time as

$$\tau'_0(t) = \int_{-\infty}^t A(t, t_0) dt_0 \int_{-\infty}^t \left( -\frac{dA(t, t_0)}{dt} \right) dt_0 \quad (6)$$

which is not, in general, equal to  $\tau'_0(t)$ . It is of interest to explore briefly the consequences of the latter definition. Under many circumstances it may be possible to describe the rate of removal of material from the reservoir according to a first-

order process with time-dependent rate coefficient  $k(t)$ ,

$$-\frac{dA(t, t_0)}{dt} = k(t)A(t, t_0) \tag{7}$$

Under such conditions the definition (6) yields the result that the turn-over time  $\tau_0''(t)$  is equal to  $k(t)^{-1}$ , the inverse of the instantaneous rate coefficient for removal. Thus, despite the appearance to the contrary in (6), it is seen that  $\tau_0''(t)$  is an instantaneous property of the system that in no way reflects any average over the period of time that the sample has been in the reservoir. Such a quantity would strongly reflect any short, intense removal processes. In terms of the analogy to human populations,  $\tau_0'$  is the ratio of the population to the birth rate;  $\tau_0''$  is the ratio of the population to the death rate. The instantaneous value of the latter quantity would exhibit extreme variation, for example, in wartime that would limit its usefulness as a measure of human lifetimes. Similarly,  $\tau_0'$  might exhibit a decrease during a period of high birth rate, or "baby boom", that would lead to a similar distortion. The sensitivity of the population-based turn-over time defined by either of the two choices of flux to short duration influences is a consequence of the fact that the  $\tau_0'$ 's do not refer to a fixed set of material, but refer rather to a set of material that is always changing as new material is added to the material already present in the reservoir. As such they are hybrid quantities reflecting the time dependence of the rate that material is introduced into the reservoir as well as the rate at which it is removed. Only for the rate of introduction  $A(t, t)$  independent of time does  $\tau_0'$  become representative of removal processes only.

(b) *Mean age.* This quantity represents the average age of the material present in the reservoir at time  $t$ , and is thus (cf. Bolin and Rodhe, 1973) computed as an average over the distribution  $A(t, t_0)$ . Again the integrals are taken over the time of introduction  $t_0$ :

$$\tau_a(t) = \int_{-\infty}^t (t - t_0)A(t, t_0) dt_0 / \int_{-\infty}^t A(t, t_0) dt_0 \tag{8}$$

$$= \frac{1}{M_A(t_0)} \int_{-\infty}^t (t - t_0) A(t, t_0) dt_0 \tag{9}$$

(c) *Mean transit time.* This quantity represents the average age of the material leaving the reservoir at an observation time  $t$ . For primary

materials the mean transit time may be computed as an average over the distribution  $(-dA(t, t_0)/dt)$ , since the only contribution to this time derivative is the rate of removal of material from the reservoir. Under steady-state conditions the mean transit time is equal to the turn-over time (Bolin and Rodhe, 1973). Under non-steady-state conditions the mean transit time is a function of observation time and is computed as an average taken over the time of introduction of material into the reservoir:

$$\tau_t(t) = \frac{\int_{-\infty}^t (t - t_0) \left( -\frac{dA(t, t_0)}{dt} \right) dt_0}{\int_{-\infty}^t \left( -\frac{dA(t, t_0)}{dt} \right) dt_0} \tag{10}$$

Equation (8) does not in general simplify further (as does the corresponding steady-state expression), and the mean transit time not generally equal to the turn-over time. However, for the special case of a removal process that is first order in the amount of material present in the reservoir, as described by eq. (7) we observe that the rate coefficient  $k(t)$  is independent of the variable of integration  $t_0$ , and may thus be brought outside the integrals in (10) even though  $k(t)$  is a function of time. Hence, under the condition (7) we obtain the result that the population-based mean transit time  $\tau_t$  is equal to the mean age  $\tau_a$ ; i.e., the mean age of the material *leaving* the reservoir is equal to the mean age of the material *present* in the reservoir. This result is a consequence of the stochastic nature of the first-order removal process, eq. (7).

2.2 Cohort-based residence times

As noted above, definitions of residence times based upon the material present in the reservoir at a given time of observation  $t$  are not entirely satisfactory, since these quantities may incorporate the time dependence of both introduction and removal processes or are subject to short-duration transients. One is motivated, therefore, to develop definitions for these several time quantities that are long-term average measures of the persistence of material in the reservoir. This has led to a set of definitions pertinent to a class of material, or "cohort", that enters the reservoir at a given time  $t_0$ . The resulting expressions, while perhaps initially seeming somewhat artificial, turn out to be particularly useful in assessing the effect of a source upon the reservoir into which it emits, as a function

of the time of emission, as in consideration of the long-range impact of atmospheric pollutants from distributed sources (Schwartz, 1979).

(a) *Turn-over time.* As before we take the turn-over time to be the ratio of the amount of material in the reservoir to the flux through the reservoir. The flux through the reservoir attributable to a rate of introduction  $A(t_0, t_0)$  is seen unambiguously to be  $A(t_0, t_0)$ , since we have assumed that all material that enters the reservoir is ultimately removed. What is the amount of material in the reservoir attributable to this rate of introduction? It is proposed that the appropriate measure of this quantity is given by

$$N_A(t_0) = \int_{t_0}^{\infty} A(t_0, t) dt \quad (11)$$

where the integral is taken over the domain of *observation* time. The choice of (11) to represent the mass loading attributable to the rate of introduction  $A(t_0, t_0)$  can be motivated as follows. Let us consider a rate of introduction  $A(t_0, t_0)$  for a short period, of duration  $h$ , from  $t_0 - h/2$  to  $t_0 + h/2$ , and zero at all other times. At any subsequent observation time  $t$  the burden of material in the reservoir is given approximately by  $h \times A(t, t_0)$ . The integrated burden (burden integrated over observation time) is  $h \times \int_{t_0}^{\infty} A(t, t_0) dt$ . In turn, the integrated burden per unit time in the emissions domain is given by  $N_A(t_0)$ , eq. (11).  $N_A(t_0)$  thus represents a "committed burden" attributable to the rate of introduction  $A(t_0, t_0)$ ,<sup>1</sup> albeit not an amount of material that is present in the reservoir at any given observation time.

Further insight into the parallelism between the burden of material present at a given observation time,  $M_A(t)$ , and the committed burden attributable to the emission rate at a given time of introduction,  $N_A(t_0)$ , may be obtained by expressing the latter in terms of the age subsequent to introduction,  $u = t - t_0$ ,

$$N_A(t_0) = \int_0^{\infty} A(t_0 + u, t_0) du \quad (12)$$

Comparison of (12) with (3) establishes the essential similarity of the two quantities, and also points out the inherent difference, viz. that  $M_A(t)$  represents an integration over "past" time in the emissions domain whereas  $N_A(t)$  represents an

integration over "future" time in the observation domain.

If we accept the interpretation of the committed burden  $N_A(t)$  as a measure of the amount of material in the reservoir attributable to the rate of introduction  $A(t, t_0)$ , then the resulting expression for the turn-over time pertinent to the material introduced at  $t_0$  becomes

$$\theta_0(t_0) = \frac{1}{A(t_0, t_0)} \int_{t_0}^{\infty} A(t, t_0) dt \quad (13)$$

Here the symbol  $\theta(t_0)$  is introduced to represent a residence time pertinent to a cohort of material entering the reservoir at a given time  $t_0$ ; the symbol  $\tau(t)$  is reserved for residence times pertaining to the population present at time  $t$ . The turn-over time  $\theta_0$  may be interpreted as representing the *committed burden of material in the reservoir per unit emissions rate*, and will be of interest to examine how this quantity may depend upon temporal or spatial parameters characterizing the introduction of the material.

(b) *Mean age.* The age at time  $t$  of the cohort of material introduced at time  $t_0$  is  $t - t_0$ . With increasing age the fraction of the original material remaining decreases, as material is removed from the reservoir. The mean age of the cohort addresses, retrospectively, the average age of the material in the reservoir, weighted by the amount of material remaining in the reservoir, and is thus evaluated as

$$\theta_a(t_0) = \int_{t_0}^{\infty} (t - t_0) A(t, t_0) dt / \int_{t_0}^{\infty} A(t, t_0) dt \quad (14)$$

(c) *Mean transit time.* This quantity is computed similarly to the mean age, except that the weighting function is now the rate of removal of material from the reservoir,  $(-dA(t, t_0)/dt)$ . Thus,

$$\theta_t(t_0) = \frac{\int_{t_0}^{\infty} (t - t_0) \left( -\frac{dA(t, t_0)}{dt} \right) dt}{\int_{t_0}^{\infty} \left( -\frac{dA(t, t_0)}{dt} \right) dt} \quad (15)$$

This expression may be simplified considerably, in complete analogy to the corresponding expression for the steady-state situation, by observing that

$$\int_{t_0}^{\infty} \left( -\frac{dA(t, t_0)}{dt} \right) dt = -\int_{t_0}^{\infty} dA(t, t_0) = A(t_0, t_0) \quad (16)$$

i.e., that the total amount of material removed from

<sup>1</sup>I am indebted to Dr Henning Rodhe for having suggested the term "committed burden" for the quantity represented by eq. (11).

the reservoir attributable to the rate of introduction  $A(t_0, t_0)$  is equal to the rate of introduction. Also, by integrating the numerator of (15) by parts we obtain

$$\int_{t_0}^{\infty} (t - t_0) \left( -\frac{dA(t, t_0)}{dt} \right) dt = \int_{t_0}^{\infty} A(t, t_0) dt \quad (17)$$

Consequently we have the result

$$\theta_i(t_0) = \frac{1}{A(t_0, t_0)} \int_{t_0}^{\infty} A(t, t_0) dt \quad (18)$$

that is, the equivalence of the mean transit time and the turn-over time pertinent to a cohort. This situation contrasts with that noted above for the corresponding residence times pertinent to a population, where this equivalence does not in general obtain.

### 2.3. Relation to steady-state expressions

In the steady-state condition it is required that the two sets of residence times, those pertinent to a cohort of co-introduced materials, the  $\theta$ 's, and those pertinent to the population present, the  $\tau$ 's, should become independent of time, mutually identical, and identical as well to the steady-state, population-based expressions developed by Bolin and Rodhe (1973). Similarly the expressions for the burden and the "committed burden" should coincide. That these requirements are met is readily established by noting that, in the present notation, the criterion for attainment of steady state is that the quantity  $A(t, t_0)$  be a function only of the age or "relative" time  $u = t - t_0$ , and not of "absolute" time  $t$  or  $t_0$ . Under this condition it is clear by inspection, say of eqs. (3) and (12), that the two expressions for burden become identical, and the same holds true for the several residence times. The interested reader will also note that the expression for the mean age  $\tau_a$  (eq. (14)) may be written in terms of the distribution function

$$\psi(t, u) \equiv A(t, t - u) / \int_0^{\infty} A(t, t - u') du' \quad (19)$$

as

$$\tau_a(t) = \int_0^{\infty} u \psi(t, u) du \quad (20)$$

For  $\psi(t, u)$  a function of relative time  $u$  only (i.e., independent of time  $t$ ), the expressions (19) and (20) become identical to those of Bolin and Rodhe (1973), thus establishing the connection to that work under steady-state conditions.

One further observation regarding steady-state conditions concerns the important special case in which the rate of removal of the material from the reservoir is first order in the amount of that material, with constant coefficient  $k_1$ ,

$$-\frac{dA(t, t_0)}{dt} = k_1 A(t, t_0) \quad (21)$$

corresponding to the exponential decay function

$$A(t, t_0) = A(t_0, t_0) e^{-k_1(t-t_0)} \quad (22)$$

In this special case all of the above-defined residence times become identical and equal to the inverse of the first-order rate coefficient, i.e.,

$$\theta_a = \theta_t = \theta_0 = \tau_a = \tau_t = \tau_0 = k_1^{-1} \quad (23)$$

### 2.4. Secondary materials

We turn now to the extension of the definitions of the several residence times to encompass secondary materials. In the interest of brevity, and because of the greater physical insight afforded, this discussion is restricted to consideration of the residence times pertinent to material introduced at a given time, where now the material introduced is the primary precursor to the secondary material of interest, i.e., residence times defined analogously to the  $\theta$ 's above.

(a) *Turn-over time.* The turn-over time of a secondary material may, by analogy to that of a primary material, be defined as the ratio of the committed burden of this material to the flux of this material through the reservoir. The committed burden may be expressed by analogy to (11) as

$$N_B(t_0) = \int_{t_0}^{\infty} B(t, t_0) dt \quad (24)$$

where  $B(t, t_0)$  represents the amount of secondary material present in the reservoir at time  $t$  resulting from the emission of primary material at time  $t_0$ , per unit time in the  $t_0$  domain. The flux of secondary material through the reservoir, or yield, may be evaluated as

$$Y(t_0) = \int_{t_0}^{\infty} \left( \frac{dB(t, t_0)}{dt} \right)_+ dt \quad (25)$$

Here the plus sign as a subscript to the differential denotes that this quantity represents only the contribution to  $dB/dt$  resulting from formation of the secondary material from the primary precursor;

i.e.,

$$\frac{dB(t, t_0)}{dt} = \left( \frac{dB(t, t_0)}{dt} \right)_+ + \left( \frac{dB(t, t_0)}{dt} \right)_- \quad (26)$$

where the two terms on the right-hand side represent the formation and loss terms respectively. The turn-over time for the secondary material is now given as

$$\sigma_0(t_0) = N_B(t_0)/Y(t_0) \quad (27)$$

where the symbol  $\sigma(t_0)$  is introduced to represent residence times of secondary materials pertinent to a cohort of primary material introduced into the reservoir at time  $t_0$ .

(b) *Mean age.* Of all the secondary material formed by reaction of a primary material introduced into the reservoir at time  $t_0$ , what is the age of this material, measured from the time of introduction of the primary material, averaged over the time that the secondary material is present in the reservoir? I choose to measure this age from the time of introduction of the primary material because it is this quantity, not the mean age subsequent to the *formation* of the secondary material, that is relevant in consideration of material transport.

By analogy to eq. (14) this average age is given by

$$\sigma_a(t_0) = \int_{t_0}^{\infty} (t - t_0) B(t, t_0) dt / \int_{t_0}^{\infty} B(t, t_0) dt \quad (28)$$

(c) *Mean transit time.* Of all the secondary material formed by reaction of a primary material introduced at time  $t_0$ , what is the average age of this material at the time that the secondary material is removed from the reservoir? As before, this mean transit time is to be computed over the distribution of the rate of loss of material from the reservoir:

$$\sigma_t(t_0) = \frac{\int_{t_0}^{\infty} (t - t_0) \left( -\frac{dB(t, t_0)}{dt} \right)_- dt}{\int_{t_0}^{\infty} \left( -\frac{dB(t, t_0)}{dt} \right)_- dt} \quad (29)$$

Equation (29) may be simplified analogously to eq. (15), but, since  $(dB/dt)_-$  is not a perfect differential, this is not quite so straightforward. In order to proceed we make use of (26) to write first

the denominator of (29) as

$$\int_{t_0}^{\infty} \left( -\frac{dB(t, t_0)}{dt} \right)_- dt = \int_{t_0}^{\infty} \left( \frac{dB(t, t_0)}{dt} \right)_+ dt + \int_{t_0}^{\infty} \left( -\frac{dB(t, t_0)}{dt} \right) dt \quad (30)$$

The term on the right-hand side of (30) is recognized as the yield, eq. (25). The second term may be integrated directly to give

$$\int_{t_0}^{\infty} \left( -\frac{dB(t, t_0)}{dt} \right) dt = B(t_0, t_0) - B(\infty, t_0) = 0 \quad (31)$$

where we have made use of the definition that the secondary material is not directly introduced into the reservoir, and is thus not present at time  $t_0$ , and also of the fact that this material, analogously to primary materials, is ultimately removed at large time. We thus obtain the result

$$\int_{t_0}^{\infty} \left( -\frac{dB(t, t_0)}{dt} \right)_- dt = Y(t_0) \quad (32)$$

i.e., the statement, obvious in retrospect, that the total amount of secondary material removed from the reservoir is equal to the total amount formed.

We turn now to evaluation of the numerator of (29). Again we make use of (26) to write

$$\sigma_t(t_0) = \frac{1}{Y(t_0)} \left\{ \int_{t_0}^{\infty} (t - t_0) \left( \frac{dB(t, t_0)}{dt} \right)_+ dt + \int_{t_0}^{\infty} (t - t_0) \left( -\frac{dB(t, t_0)}{dt} \right) dt \right\} \quad (33)$$

and again making use of the fact that  $dB/dt$  is a perfect differential we integrate by parts analogously to (17) to obtain the result

$$\sigma_t(t_0) = \frac{1}{Y(t_0)} \left\{ \int_{t_0}^{\infty} (t - t_0) \left( \frac{dB(t, t_0)}{dt} \right)_+ dt + \int_{t_0}^{\infty} B(t, t_0) dt \right\} \quad (34)$$

The two terms in eq. (34) readily lend themselves to physical interpretation. The first term may be considered the transit time associated with the primary precursor to the secondary pollutant of interest. We introduce the symbol

$$\theta_*(t_0) \equiv \frac{1}{Y(t_0)} \int_{t_0}^{\infty} (t - t_0) \left( \frac{dB(t, t_0)}{dt} \right)_+ dt \quad (35)$$

to denote that this residence time represents that component of the transit time of the secondary species that is associated with the primary precursor. The second term in (34) is the mean transit time associated with the secondary pollutant itself and is recognized as equal to the secondary pollutant turn-over time, eq. (27). Equation (34) may thus be written as

$$\sigma_t(t_0) = \sigma_0(t_0) + \theta_*(t_0) \quad (36)$$

i.e., the mean transit time of the secondary pollutant is equal to the sum of the turn-over time of that species plus the residence time of the precursor as evaluated by eq. (35). Which, if either, of these two terms will dominate for any given system will depend upon the rates of the chemical and physical processes of transformation and removal. For atmospheric sulfur compounds as we shall see below, the removal rate of the secondary material, sulfate aerosol, appears to be substantially less than that of the precursor  $\text{SO}_2$ , and thus  $\sigma_0$  greatly exceeds  $\theta_*$ .

As with the residence times  $\theta$  and  $\tau$  pertinent to material directly introduced into the reservoir, the mean age  $\sigma_a$  and transit time  $\sigma_t$  for secondary materials coincide when the rate of removal is first order with constant coefficient,

$$\left( -\frac{dB(t, t_0)}{dt} \right) = k_2 B(t, t_0) \quad (37)$$

This is readily established by comparison of eqs. (28) and (29). However, as noted above, the turn-over time  $\sigma_0$  will *not* be equal to  $\sigma_a$  and  $\sigma_t$ . For the important special case in which the rate law for removal of the primary precursor  $A$  is itself first order with constant coefficient, eq. (21), with formation of the secondary material  $B$  first order in  $A$ , and loss of  $B$  given by (37) we have the following results:

$$\sigma_a = \sigma_t = k_1^{-1} + k_2^{-1} \quad (38)$$

i.e., the mean age (or transit time) of the secondary material, referenced to the time of emission of the primary material, is equal to the sum of the mean age (or transit time) of the primary material and that of the secondary material, considered from the time of its *in situ* formation. However, the turn-over time is simply

$$\sigma_0 = k_2^{-1} \quad (39)$$

the mean age (or transit time) of the secondary material measured from the time of formation.

Before concluding this section, it is of interest to define two further quantities pertinent to the burden of secondary materials in reservoirs. First, I consider the relative yield of secondary material normalized to the emission rate of primary material,

$$\alpha(t_0) = Y(t_0)/A(t_0, t_0) \quad (40)$$

This dimensionless quantity, which may be evaluated by eq. (25), represents the fraction of primary material that reacts to form the secondary material as a function of time of introduction of the primary material into the reservoir, and is a generalization of the time-independent, steady-state quantity that has been introduced previously (Rodhe, 1978).

The final quantity of interest that I wish to introduce is the relative burden, or the ratio of the committed burden of secondary material in the reservoir to that of primary material. The relative burden is useful in comparison with observation since, under the assumption that the two materials are equivalently distributed within the reservoir, it will be equal to the ratio of their concentrations. Considered as a function of  $t_0$ , the time of introduction of the primary material, the relative burden may be computed by eqs. (13) and (27) as

$$\beta(t_0) \equiv \frac{M_B(t_0)}{M_A(t_0)} = \frac{Y(t_0)}{A(t_0, t_0)} \frac{\sigma_0(t_0)}{\theta_0(t_0)} = \alpha(t_0) \frac{\sigma_0(t_0)}{\theta_0(t_0)} \quad (41)$$

Within the model of constant first-order processes both the yield and the relative burden assume particularly simple interpretations. Letting  $k_1$  represent the total rate coefficient for removal of primary material and  $b$  represent the rate coefficient for primary to secondary conversion, then by eqs. (23) and (25) the relative yield is

$$\alpha = b/k_1 = b\theta_0 \quad (42)$$

In turn the relative burden may be evaluated (eqs. (23) and (39)) as

$$\beta = b/k_2 = b\sigma_0 \quad (43)$$

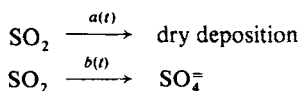
Thus for constant first-order processes the relative yield and relative burden may be evaluated as the ratio of the conversion coefficient to the coefficients for removal of the primary and secondary



materials, respectively, or equivalently as the product of the conversion rate coefficient multiplied by the respective turn-over times.

### 3. Application to atmospheric sulfur compounds

In this section the definitions and formulae developed above are applied to a consideration of the residence times describing atmospheric  $\text{SO}_2$  and aerosol sulfate. This discussion is motivated generally by the widespread concern regarding the fate of these industrial pollutants and in particular by the recent work by Husar et al. (1978) reporting the extent of conversion of  $\text{SO}_2$  to sulfate in a power plant plume as a function of time of day, from which it was possible to infer the time dependence of the rate processes for conversion of  $\text{SO}_2$  to sulfate aerosol and for  $\text{SO}_2$  deposition. Both processes were described as first order in  $\text{SO}_2$ ,



with empirical, rate coefficients dependent on the time of day as shown in Fig. 1. Here the time dependence of the coefficient for dry deposition reflects the enhancement of this process under well-mixed daytime conditions; the diurnal dependence of the conversion rate may reflect secondary photochemical activity (Calvert, 1978) or enhanced mixing, or both. The  $\text{SO}_2$  oxidation rate inferred for non-cloud processes ( $3\% \text{ h}^{-1}$ , maximum;  $1.2\% \text{ h}^{-1}$ , 24-hour average) is consistent with present understanding (Calvert, 1978) of the concentrations of free radicals, principally HO and  $\text{HO}_2$ , and of rates of reaction of these species with  $\text{SO}_2$ . The reported oxidation rates are somewhat higher than those reported in other recent studies in stack plumes (Forrest and Newman, 1977; Lusic and Wiebe, 1976) although the latter studies have not been extended to such great distances and for such extensive exposure to solar radiation as those of Husar et al. (1978). On the other hand,  $\text{SO}_2$  oxidation rates recently reported for urban plumes and atmospheres have tended to be somewhat higher:  $2\text{--}10\% \text{ h}^{-1}$  (Smith and Jeffrey, 1975);  $1\text{--}13\% \text{ h}^{-1}$  (Roberts and Friedlander, 1975);  $10\text{--}14\% \text{ h}^{-1}$  (Alkezweeny and Powell, 1977); and

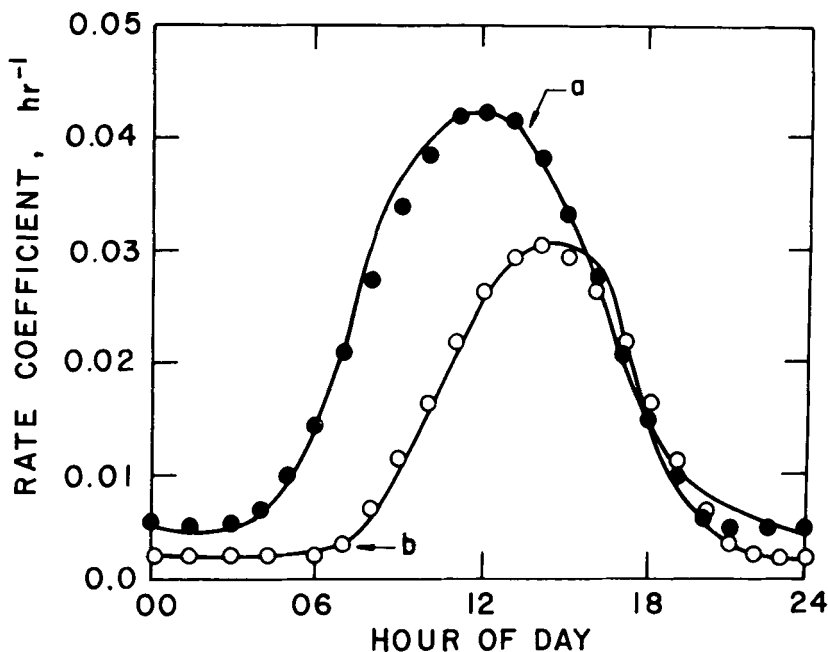


Fig. 1. Diurnal profiles of time-dependent rate coefficients for  $\text{SO}_2$  deposition (a) and  $\text{SO}_2$ -to-sulfate conversion (b). The curve represent the time dependence proposed by Husar et al. (1978). The circles represent the analytical approximation (eq. (44)) employed in the present analysis.

6–25% h<sup>-1</sup> (Benarie et al., 1972), although we have recently reported a study that set an upper bound of 4% h<sup>-1</sup> for the oxidation rate under bright sun, urban atmosphere conditions (Forrest et al., 1979).

The rather strong time dependence reflected, for example, in Fig. 1, and also the substantial modulation expected for the rate of homogenous oxidation reactions (Calvert, 1978) have led to the recommendation (ISSA, 1978) that future efforts toward modeling concentrations of atmospheric sulfur compounds incorporate such diurnal patterns rather than utilize constant, average values for the rate coefficients. In this section the model of Husar et al. (1978) is treated as an example of the application of the methodology developed above to a chemical system characterized by a strong diurnal dependence in removal and transformation rates. This will permit a comparison between the understanding that is reached by means of the steady-state approach and that of the time-dependent approach, and will also permit examination of the dependence of the several quantities of interest upon time of day of emission of the primary material SO<sub>2</sub>. In order to simplify the computations, the rate coefficients in Fig. 1 were approximated as a function of time of day  $t$  as follows, in units of h<sup>-1</sup>:

$$a(t) = 0.0050 + 0.0375L(03,21) \cos^2 \left( (t-12) \frac{\pi}{18} \right)$$

$$b(t) = 0.0025 + 0.0275L(06,22) \cos^2 \left( (t-14) \frac{\pi}{16} \right)$$
(44)

Here  $L(t_1, t_2)$  represents an on-off function,

$$L(t_1, t_2) = 1, \quad t_1 \leq t \leq t_2$$

$$L(t_1, t_2) = 0, \quad t < t_1 \text{ or } t > t_2$$
(45)

The functions  $a$  and  $b$  given by (44) are also shown in Fig. 1, and serve as the basis of the further discussion.

Before treating the time-dependent problem it is of interest for comparison to consider the steady-state case with rate coefficients  $a_{ss}$  and  $b_{ss}$  given by the average values of the time-dependent functions (44),

$$a_{ss} = \bar{a} = 0.0191 \text{ h}^{-1}$$

$$b_{ss} = \bar{b} = 0.0117 \text{ h}^{-1}$$
(46)

For these values of the steady-state rate coefficients we obtain eq. (23)

$$\theta_{ss} = (\bar{a} + \bar{b})^{-1} = 32.5 \text{ h}$$
(47)

The yield of sulfate normalized to SO<sub>2</sub> emissions is evaluated by (42) as

$$\alpha_{ss} = \frac{b_{ss}}{k_{ss}} = \frac{\bar{b}}{\bar{a} + \bar{b}} = 0.380$$
(48)

We now turn to an examination of the several residence times as a function of the hour of day at which the SO<sub>2</sub> is emitted for the  $\theta$ 's, and as a function of the hour of day of observation for the  $\tau$ 's. In these calculations a constant emission rate  $A(t_0, t_0)$  was assumed. The infinite-time integrals were computed by numerical integration over the initial 24-hour period and appropriate series summations for subsequent days. The results of the calculations are shown in Fig. 2. It may be seen that the several residence times exhibit rather different properties. First, the instantaneous turn-over time,  $\tau_0'' = (a(t) + b(t))^{-1}$ , exhibits the rather large fluctuations assumed for these coefficients. The remaining residence times, being average quantities, oscillate somewhat more gently about the steady-state value  $\theta_{ss} = (\bar{a} + \bar{b})^{-1}$ . The several lifetimes  $\theta$  considered as a function of hour of emission  $t_0$  are shortest for emission in the morning, reflecting the greater rate of SO<sub>2</sub> removal in the daytime hours, whereas the lifetimes  $\tau_0'$  and  $\tau_a$  reach a minimum in the afternoon and night, reflecting the diminished age of the population as a consequence of the daytime removal process. Perhaps the most significant feature of the several computed quantities is the strong attenuation in the amplitude of modulation, or "damping", that is exhibited in comparison to the rather strong modulation characterizing the rate coefficients shown in Fig. 1. Thus the fractional standard deviation in the turn-over times  $\tau_0'$  and  $\theta_0$  as a function of time of measurement or of emission respectively is 8.6%, and in the mean ages  $\tau_a$  and  $\theta_a$ , 1.0%, compared to 76% in the total rate coefficient for removal,  $k_1(t) = a + b$ . This damping may be attributed to the relatively large fraction,  $\exp(-\bar{k}_1 \times 24 \text{ h}) = 0.48$ , of emitted SO<sub>2</sub> that remains in the reservoir after one period of the diurnal cycle; in other words, a significant proportion of SO<sub>2</sub> emitted into the reservoir experiences the full diurnal cycle, irrespective of the

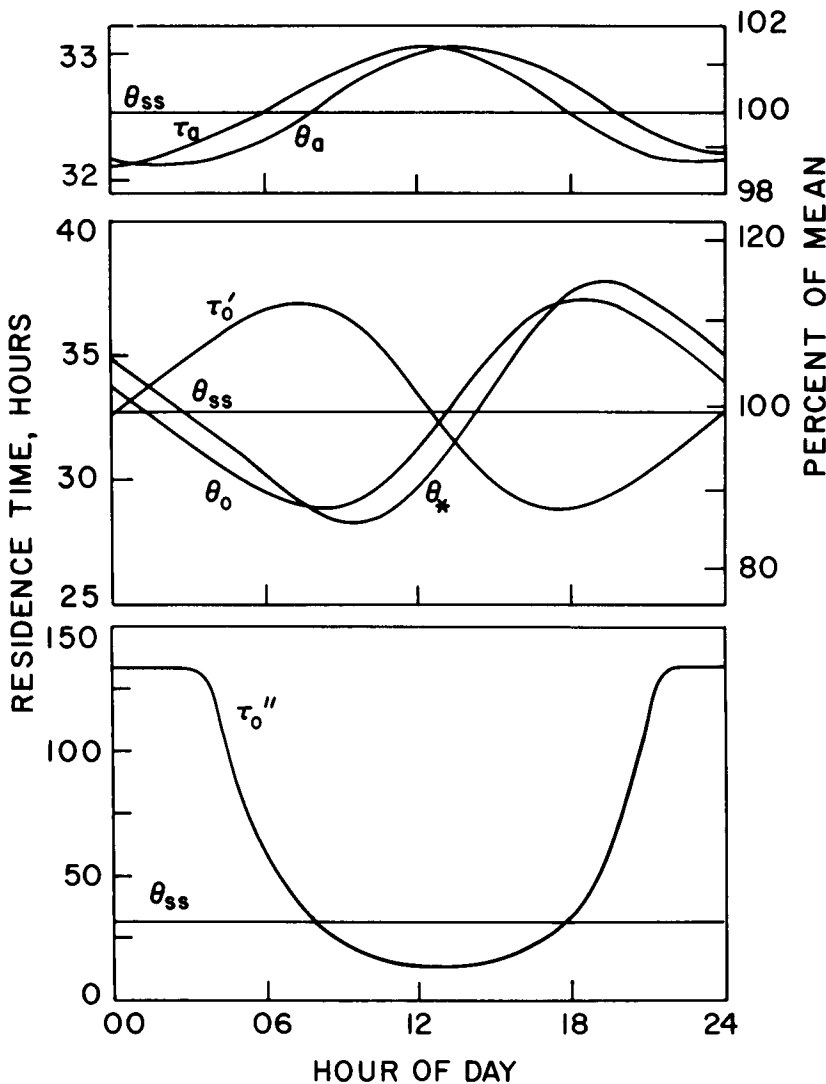


Fig. 2. Residence times of  $\text{SO}_2$  in the atmosphere according to the several definitions given in the text for the time-dependent rate coefficients given in Fig. 1. The  $\theta$ 's are shown as a function of hour of introduction of  $\text{SO}_2$  into the atmosphere; the  $\tau$ 's as a function of the hour of observation. A constant  $\text{SO}_2$  emission rate was assumed.

hour of introduction. It will be recalled that the turn-over time  $\theta_0$  is the burden of material present in the reservoir per unit emission rate. In the present example it may be seen that despite the considerable (greater than 9-fold) variation in the  $\text{SO}_2$  removal rate over the diurnal cycle, the atmospheric burden of  $\text{SO}_2$  resulting from emissions at different times of day departs from the mean or steady-state values at most by only  $\pm 13\%$ . Finally, we note that the average age of  $\text{SO}_2$  in the

atmosphere exhibits a much greater degree of damping than does the turn-over time since the former represents an average over the amount of material, whereas the latter is an average over the more strongly varying removal rate. The low variation in these residence times as a function of hour of day suggest that for many purposes (e.g., modeling long-time average concentrations as governed by transport, diffusion, and reaction) it may be suitable to employ the steady-state model.

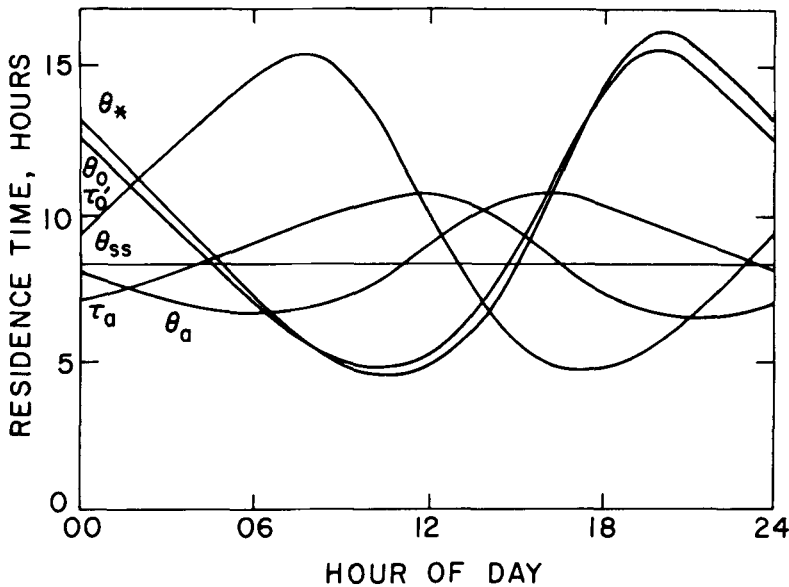


Fig. 3. Characteristic residence times of  $\text{SO}_2$  in the atmosphere for the rapid  $\text{SO}_2$  oxidation rate ( $b_{\text{max}} = 30\% \text{ h}^{-1}$ ,  $b = 10\% \text{ h}^{-1}$ ) given by eq. (49).

In order to examine the degree to which the several residence times may exhibit a stronger dependence upon the hour of day as the rate of removal is increased, I have considered a somewhat extreme case in which the maximum rate of oxidation was increased to  $30\% \text{ h}^{-1}$ ; i.e., the conversion function  $b(t)$ , eq. (44), is replaced by

$$b(t) = 0.0025 + 0.2975L(06,22) \times \cos^2\left((t-14)\frac{\pi}{16}\right) \quad (49)$$

With this high rate of conversion ( $\bar{b} = 10.2\% \text{ h}^{-1}$ ;  $\bar{k}_1^{-1} = 8.3 \text{ h}$ ) the fraction of  $\text{SO}_2$  remaining in the reservoir after 24 hours is reduced to 6%. The computed values of the several residence times, shown in Fig. 3, exhibit substantially greater variation as a function of time of day than did those computed for the previous example. Thus the relative standard deviation in the turn-over times is 38% in this example, corresponding to greater than a factor-of-three spread in these quantities as a function of the time of measurement or emission. In this case, in contrast to the previous example, it may be seen that the hour of day at which the  $\text{SO}_2$  is emitted into the atmosphere has a major influence upon the burden of this material. Similarly, the amount of  $\text{SO}_2$  in the reservoir, and,

assuming a well-mixed reservoir, the concentration of  $\text{SO}_2$ , would be expected to exhibit a corresponding high degree of modulation.

It is of interest to compare the curves  $\tau'_0$  to measured diurnal profiles of  $\text{SO}_2$  concentrations, since, for a constant rate of emission of  $\text{SO}_2$  into the atmosphere,  $\tau'_0$  represents the burden of  $\text{SO}_2$  present in the atmosphere per unit emissions of  $\text{SO}_2$ . Blade and Ferrand (1969) have presented such average profiles on a month by month basis based on measurements in New York City over a 12-year period as shown in Fig. 4. It would appear from the bimodal profile shown for February that the  $\text{SO}_2$  concentration is affected to a great extent by the diurnal profile of emissions, which, during this period, were dominated by space heating (Simon and Ferrand, 1972). In the profile for August, however, the bimodal effect appears much weaker, and there is a pronounced afternoon minimum in concentration that would be consistent with an enhanced daytime rate of removal of  $\text{SO}_2$ . While this conclusion must be considered very tentative in view of the unknown magnitude of such effects as enhanced daytime mixing upon the measured diurnal concentration profiles, the depth of the modulation suggests a midday rate of  $\text{SO}_2$  removal (conversion plus deposition) of the order of  $10\% \text{ h}^{-1}$ .

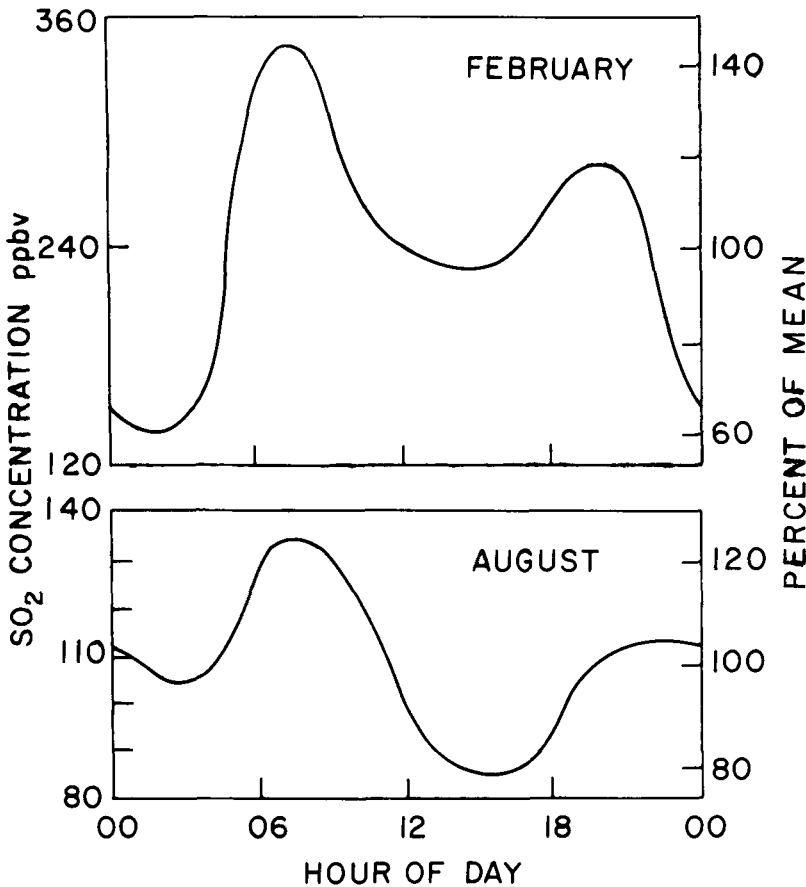


Fig. 4. Twelve-year-average diurnal profiles of New York City SO<sub>2</sub> concentrations, after Blade and Ferrand (1969).

An additional quantity of interest that may be evaluated on the basis of the present treatment is the sulfate yield as a function of hour of day of SO<sub>2</sub> emission that reflects the competition between oxidation and deposition. As seen in Fig. 5, computed for oxidation and deposition rates as given by eq. (44) ( $\bar{b} = 1.2\% \text{ h}^{-1}$ ), this yield is only weakly dependent upon the hour of emission, since both processes were assumed (Fig. 1) to exhibit rates that increased similarly during the daylight hours. The numerical value of the computed yield, 36–38%, is comparable to previous estimates of this quantity (Rodhe, 1978; ISSA, 1978) based upon a steady-state treatment. For the rapid SO<sub>2</sub> oxidation rate,  $\bar{b} = 10\% \text{ h}^{-1}$  (eq. (49)), the sulfate yield is substantially increased, as expected, and is also somewhat more strongly a function of the hour of emission. It is interesting to observe that in both cases the steady-state sulfate yield somewhat

exceeds the average based upon the amount of sulfate formed according to the instantaneous rate coefficients.

In order to proceed to a consideration of the residence times and burden of secondary aerosol sulfate it is necessary to postulate a rate expression governing not only the formation, but also the removal of this material from the atmosphere. In comparison to the above picture regarding SO<sub>2</sub>, the present understanding of processes governing removal of aerosol sulfate from the atmosphere is rather less well developed. Thus, for example, Sehmel and Hodgson (1976) and Wesely et al. (1977) consider dry deposition of aerosols in the size range 0.1 to 1  $\mu\text{m}$  to be moderately fast—deposition velocities in the range 0.1 to 1 cm/s, depending on atmospheric stability. For an assumed mixing height of 1 km these deposition velocities correspond to a removal rate coefficient,

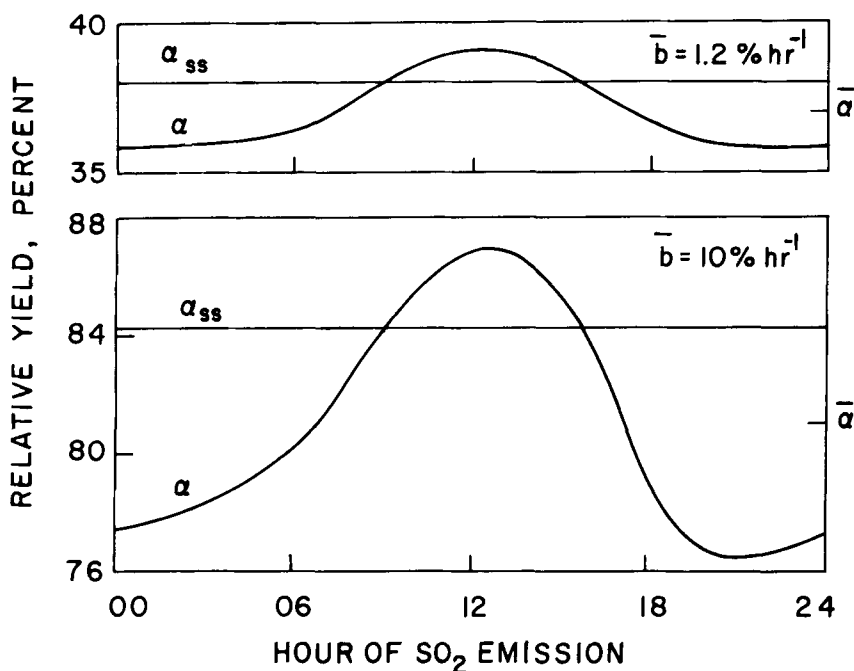


Fig. 5. Diurnal profiles of the relative yield of sulfate, i.e., amount of sulfate formed per unit amount of  $\text{SO}_2$  emitted (mole basis), for assumed deposition and oxidation rates given by eq. (44) and (49), as a function of the hour of day of introduction of  $\text{SO}_2$  into the atmosphere.

$c$ , in the range  $0.004$  to  $0.04 \text{ h}^{-1}$ . On the other hand, Garland (1978) considers dry deposition to be negligibly slow and suggests rather that aerosol sulfate is removed principally by precipitation scavenging. Assuming negligible dry deposition, Rodhe and Grandell (1972) have treated precipitation scavenging according to a probabilistic model that led to an approximately exponential decay function, with the average removal coefficient  $\bar{c}$  ranging from  $0.007$  to  $0.02 \text{ h}^{-1}$ , depending upon season.

Based upon the above discussion it is apparent that any detailed examination of the persistence and removal of secondary sulfate aerosol will have to incorporate a model for the removal process that reflects the intermittent nature of rainfall events, as well as the diurnal variation of the dry deposition rate. At the present time, however, in view of the rather large uncertainty in the understanding of the rates of aerosol removal processes, the use of a model of any greater complexity than that of a constant first-order process would not seem justified. The use of this model gains further

support in the fact that the fraction of sulfate persisting for 24 hours will be rather great thus damping our diurnal variation in the removal rate.

Based upon the above discussion I have somewhat arbitrarily selected for illustrative purposes a removal rate for sulfate aerosol  $c = 0.01 \text{ h}^{-1}$  to represent the sum of wet and dry removal processes, although it would appear that the average value of this quantity might differ from this value by a factor of 2 or more. The turn-over time for sulfate is thus (eq. (39)) taken as

$$\sigma_0 = c^{-1} = 100 \text{ h} \quad (50)$$

Also, since a constant rate coefficient is assumed for removal of the secondary species, the mean age and mean transit time of this species are identical, as was pointed out in connection with eq. (37). In this example these quantities are evaluated according to eq. (36) as

$$\sigma_a = \sigma_t = \sigma_0 + \theta_* = 100 \text{ h} + \theta_* \quad (51)$$

Values of  $\theta_*$  computed for the two assumed expressions for the rate of  $\text{SO}_2$  oxidation are shown

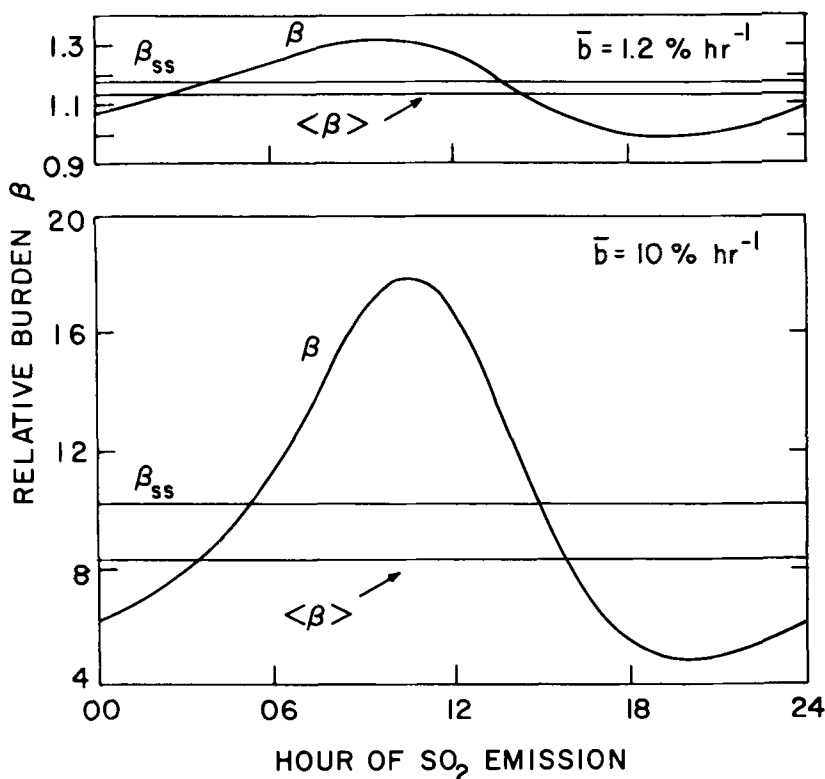


Fig. 6. Diurnal profiles of the relative sulfate burden, i.e., the ratio of the atmospheric burden of sulfate to that of  $\text{SO}_2$ , for assumed deposition and oxidation rates given by eq. (44) and (49), as a function of the hour of introduction of  $\text{SO}_2$  into the atmosphere.  $\langle \beta \rangle$  is the ratio of the average burdens, for a constant  $\text{SO}_2$  emission rate.

in Figs. 2 and 3. This characteristic time is comparable in magnitude to  $\theta_p$ , but is seen to lag the latter somewhat as a function of hour of day at which the  $\text{SO}_2$  is emitted, reflecting the assumed lag in the conversion coefficient  $b(t)$  relative to the total coefficient for removal of  $\text{SO}_2$ ,  $k_1 = a + b$ . Comparison of the assumed 100-hour turn-over time for sulfate aerosol with the value computed for  $\theta_*$  shows that the former dominates the mean age and mean transit time of secondary aerosol sulfate. In turn, the geographical scale of transport of sulfate relative to sources of the primary  $\text{SO}_2$  will be governed principally by the turn-over time characteristic of the sulfate. We observe further that even if there is a significant variation of  $\theta_*$  with the time of emission of the primary  $\text{SO}_2$ , the relative effect of this variation upon  $\sigma_a$  or  $\sigma_r$  is greatly diminished by the magnitude of the assumed value of  $\sigma_0$ .

Finally we consider briefly the committed burden

of secondary aerosol sulfate as a function of the time of emission of the primary  $\text{SO}_2$ . As indicated by eq. (27) this committed burden is given by

$$N_B(t_0) = \sigma_0(t_0) Y(t_0) \quad (52)$$

and is thus, for  $\sigma_0$  assumed independent of  $t_0$ , proportional to the sulfate yield as shown in Fig. 5. The burden of sulfate relative to that of  $\text{SO}_2$ ,  $\beta(t_0)$ , eq. (41), is shown in Fig. 6 as a function of hour of emission of  $\text{SO}_2$  for each of the cases treated, i.e., average oxidation rates of  $1.2\% \text{ h}^{-1}$  and  $10\% \text{ h}^{-1}$ ; the average value  $\langle \beta \rangle$  was computed as the ratio of the mean burdens of sulfate and  $\text{SO}_2$ . Also shown is the corresponding steady-state value computed as  $\beta_{ss} = \bar{b}\sigma_0$  (eq. (43)). It is of interest to compare these computed burdens to ratios of observed long-term average atmospheric concentrations of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ , since, if these materials were distributed equivalently in the atmosphere, the relative burden would be equal to this ratio.

As it turns out, the assumption of equivalent distribution is far from satisfied, since in industrial regions the ratio of  $\text{SO}_4^-$  to  $\text{SO}_2$  concentrations is not constant, but increases with increasing age and thus distance subsequent to emission. Thus in the northeastern coastal region of the United States for example, Altshuller (1976) reports annual average  $(\text{SO}_4^-)/(\text{SO}_2)$  typically 0.08–0.15 (mole basis) at urban sites increasing to  $\sim 0.5$  at non-urban sites. This increase reflects the transformation of  $\text{SO}_2$  to sulfate and the preferential deposition of  $\text{SO}_2$  as these materials are advected from the region of greatest source density. Consequently, any detailed comparison of the relative burden predicted by the present model with the ratio of the amounts of sulfate and  $\text{SO}_2$  in the atmosphere will require integration of the two concentrations over a geographical extent sufficiently large to encompass the great majority of both materials that are attributable to a given source region. Nevertheless, even without carrying out that integration it seems safe to say that an average relative burden as great as 8 to 10, as predicted by the higher assumed oxidation rate,  $\bar{b} = 10\% \text{ h}^{-1}$ , for an assumed turn-over time for sulfate aerosol of 100 h, can be ruled out on the basis of observation, even considering the uncertainty in the present knowledge of the turn-over time for sulfate. On the other hand, a relative burden of the order of unity, as predicted by the lower oxidation rate,  $\bar{b} = 1.2\% \text{ h}^{-1}$ , while somewhat higher than the average given by Altshuller (1976) for the non-urban sites, is in fact occasionally exceeded at some sites on an annual average basis, and may thus be consistent with the observations. A more detailed comparison with observation, which would require carrying out the spatial integration that is indicated above, is beyond the scope of the present article. Nevertheless, the brief discussion presented here should serve to indicate the utility of the relative burden as an observable quantity against which to compare model predictions.

#### 4. Summary and conclusion

The definitions given by Bolin and Rodhe (1973) for the mean age, mean transit time, and turn-over time describing the residence of material in reser-

voirs under steady-state conditions have been extended to encompass time-dependent rates of introduction and/or removal of such materials. This extension leads to two sets of such residence times, pertinent either to material present in the reservoir at a given time of observation or to material that entered the reservoir at a given time. Under steady-state conditions there two sets of definitions are shown to become identical to each other and identical as well to those given previously by Bolin and Rodhe (1973) in terms of the frequency distribution for the persistence of the material in the reservoir. Additionally, the several definitions have been extended to secondary materials, i.e., materials formed *in situ* by reaction of materials directly introduced. In particular, the mean transit time of the secondary material is shown to be equal to the turn-over time of the secondary material plus a contribution due to the primary material but not necessarily equal to its mean transit time.

The formalism developed herein was applied to a consideration of the residence times and burdens of primary  $\text{SO}_2$  and secondary aerosol sulfate in the atmosphere for an assumed diurnal profile of the rates of  $\text{SO}_2$ -to-sulfate conversion and dry deposition, in order to examine the extent to which the results of this time-dependent treatment differ from those of the steady-state approach. It was found that even for the assumed rates of  $\text{SO}_2$  removal and conversion exhibiting a high degree of modulation the results of the time-dependent treatment do not differ greatly from those of the steady-state treatment unless the extent of  $\text{SO}_2$  removal in a 24-hour period substantially exceeds 50%, which seems highly unlikely in the context of the present understanding.

A further quantity that is useful in considerations of secondary materials is the relative burden, or the ratio of the amount of secondary material present in the reservoir to that of the primary material. Within the steady-state approximation this relative burden is equal to the product of the rate coefficient for conversion from primary to secondary material multiplied by the turn-over time of the secondary material. Examination of observed ratios of concentrations of the secondary and primary materials may permit bounds to be placed upon this product, and thus serve as a further means of evaluating our understanding of these processes.



## 5. Acknowledgements

I appreciate helpful discussions with Drs Paul Michael and Leonard Newman. Dr Henning Rodhe reviewed an earlier version of this paper and made many helpful suggestions.

## 6. Nomenclature

$A(t, t_0)$	Amount of material introduced into reservoir at time $t_0$ present at time $t$ , per unit time of introduction.
$B(t, t_0)$	Amount of secondary material present in reservoir at time $t$ resulting from primary material introduced at time $t_0$ , per unit time $t_0$ .
$t$	Time of observation.
$t_0$	Time at which primary material is introduced into reservoir.
$u$	Relative time, or age of material in reservoir, $t - t_0$ .
$\theta(t_0)$	Residence times pertinent to a class of primary material introduced at time $t_0$ .
$\tau(t)$	Residence times pertinent to the primary material present at time $t$ .
$\sigma(t_0)$	Residence times pertinent to secondary material arising from reaction of primary material introduced at time $t_0$ .
$M_A(t)$	Burden of primary material in reservoir at time $t$ .

$N_A(t_0), N_B(t_0)$	Committed burden of primary or secondary material, respectively, due to material introduced into reservoir at time $t_0$ .
$F''(t)$	Flux out of reservoir at time $t$ .
$\psi(t, u)$	Probability of persistence of primary material in reservoir, eq. (19).
$Y(t_0)$	Total amount or yield of secondary material resulting from primary material introduced at time $t_0$ , per unit time $t_0$ .
$\alpha(t_0)$	Relative yield of secondary material, i.e., fraction of primary material introduced at time $t_0$ that reacts to form secondary material.
$\beta(t_0)$	Relative burden, $N_B(t_0)/N_A(t_0)$ .
$k_1, k_2$	Rate coefficients for removal of primary or secondary materials from reservoir, respectively.
$a(t)$	Rate coefficient for dry deposition of $\text{SO}_2$ .
$b(t)$	Rate coefficient for $\text{SO}_2$ -to-sulfate conversion.
$c(t)$	Rate coefficient for removal of sulfate.
$L(t_1, t_2)$	On-off function, eq. (45).

### Subscripts to residence times

$a$	Denoting mean age.
$t$	Denoting mean transit time.
$0$	Denoting turn-over time.
$*$	Denoting primary contribution to mean transit time of secondary material.
$ss$	Denoting steady state.

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#### ВРЕМЕНА ПРЕБЫВАНИЯ В РЕЗЕРВУАРАХ ПРИ НЕСТАЦИОНАРНЫХ УСЛОВИЯХ: ПРИМЕНЕНИЕ К АТМОСФЕРНОМУ SO<sub>2</sub> И СУЛЬФАТНЫМ АЭРОЗОЛЯМ

Были расширены определения времен пребывания, описывающих вывод материалов из естественных резервуаров, таких, как средний возраст, среднее время прохождения и время оборота, для того чтобы включить в эту схему зависящие от времени скорости ввода и вывода. Такой подход ведет к двум рядом времен пребывания, причем первый основывается на времени, за которое материал вводится в резервуар, а второй—на времени пребывания материала в резервуаре для любого данного времени наблюдения. Первые величины являются свойствами только скоростей процессов удаления, в то время как последние отражают также зависимость от скоростей ввода материала в резервуар. Обследуются соотношения между различными временами пребывания, так же как и нагрузка материала в резервуаре при заданной скорости его ввода. Дополнительно расширяются различные определения для учета вторичных материалов, таких, которые образуются на месте в результате реакций между материалами, вводимыми непосредственно.

В этих рамках рассматриваются времена пребывания и нагрузки для атмосферного SO<sub>2</sub> и сульфатного аэрозоля при предполагаемых зави-

сших от времени скоростях превращения SO<sub>2</sub> в сульфаты и скоростях их сухого осаждения. Найдено, что даже при таких скоростях, выявляющих сильную суточную модуляцию, как это ожидается из рассмотрений скоростей фотохимических реакций и от хода устойчивости атмосферы, времена оборота и атмосферные нагрузки SO<sub>2</sub> и сульфатов выявляют относительно малую суточную модуляцию до тех пор, пока часть SO<sub>2</sub>, удаляемая за сутки, не превосходит существенно 50%. Эти рассмотрения показывают, что для многих целей может оказаться адекватным моделировать подобные процессы с использованием коэффициентов скоростей, осредненных за сутки.

Что касается вторичных материалов, то еще одной полезной величиной является относительная нагрузка, или отношение количеств вторичных материалов к первичным, имеющимся в резервуаре. Эта величина прямо сопоставима с отношением наблюдаемых концентраций этих материалов и поэтому служит дополнительным условием, которое должно быть удовлетворено в моделях, описывающих трансформацию и удаление материалов.