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**RELATIONSHIPS BETWEEN REMOVAL PROCESSES AND
RESIDENCE TIMES FOR ATMOSPHERIC POLLUTANTS***

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ABSTRACT

This report is concerned with improving estimates for the residence times of atmospheric trace constituents in various reservoirs. Residence times are defined only for steady-state conditions; i.e., when the net growth rate vanishes. The most useful case of vanishing net growth rate is when the total growth rate is equal to the decay rate. It is demonstrated that the most important advance towards improving estimates of pollutant residence times is through proper choices of reservoirs.

Chosen reservoirs should possess the following features: steady-state conditions, uniform mixing ratio throughout or throughout specified subreservoirs, and subreservoirs chosen in which removal rates can be treated as approximate constants. An example of a poorly mixed reservoir, the stratosphere, is discussed. In another example, it is suggested that commonly used reservoirs for atmospheric CO₂ have been chosen poorly and that a substantial portion of the anthropogenic CO₂ released during the past 50 years may still be mixing into the stratosphere. In another example, it is suggested that determination of the dry deposition velocity for accumulation-mode aerosol particles may not be so important as previously thought. To improve estimates for the atmospheric residence times of these particles, it is important to increase knowledge of what is called the "ascension velocity."

RELATIONSHIPS BETWEEN REMOVAL PROCESSES AND RESIDENCE TIMES FOR ATMOSPHERIC POLLUTANTS

INTRODUCTION

Qualitatively, it is obvious that there must be a relationship between a pollutant's residence time in the atmosphere and the effectiveness of the removal processes that act on the pollutant. For example, the more effective are the removal processes, the shorter will be the pollutant's residence time. The purpose of this report is to describe some of these relationships, for different pollutants, quantitatively. Before undertaking this task, however, it may be useful to record some general observations about residence times, reservoirs, and removal processes.

One of these observations is that when reference is made to a pollutant's residence time, what is meant is the residence time in a certain reservoir. For example, in the first paragraph, the reservoir mentioned explicitly was the atmosphere, as opposed to the hydrosphere, some other geosphere, or the biosphere. Later in this report, reservoirs that will be considered include the troposphere, the atmosphere's mixed layer and the ocean's mixed layer. Indeed, as is illustrated by two of the reservoirs just mentioned, not only is it understood that the residence time refers to a specific reservoir, usually it is assumed that the reservoir is well mixed. Later in this report, it will be seen what the "well-mixed" condition means, why the condition simplifies the analysis, and how poorly-mixed reservoir might be treated.

Another general observation about a pollutant's residence time in a reservoir is that the residence time obviously depends on the reservoir, as well as on the pollutant. For example, for a small reservoir with rapid

mixing both internally and at the reservoir's (permeable) boundaries, then the residence time in the reservoir would normally be small, regardless of the pollutant. The obvious dependence of the residence times on the removal efficiencies for different pollutants was already mentioned. Thus, in summary, a pollutant's residence time in a reservoir can be expected to depend on the pollutant, the reservoir, the mixing, and the efficiency of the removal processes.

As for general observations about relationships between removal processes and residence times, it is noted, first, that by the very nature of (spatially, large) reservoirs, residence times must be, in some sense, spatial averages of the removal processes. Further, as will be seen, residence times are defined only for steady-state conditions. In contrast, it is of course true that removal processes proceed in spatially inhomogeneous conditions and usually in a time dependent manner. For example, precipitation scavenging (or wet removal) of pollutants from the atmosphere occurs during spatially inhomogeneous conditions (e.g., a rain storm) and terminates with the precipitation. Therefore it is clear that knowledge about removal processes might be used to define residence times (if suitable averages are taken) but not *vice versa*. Consequently, an analysis of relationships between removal processes and residence times should start from a formalism in which the removal processes are explicit. To this we now turn.

CONSERVATION OF MASS

The reservoirs to be considered in this report are control volumes for which account is made of all pollutant mass. An equation describing conservation of mass in which removal (and gain) terms appear explicitly is the

continuity equation:

$$\frac{\partial \chi}{\partial t} = -\nabla \cdot \vec{F} + G - L \quad (1)$$

where $\chi = m\rho$ is the pollutant's mass concentration (M/L^3) in which m is the (mass) mixing ratio and ρ is the density of air; $\vec{F} = \vec{F}(\vec{r}, t)$ is the total (or net) pollutant flux (M/L^2T) at position \vec{r} and time t ; and G and L represent general gain and loss rates per unit volume, respectively (M/L^3T).

Equation (1) can be viewed as the equation for conservation of mass in a reservoir of unit volume, small enough so that G and L can be treated as constants within the volume and small enough so that the differences in fluxes at opposite sides of the reservoir can be approximated by differentials.

To obtain a statement of conservation of mass in a reservoir of arbitrary (but fixed) volume, V , Eq. (1) is integrated over V . Then, with use of the divergence theorem, there results:

$$\frac{\partial Q}{\partial t} = - \oint_S \vec{F} \cdot \hat{n} \, dS + \int_V G \, dV - \int_V L \, dV \quad (2)$$

where $Q = \int \chi \, dV$ is the total amount (usually, total mass) of the pollutant in the reservoir, whose surface is denoted by S . In Eq. (2), \hat{n} is the familiar unit vector, normal to dS , with the positive direction chosen to be outward from the volume.

It will be convenient to have introduced the following symbols:

(a) the total, mass production rate (M/T)

$$P = \int G \, dV \quad (3a)$$

(b) the total, mass removal rate (M/T)

$$R = \int L \, dV \quad (3b)$$

(c) the total, mass inflow rate (M/T)

$$I = \oint_S \vec{F} \cdot \hat{n} \, dS \quad , \quad \vec{F} \cdot \hat{n} < 0 \quad (3c)$$

(d) the total, mass outflow rate (M/T)

$$O = \oint_S \vec{F} \cdot \hat{n} \, dS \quad , \quad \vec{F} \cdot \hat{n} > 0 \quad (3d)$$

With these definitions, then Eq. (2) becomes

$$\frac{\partial Q}{\partial t} = (P + I) - (R + O) \quad (4)$$

Admittedly, such an obvious statement of mass conservation in the reservoir, as is Eq. (4), could have been written immediately, without the intervening steps. However, later in this report it will be demonstrated that precise definitions (e.g., of I and O) are important. Imprecise definitions have led to residence times quoted in the scientific literature (e.g., Slinn, 1978) which are incorrect by more than two orders of magnitude.

GROWTH, DECAY, AND NET GROWTH RATES

So far in this analysis, no restrictions have been made, e.g., to homogeneous, well-mixed, or steady-state conditions. In the general case, then, a characteristic time constant for the pollutant in the reservoir can be defined from Eq. (4) as follows:

$$\frac{1}{\sigma} \equiv \frac{1}{Q} \frac{\partial Q}{\partial t} = \frac{(P+I)}{Q} - \frac{(R+O)}{Q} \quad (5)$$

From this definition, clearly σ^{-1} is the net, fractional rate of increase of the amount of the trace constituent in the reservoir. We shall refer to σ^{-1} as the net growth rate.

It is useful to define a number of other characteristic time constants:

(a) The production rate (T^{-1})

$$\tau_P^{-1} = P/Q \quad (6a)$$

(b) The inflow rate (T^{-1})

$$\tau_I^{-1} = I/Q \quad (6b)$$

(c) The removal rate (T^{-1})

$$\tau_R^{-1} = R/Q \quad (6c)$$

(d) The outflow rate (T^{-1})

$$\tau_O^{-1} = O/Q \quad (6d)$$

With the definitions for these rates (which are inverses of appropriate time constants) two other rates follow:

(a) The (total) growth rate, τ_G^{-1} (T^{-1})

$$\frac{1}{\tau_G} = \frac{1}{\tau_P} + \frac{1}{\tau_I} \equiv \frac{P}{Q} + \frac{I}{Q} \quad (7a)$$

(b) The decay rate, τ_D^{-1} (T^{-1})

$$\frac{1}{\tau_D} = \frac{1}{\tau_R} + \frac{1}{\tau_O} \equiv \frac{R}{Q} + \frac{O}{Q} \quad (7b)$$

Finally, with these definitions, conservation of mass in the reservoir, Eq. (4), gives us

$$\frac{1}{\sigma} = \frac{1}{\tau_G} - \frac{1}{\tau_D} \quad (8)$$

Equation (8) states the obvious result that the net growth rate is the difference between the total growth rate and the rate of decay.

Although no restrictions have been placed on the analysis to arrive at Eq. (8), nevertheless an ambiguity can arise. This ambiguity is derived from what is chosen for the fluxes past the reservoir's boundaries. In this report, *all* components of the fluxes from the reservoir to its exterior will be included in the mass outflow rate, O , and similarly, *all* components of the fluxes into the volume will be included in I . In contrast, in other reports, sometimes the *net* outflow (or inflow, as the case may be) is used: $O^* = O - I$. This leads to the definitions $\tau_G^* = Q/P$ and $\tau_D^* = Q/(R + O^*)$ and obviously, therefore, significantly different values for the characteristic times. Most importantly, if net outflow (or net inflow) is used, significantly different and totally unrealistic values for the residence time can result. We now turn to the definition for the residence time.

STEADY-STATE AND THE RESIDENCE TIME

The rest of the analysis in this report is restricted to steady-state conditions. From Eq. (8), it is seen that steady condition can arise for two cases. The first, and less interesting case, is when the net growth rate goes to zero (i.e., $\sigma \rightarrow \infty$) because both τ_G and $\tau_D \rightarrow \infty$. Apparently, none of the trace constituents in the atmosphere behave in this manner (Junge, 1972). Even helium, the gas with the longest known residence time ($\sim 10^7$ years) has a finite rate of growth (mostly via alpha decay of U^{238} and Th^{232}) and finite decay (via transport through the exosphere). Thus the case $\sigma \rightarrow \infty$ because τ_G and $\tau_D \rightarrow \infty$ does not appear to be of practical significance.

The more relevant steady-state case is when dynamic equilibrium prevails with $\tau_G = \tau_D$. In this case of $\sigma \rightarrow \infty$, the trace constituent's residence or turnover time in the reservoir can be defined via

$$\frac{Q}{P+I} = \tau_G = \tau = \tau_D = \frac{Q}{R+O} \quad (9)$$

This definition of τ is similar to the usual definition of the residence time (e.g., see Junge, 1963). However, in Eq. (9), the terms representing inflow and outflow are explicit. Further, as was mentioned earlier, these mass flow rates, defined in Eqs. (3c) and (3d), explicitly contain the total rather than the net flows.

We also wish to repeat that the only restriction on the analysis leading to the definition of the residence time in Eq. (9) is that steady-state conditions must prevail. ~~Rapid~~ mixing or homogeneity in the reservoir is not required. However, it should be mentioned that the requirement of steady-state conditions is actually quite severe. In reality, steady-state conditions for the amount of a pollutant in the atmosphere, rarely prevail. In general it might be expected that the longer the pollutant's residence time compared with the time scales for atmospheric fluctuations, the smaller would be the deviations from steady-state conditions for Q , provided the production rate does not vary substantially. Indeed, Junge (1974) has demonstrated that the residence times for most atmospheric trace constituents are related to the coefficients of dispersion for the concentration fluctuations, $f = (\delta\chi)/\chi$, by the empirical result $f = (0.14 \text{ yrs})/\tau$. Of course, time variations in Q would normally be substantially smaller than variations in χ , and decrease with increasing reservoir volume. Consequently we can expect that the larger the

reservoir and the longer the residence time, the more nearly will steady-state conditions prevail.

ILLUSTRATIONS OF EQUATION (9)

Two examples that illustrate Eq. (9) may be of interest. For the first example, let Q be the total population of the U.S., say $Q = 210 \times 10^6$ people. Further, assume a steady-state (but not homogeneous!) case with: (a) the birth rate, $P = 3 \times 10^6/\text{yr} = R$, the death rate, and (b) the immigration rate $= I = o = 0$, the emigration rate. Then in this case the residence time is given by

$$\tau = \tau_G = \tau_P = \tau_R = \tau_D = 210 \times 10^6 / (3 \times 10^6/\text{yr}) = 70 \text{ years.} \quad (10)$$

Incidentally, it might be useful to notice that there is a difference between the residence time (or turnover time, transit time, or lifetime) and the average age (e.g., see Eriksson, 1971, although his terminology is different). Thus, for the example just presented, the residence time (or lifetime) is 70 years but the average age of U.S. citizens is about 30 years. A difference between the average lifetime and the average age does not imply that conditions are unsteady.

For atmospheric trace constituents, Bolin and Rodhe (1973) point out that whenever the sources and sinks in the reservoir are separated by a substantial distance (e.g., for those halogenated hydrocarbons whose sources are at the earth's surface and whose sink is in the stratosphere) then it can be expected that the residence time will be longer than the average age. In contrast, if the sources and sink are adjacent (e.g., the oceans are both the dominant source and the dominant sink for atmospheric H_2O) then the average age will

be longer than the residence time. Bolin and Rodhe indicate that if a reservoir is well-mixed, that is, if all elements in the reservoir instantly have an equal probability of being exposed to the sinks in the reservoir, then the probability density function (pdf) for the distribution of ages in the reservoir will be exponential. A simple example is when the only sink is radioactive decay. The result that the pdf for the ages is exponential is sufficient to insure that the average age is the same as the (average) residence time.

As a second illustration of Eq. (9), consider all compounds of sulfur in the troposphere. If the average mixing ratio of these compounds is about 1 ppb, then since the mass of the troposphere is about 4×10^{21} g, $Q \approx 4$ Tg. Natural and anthropogenic sources of sulfur contribute to give a total P (or I at the earth's surface) of about 200 Tg/yr, within a factor of about 2. Consequently, the residence time of sulfur compounds in the troposphere, $\tau \approx 4 \text{ Tg} / (200 \text{ Tg/yr}) \approx 1$ week, to within a factor of about 2 to 4.

This uncertainty in the estimate for the tropospheric residence time of sulfur compounds, mentioned at the end of the previous paragraph, coupled with great economic and ecological interests in controls on anthropogenic sulfur emissions, are incentives to improve the accuracy of estimates for τ . Thus, for example, if τ for sulfur compounds is only a few days, then the U.K. does not contribute much to the acid rain problem in Scandinavian countries (e.g., see Odén, 1976). On the other hand, if τ is a number of weeks, then even the U.S. contributes to the acid rain problem in Scandinavia. Clearly, then, accurate estimates for τ are important.

To improve the accuracy of estimates for τ , it is obvious from Eq. (9) that what is needed are accurate estimates for Q and either $(P+I)$ or $(R+O)$

- or both! However, as will be seen, it is generally not easy to improve the accuracy of any of these terms if, as is usually the case, there are significant spatial inhomogeneities in the reservoir. These inhomogeneities may be in the pollutant's mixing ratio, m , or in the volumetric gain rate, G , or loss rate, L . Nonuniformities in m can also result from spatial inhomogeneities at the reservoir's boundaries and corresponding inhomogeneities in the rates of inflow and outflow.

Of course, these inhomogeneities were expected and attempts were already made to account for them by introducing the concept of a reservoir and the associated average over the reservoir's volume. However, it is terms such as L , for example, for which improved estimates can be expected to become available. As an example, suppose improvements become available for the first order removal rate, λ , that characterizes precipitation scavenging of aerosol particles: $L = \lambda(z)\chi$, where a dependence of λ on height has been displayed. Then, to evaluate R , it would be necessary to evaluate $\int \lambda(z)\chi(z)dz$. That is, to obtain improved estimates of τ it appears to be necessary to know $\chi(z)$. But if this were the case, that is, if $\chi(z)$ were known, then there would have been little advantage to introducing the concept of a reservoir in the first place.

In reality, the outlook for improved estimates of τ is not quite so bleak as intimated at the end of the previous paragraph, although there are major impediments to improvements. In the remainder of this report, methods and conditions will be considered that can lead to more accurate estimates of τ . For example, rapid mixing helps. However, in the real atmosphere, rarely is mixing in all directions sufficiently rapid to insure the mixing ratio is constant throughout the atmosphere. Instead, cases must be considered where

the mixing ratio is constant in one direction, for a limited distance, but not constant in another direction. These considerations will lead to the introduction of subreservoirs. Before introducing these, however, it is useful to consider a special case, of practical significance, in which τ is independent of χ or Q .

τ FOR THE SIMPLEST CASE

Consider a steady-state reservoir in which the following conditions are satisfied: (a) volumetric loss rate, first-order in χ with constant rate coefficient; i.e., $L = \lambda\chi$ with $\lambda = \lambda_0$, a constant; and (b) negligible outflow from the reservoir, i.e., $O = 0$. An example of this case is Kr^{85} in the entire atmosphere. The only significant "removal" of Kr^{85} is radioactive decay which, of course, proceeds at a rate independent from the nuclide's location in the atmosphere. Although the assumed conditions (a) and (b) seem quite strict, notice that no assumption has been made about the distribution of the pollutant in the atmosphere. i.e., about $\chi(z)$.

When conditions (a) and (b) of the previous paragraph are satisfied, then improvements in τ need not rely on improvements in χ or Q . This follows because from Eq. (3b) we have

$$R = \int L \, dV = \lambda_0 \int \chi \, dV = \lambda_0 Q \quad . \quad (11)$$

Now, substituting $R = \lambda_0 Q$ and $O = 0$ in Eq. (9) there results $\tau^{-1} = \tau_D^{-1} = \lambda_0$. More generally, if there are a number of separate, first-order, constant removal processes, $L = \sum \lambda_{i,0} \chi$, and if $O = 0$, then the residence time is given by

$$\frac{1}{\tau} = \frac{1}{\tau_D} = \frac{1}{\tau_R} = \sum_i \lambda_{i,o} = \frac{1}{\tau_{w,o}} + \frac{1}{\tau_{ch,o}} + \frac{1}{\tau_{ph,o}} + \dots \quad (12)$$

In Eq. (12), separate characteristic time constants have been identified with subscripts to represent removal by wet processes (τ_w), chemical transformations (τ_{ch}), physical transformations such as radioactive decay (τ_{ph}), etc. The subscript, o, on each characteristic time is used as a reminder that these coefficients are assumed to be independent of location within the reservoir.

Two important deductions can be made from Eq. (12) even though the range of applicability of Eq. (12), itself, is quite restricted. First, Eq. (12) demonstrates that separate removal paths add together to give a total residence time, like electrical resistance in parallel add to give a total resistance, even smaller than the smallest resistance. Consequently, for improvements in practical applications, focus should always be on improving estimates for the fastest removal rate. As an example, it will be shown later that improved estimates for the dry deposition velocity for submicron aerosol particles are not nearly so important as has frequently been stated in the scientific literature (e.g., see Slinn, 1977, 1978). More important than to know the dry deposition velocity is to know what we will call the dry ascension velocity. The second important result from Eq. (12) is that when $L = \lambda_o \chi$ and $O = o$, then *even for poorly-mixed reservoirs*, simple and accurate estimates for τ can be obtained provided, of course, that the removal rates can be accurately estimated.

ILLUSTRATIONS OF EQUATION (12)

Some examples of the use of Eq. (12) may be illuminating. For Kr^{85} , the most important removal is by radioactive decay, with $\tau_{ph,o} \approx 10$ yrs. In

harmony with the remarks in the previous paragraph, we focus on this fastest removal process, even though krypton has a finite solubility in water. Thus, substituting values into Eq. (12) and using the same order as the order of the terms displayed on the right-hand side of Eq. (12), there results the most accurately known residence time that will appear in this report:

$$\frac{1}{\tau} = \frac{1}{\tau_D} = \frac{1}{\infty} + \frac{1}{\infty} + \frac{1}{(10.76 \text{ yrs})} \Rightarrow \tau(\text{Kr}^{85}) = 10.76 \text{ yrs.} \quad (13)$$

In this simple case, when the pollutant has such a long residence time in the atmosphere, probably it would have been acceptable to assume the mixing ratio is constant throughout the atmosphere, except in specific Kr^{85} plumes. However, again, information on χ is not needed for τ when $L = \lambda_0 \chi$ and $O = 0$.

As a second example of the use of Eq. (12), consider tropospheric aerosol particles with radii, a , in the range $0.1 \leq a \leq 1 \mu\text{m}$, and which can act as cloud condensation nuclei (CCN). CCN are particles on which water condenses within clouds. Apparently, essentially all particles in the atmosphere that satisfy $0.1 \leq a \leq 1 \mu\text{m}$ can act as CCN after only a few hours in the troposphere (e.g., see Junge, 1977). That is, even particles that are initially non-wettable soon accumulate a sufficient number of Aitken nuclei ($a \leq 0.1 \mu\text{m}$) or act as sites for heterogeneous gas reactions, and become wettable. We focus on the particle size range between about 0.1 and 1.0 μm because coagulation is an important "removal" process for smaller particles, and gravitational settling is important for larger particles.

The dominant removal mechanism for the particles under consideration appears to be precipitation (or nucleation) scavenging (e.g., see Junge, 1963). It is noted, however, that some authors have suggested that there

are significant variations in the scavenging rate, λ_w , as a function of altitude. Undoubtedly this is true for specific releases of aerosol particles. Nevertheless, here we assume $\lambda_w = \text{constant}$ and invite the assumption to be viewed either as a first approximation or as a reasonably correct, long-term average.

The author expects that it is reasonable to take $\lambda_w = \text{constant}$ because, fundamentally, precipitation only occurs with the *lifting* of low-level, moist air. During this ascent, the particles are, of course, lifted with the air. Therefore, it seems to the author that the policy of introducing different removal rates for below-cloud vs. in-cloud scavenging is not so realistic for residence time estimates as the policy of assuming $\lambda_w = \text{constant}$ since most particles that are scavenged do not remain beneath clouds. Of course, some scavenging does occur beneath clouds and for some air trajectories in the neighborhood of some storms, the lower level air can be quite polluted. However, usually the scavenging rates are substantially smaller beneath clouds than within, and frequently the low-level air directly in the path of the precipitation is relatively clean. In fact, the author would prefer to yield to results which demonstrated that scavenging of CCN was not first order in their concentration (because a significant, additional number of CCN could influence the precipitation rate) than yield on the assumption $\lambda_w = \text{constant}$.

With $\lambda_{w,0} = \lambda_w$ and other removal rates negligible (note that dry deposition is ignored via the assumption $0 = 0$), then Eq. (12) yields

$$\tau(\text{CCN}) = \tau_w \quad . \quad (14)$$

Numerical estimates for τ_w (e.g., see Junge, 1963, 1977; Rodhe and Grandell, 1972; Slinn, 1977) yield, for temperate latitudes: $\tau_w \approx 5$ days during the

winter; ≈ 7 days during the fall and spring; and ≈ 10 days during the summer. The contributions from dry deposition to the residence time of particles with $0.1 \leq a \leq 1 \mu\text{m}$ will be addressed in a later section. There it will be suggested that dry deposition of these particles appears to have a negligible contribution to the residence time if the deposition velocity is of the order of 0.1 cm/sec or less.

As a final example to illustrate Eq. (12), consider a gas such as CH_3I whose primary removal is via (photo) chemical destruction (e.g., see Lillian *et al.*, 1975). For some gases, e.g., O_2 , the photochemical reaction rate is strongly dependent on altitude because of absorption of photons, with appropriate energies, at still higher altitudes. In the case of CH_3I , however, apparently there are photons with sufficient energy, available throughout the troposphere. In this case, λ_{ch} can be treated as a constant. Consequently, since both dry deposition (i.e., the outflow, 0) and wet removal of CH_3I are negligible (e.g., see Slinn *et al.*, 1978), then Eq. (12) can be used to obtain

$$\frac{1}{\tau} \approx \frac{1}{\infty} + \frac{1}{\tau_{\text{ch}}} + \frac{1}{\infty} \implies \tau(\text{CH}_3\text{I}) \approx \tau_{\text{ch}} \approx 1 \text{ day.} \quad (15)$$

The numerical value for τ_{ch} used in Eq. (15) is a compromise between the laboratory data in Lillian *et al.* (1975) and the estimate made by Singh *et al.* (1977).

There are, of course, many other gases in the atmosphere whose primary removal is by first order chemical reactions. A case in point is SO_2 . However, in this case, as with the scavenging of aerosol particles, arguments can be raised against the use of spatially independent removal rates. The

arguments in the case of chemical reactions are especially compelling if the dominant reactions are among different pollutants, since then the reaction rates are higher in the polluted, lower layers of the continents. The now-classic example is the complex series of reactions involving oxides of nitrogen that create "photochemical smog." For such cases, it is least defensible to use constant reaction rates. In the following sections, problems arising from spatial inhomogeneities will be addressed.

TERMINOLOGY: HOMOGENEITY VS UNIFORMITY

Before tackling details of the problems caused by inhomogeneities, a few comments about definitions may be useful. In this report, the description "well-mixed, inhomogeneous reservoir" will mean the mixing ratio is uniform but that there are inhomogeneities in the removal (or other) rates for the reservoir. That is, if the usual meaning were taken for the word inhomogeneous, then there are three types of inhomogeneities for a reservoir: (a) inhomogeneities in L (and/or G); (b) inhomogeneities in O (and/or I) caused by different conditions at different portions of the reservoir's boundaries; and (c) inhomogeneities (or, as we shall call them, "nonuniformities") in χ or, more usefully, nonuniformities in the mixing ratio, m .

In general, the three types of inhomogeneities listed in the previous paragraph are independent although it is true that the first two can cause nonuniformities in m . However, nonuniformities in m can be caused solely by poor mixing. At the other extreme, a case can be imagined for which, regardless of the inhomogeneities in L (or G) and O (or I), yet m could be uniform, if the mixing were sufficiently fast. Thus it appears to be necessary to consider carefully just what is inhomogeneous and what causes the nonuniformities in m .

To assist these considerations, terminology can be useful. In this report, the "degree of uniformity" will be used to describe the mixing ratio and the "degree of homogeneity" will refer to the various rates and fluxes. However, we shall avoid the description "uniform, inhomogeneous reservoir" and, instead, use "well-mixed, inhomogeneous reservoir."

MIXING TIMES AND THE WELL-MIXED CONDITION

Already in this report, mixing has been mentioned many times. The rapidity of mixing depends on additional characteristic time scales for the reservoir. Thus, besides the net growth rate, σ^{-1} , the total rates of growth and decay, τ_G^{-1} and τ_D^{-1} , the rates of production, inflow, removal and outflow (τ_P^{-1} , τ_I^{-1} , τ_R^{-1} and τ_O^{-1}) and the residence time, τ , there are characteristic mixing times. These mixing times are independent from the other characteristic times, because mixing depends on different physical processes. These independent mixing rates will be identified by $\tau_{M,i}$ where i identifies the direction. For example, if mixing in the z -direction is governed by diffusion with average diffusivity, K_z , then the characteristic mixing time over a length scale L_z is $\tau_{M,z} = L_z^2/K_z$; similarly for $\tau_{M,x}$ and $\tau_{M,y}$.

Given the characteristic mixing times, then a quantitative definition of a "well-mixed" reservoir can be formulated. If nonuniformities in the mixing ratio caused by inhomogeneous production and removal are to be obliterated by rapid mixing, then it is necessary that

$$(\tau_{M,x}, \tau_{M,y}, \tau_{M,z}) \equiv \tau_{M,i} \ll (\tau_P, \tau_R) \quad (16)$$

Further, if nonuniformities in χ caused by inhomogeneities in outflow and inflow are to be obliterated by mixing, then

$$\tau_{M,i} \ll (\tau_I, \tau_O) \quad (17)$$

Finally, a well-mixed (or uniform), steady-state reservoir can be defined as one which satisfies:

$$\frac{1}{\tau_{M,i}} \gg \frac{1}{\tau_G} = \frac{1}{\tau_P} - \frac{1}{\tau_I} = \frac{1}{\tau} = \frac{1}{\tau_R} - \frac{1}{\tau_O} = \frac{1}{\tau_D} \gg \frac{1}{\sigma} \quad (18)$$

For practical atmospheric problems, frequently we must deal with only partially, well-mixed reservoirs; i.e., reservoirs that can be assumed to be well-mixed in one direction, but not another. An example of a poorly-mixed atmospheric reservoir may be illuminating.

THE STRATOSPHERE AS A POORLY-MIXED RESERVOIR

According to condition (18), a reservoir is poorly mixed if at least one of the characteristic mixing times is not small compared with the trace constituent's residence time, τ . Notice that this means that a specific reservoir can be well-mixed for some pollutants and poorly mixed for others, depending on τ . Further, typically the mixing times in the atmosphere are different for different directions. Consequently, for example, the entire troposphere (vertical mixing time $\tau_{M,z} \sim 1$ week; horizontal mixing time $\tau_{M,h} \sim 1$ year) can be considered to be a well-mixed reservoir for Kr^{85} ($\tau \sim 10$ years) but even vertical mixing is not rapid compared with the residence time of sulfur compounds (~ 1 week). Thus, in summary, it is relatively easy to find examples of reservoirs that are poorly mixed for some pollutants; in fact, probably all common atmospheric reservoirs are poorly mixed for *some* pollutants.

One common atmospheric reservoir, the stratosphere, is poorly mixed for essentially *all* atmospheric trace constituents. Available data, however, can be interpreted in a misleading way. Thus, for example, there are many reports that give the "residence time" of stratospheric bomb debris to be about: 30 days, if the material is injected into the lowest layers of the stratosphere (at $z \sim 10-12$ km); ~ 1 year, for material injected at about 15 km; and ~ 5 years, if the material is injected still higher. In view of condition (18), however, it appears that these reported values are not residence times (in the sense of $\tau_G = \tau = \tau_D$) but, instead, are mixing times, for mixing from the injection altitude down to the tropopause. Thus, with $K_z = 1$ m²/sec (e.g., see Junge, 1963) it is noted that for $L_z = 1.6$ km, 5.5 km and 12.2 km, then $\tau_{M,z} = L_z^2/K_z = 30$ days, 1 year and 5 years, respectively. Consequently, it would seem to be more appropriate to refer to the reported stratospheric bomb debris "residence times" as stratospheric mixing times.

However, objections might arise from this suggested change in terminology. It can be argued that the reported time values do relate to the length of time the debris *resides* in the stratosphere. Further, it can be argued that even in this report, the definition of a pollutant's residence time does not require that the reservoir be well mixed. Only steady-state conditions were required. However, slow mixing impedes equilibration and, in the case of bomb debris, steady-state conditions have thankfully never materialized. Therefore, the author believes a strong argument can be made *against* the usage "stratospheric bomb-debris residence times" and *for* the usage "stratospheric mixing times." Indeed, when reported "reservoir residence times" appear to be independent of the type of pollution, this is a strong suggestion that the "residence times" are actually reservoir mixing times.

The question addressed now is: when can the stratosphere be considered a well-mixed reservoir? The characteristic time for vertical mixing in the entire stratosphere, $\tau_{M,z} \sim (40 \times 10^3 \text{m})^2 / (1 \text{m}^2/\text{s}) \sim 50$ years. Consequently, the stratosphere can be considered as well-mixed, only for an atmospheric trace constituent with $\tau \gg 50$ years; e.g., helium. In the case of helium, though, there is actually little advantage to isolating the stratosphere as a separate reservoir since there are no volume sources or sinks of He within the stratosphere. That is, the stratosphere, as part of an entire atmospheric reservoir, merely impedes mixing between sources of He at the earth's surface and the sink, which is escape through the exosphere. Further, though, the stratosphere's impediment to the mixing of He is not important, since $\tau \gg \tau_{M,z}$. Thus helium's residence time can be calculated by ignoring special properties of the stratosphere, and taking the mixing ratio to be essentially constant throughout the atmosphere.

In summary, it is relatively easy to find commonly used atmospheric reservoirs that are poorly mixed for some pollutants. The stratosphere is a particularly vivid example since it is poorly mixed for essentially all atmospheric trace constituents. An exception is that the stratosphere can be considered to be well mixed for helium. However, for helium, there is no apparent advantage in considering the stratosphere as a separate reservoir. In the next section, we begin considerations of inhomogeneities in reservoirs and will see the substantial simplifications that can result if it can be assumed that the mixing ratio is uniform.

INHOMOGENEOUS BOUNDARY CONDITIONS

To initiate the study of inhomogeneities, consider a steady-state reservoir that has homogeneous conditions within the reservoir but may have non-uniformities in the mixing ratio because of inhomogeneous boundary conditions. An example of a case with inhomogeneous boundary conditions is for CO₂ in the northern troposphere: the fluxes to the ocean, to the southern hemisphere, and to the stratosphere are quite different. The trace constituent's residence time in such a reservoir is given by Eq. (9); i.e.,

$$\frac{1}{\tau} = \frac{1}{\tau_D} = \frac{1}{\tau_R} + \frac{1}{\tau_O} \equiv \frac{R}{Q} + \frac{O}{Q} \quad (19)$$

In this section, the focus will be on the outflow rate, τ_O^{-1} .

To calculate the pollutant's mass outflow rate, O , it is useful to distinguish two types of boundaries: (a) boundaries between other portions of the atmosphere; and (b) boundaries between the atmospheric reservoir and other geospheres or the biosphere. For the second type of interface, e.g., at the air/ocean interface, there is negligible flux of air past the interface although there may be a substantial flux of pollutant. This pollution flux will be parameterized in terms of a deposition velocity. Thus, for interface j between the reservoir and another geosphere or the biosphere, the outward flux of pollution past this interface will be written as

$$\vec{F}_j = v_{d,j} \chi_j \hat{n}_j = v_{d,j} m_j \rho_j \hat{n}_j \quad (20)$$

where χ_j , m_j and ρ_j are evaluated at the interface. If, in total, there are J such interfaces, then the total mass outflow rate, other than to other portions of the atmosphere, is

$$O_b = \sum_{j=1}^J \int_{S_j} v_{d,j} m_j \rho_j dS_j \equiv \sum_{j=1}^J v_{d,j} Q / h_j \quad (21)$$

where it has been assumed that the deposition velocity is constant at each interface. In Eq. (21), Q is the total mass of the pollutant in the reservoir and

$$\frac{1}{h_j} = \frac{1}{Q} \int_{S_j} m_j \rho_j dS_j = \frac{\int \chi_j dS_j}{\int \chi dV} \quad (22)$$

is a characteristic height scale whose significance will become apparent.

For the first type of interfaces mentioned in the previous paragraph, i.e., at boundaries between different portions of the atmosphere, then normally there would be a significant exchange of air past the interface. We will characterize this exchange in terms of a transfer velocity, v_t , and assume that the pollution is transported past these interfaces with the same transfer velocity as the air. Thus, the outward flux from the reservoir at interface k will be written as

$$\vec{F} = v_{t,k} m_k \rho_k \hat{n} \quad (23)$$

where it is noted that $\rho_k v_{t,k} \hat{n}$ is the flux of air out of the reservoir past the k 'th interface. If there are K such interfaces, then the total mass outflow of pollutant from the reservoir to other portions of the atmosphere becomes

$$O_a = \sum_{k=1}^K \int_{S_k} m_k v_{t,k} \rho_k dS_k \equiv \sum_{k=1}^K \bar{m}_k a_k \equiv \sum_{k=1}^K v_{t,k} \frac{Q}{h_k} \quad (24)$$

where Q_k is the total mass outflow rate for air, \bar{m}_k is the mass-flow weighted, average mixing ratio at the interface, and h_k is defined as in Eq. (22).

The total outflow from the reservoir, $O = O_a + O_b$, is obviously

$$O = \left[\sum_{j=1}^J (v_{d,j}/h_j) + \sum_{k=1}^K (v_{t,k}/h_k) \right] Q \quad (25)$$

Consequently, the outflow rate is given by

$$\frac{1}{\tau_O} = \frac{O}{Q} = \sum_{j=1}^J \frac{1}{\tau_{d,j}} + \sum_{k=1}^K \frac{1}{\tau_{t,k}} \quad (26)$$

where $\tau_{d,j} = h_j/v_{d,j}$ and $\tau_{t,k} = h_k/v_{t,k}$. For the special case that the removal processes are described by $L = \sum \lambda_{r,i} \chi \equiv \sum (1/\tau_{r,i}) \chi$, with $\tau_{r,i}$ constants, then, as was seen for the development of Eq. (12), the residence time becomes

$$\frac{1}{\tau} = \sum_{i=1}^I \frac{1}{\tau_{r,i}} + \sum_{j=1}^J \frac{1}{\tau_{d,j}} + \sum_{k=1}^K \frac{1}{\tau_{t,k}} \quad (27)$$

where, again, $\tau_d = h_j/v_{d,j}$, $\tau_{t,k} = h_k/v_{t,k}$ and h_j and h_k are the characteristic heights given by Eq. (22).

Eq. (27) appears to be quite transparent and simple. Similar to Eq. (12), Eq. (27) displays that to improve estimates for τ , it is most important to improve estimates for the fastest of the removal and outflow rates. In general, however, Eq. (27) is not simple and, indeed, it is not of much practical value unless the characteristic heights, h_j , can be evaluated. But as can be seen from Eq. (22), to determine h_j requires that the pollutant's distribution in the reservoir must be known. In general, of course, the

distribution is not known; if it were, there would not have been much point to introduce the concept of a reservoir. In some cases, though, χ can be assumed to be zero at an interface or it can be seen that regardless of (reasonable values for) the concentration, the resulting contribution of the appropriate term in Eq. (27), to the evaluation of τ , will be negligible. However, in most cases, the only practical way to overcome these problems caused by inhomogeneous boundary conditions is to make assumptions about the mixing ratio.

The most common solution to the confronting problem is to choose the reservoir in such a way that it is an acceptable approximation to assume the mixing ratio is constant. Then

$$\frac{1}{h_j} = \frac{\int m_j \rho_j dS_j}{\int m \rho dV} = \frac{1}{M} \int \rho_j dS_j \quad (28)$$

and similarly for h_k , where M is the total mass of air in the reservoir. For example, if the j 'th interface is at the earth's surface, E , and if the reservoir extends throughout the entire atmosphere, then h_E becomes the familiar scale height for the atmosphere

$$h_E = H = \int_0^{\infty} (\rho/\rho_0) dz \quad ; \quad (29)$$

for an isothermal atmosphere, $h_E = 8$ km.

Thus, in summary, the most common solution to the problem of needing χ at the reservoir's boundaries before either homogeneous or inhomogeneous outflow can be evaluated, is to assume that the reservoir is well-mixed. In practice, this means that if the outflow from the reservoir appears to be

significant, then it is necessary to choose only those reservoirs for which it appears reasonable to assume $m = \text{constant}$. Incidentally, it is clear that the larger the reservoir, then generally the larger will be the characteristic heights; therefore the less important will be the outflow terms. This result is the familiar one that surface effects become less important as the volume to surface ratio increases. A simple illustration of the development in this section may be illuminating.

HALOGENATED HYDROCARBONS

To illustrate the use of Eq. (27), consider those halogenated hydrocarbons (or halocarbons) in the troposphere whose dominant removal is via chemical reactions with ozone in the stratosphere. Actually, there are a number of complicating features of this example which we would prefer to avoid at the present time. Thus, for reasons that will be clearer in the final section of this report, we will choose the actual reservoir to be the troposphere plus the mixed-layer of the oceans. Then the flux past the thermocline, to the deep oceans, will be ignored. It will be assumed that this entire reservoir is well mixed; the reasonableness of the assumption can be checked after the residence time has been found. Recall that, for a uniform mixing ratio, it is required that $\tau \gg \tau_{M,i}$.

For the case under consideration, Eq. (27) simplifies to

$$\frac{1}{\tau} = \frac{1}{\tau_w(T)} + \frac{1}{\tau_{ch}(T)} + \frac{1}{\tau_s(T/S)} \quad (30)$$

where the symbols T and S represent troposphere and stratosphere, respectively. In the case of the halocarbons of interest, whose dominant interaction is with

ozone in the stratosphere, it appears that wet removal from the troposphere and chemical reactions with ozone in the troposphere are ignorable compared with transport to the stratosphere. Consequently, Eq. (30) simplifies to

$$\tau \approx \tau_t(T/S) = \frac{h(T/S)}{v_t(T/S)} = \frac{Q(T)}{O(T/S)} \quad (31)$$

Actually, as indicated by the last equality in Eq. (31), in this example it is easier to estimate h/v_t by returning to Q/O . In a later section, other examples will be presented in which $\tau_t = h/v_t$ will be used.

To estimate the outflow of halocarbons from the troposphere to the stratosphere, we propose to use a crude estimate of the diffusive flux. Thus

$$\frac{O(T/S)}{(\text{AREA})} \approx -K_z \frac{\partial \chi}{\partial z} \approx -K_z \left[\frac{\chi(S) - \chi(T)}{(\sim 10 \text{ km})} \right] \approx \frac{K_z \chi(T)}{(10 \text{ km})} \quad (32)$$

Then, for the height of the troposphere $h(T) \approx 10 \text{ km}$, Eqs. (31) and (32) lead to

$$\tau = \frac{Q(T)}{O(T/S)} \approx \frac{\chi(T) h(T)}{K_z \chi(T) / (10 \text{ km})} \approx 3 \text{ years} \quad (33)$$

for $K_z \approx 1 \text{ m}^2/\text{s}$. The estimate given by Eq. (33) is a commonly accepted value. Theoretically at least, this estimate can easily be improved, given the reaction rate between the particular halocarbon and ozone, the ozone concentration in the stratosphere (and troposphere), and given $K_z(z)$. However, pursuing these matters now would lead this report too far astray. The purpose of the previous two sections has been to demonstrate how inhomogeneities at the reservoir's boundaries could be treated. Now, we desire to investigate the important problems caused by the removal processes within the reservoir.

REMOVAL INHOMOGENEITIES AND SUBRESERVOIRS

Consider a large reservoir in which there are spatial inhomogeneities in the removal processes. In the general case, to improve the accuracy of estimates for a pollutant's residence time in this large reservoir, there appears to be no option other than to divide the large reservoir into subreservoirs, small enough so that the removal processes can be treated as constants, in each. Then the pollutant's residence time can be determined in each of the subreservoirs. The problem addressed in this section is how to calculate the pollutant's residence time in the original, large reservoir after the residence time in each of the subreservoirs has been determined.

From Eq. (9), the pollutant's residence time in the entire reservoir is given by

$$\frac{1}{\tau} = \frac{1}{\tau_0} = \frac{Q_0}{Q} + \frac{R}{Q} \equiv \frac{1}{\tau_0} + \frac{1}{\tau_R} \quad (34)$$

If the large reservoir is subdivided into N smaller reservoirs (e.g., for the usual atmospheric case, with reservoir n located in the altitude range $z_n \leq z \leq z_{n+1}$) then the residence time in the n th reservoir is

$$\frac{1}{\tau_n} = \frac{Q_0}{Q_n} + \frac{R}{Q_n} \equiv \frac{1}{\tau_{0,n}} + \frac{1}{\tau_{R,n}} \quad (35)$$

To relate τ to τ_n we first note that

$$R = \int L dV = \sum_{n=1}^N \int L_n dV_n \equiv \sum_{n=1}^N R_n \quad (36)$$

Therefore, in Eq. (34)

$$\frac{1}{\tau_R} = \frac{Q}{Q} = \sum_{i=1}^N \frac{Q_i}{Q} = \sum_{i=1}^N \frac{Q_i}{Q} \tau_{R,i}^{-1} \quad (37)$$

Consequently, for the entire reservoir,

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \sum_{i=1}^N \frac{Q_i}{Q} \tau_{R,i}^{-1} \quad (38)$$

Equation (38) is an obvious result but nevertheless it contains some interesting features. Since τ_0 contains only those terms describing outflow from the entire reservoir, then Eq. (38) indicates the expected result that internal mixing has no explicit influence on the overall residence time. For example, let the large reservoir be the entire troposphere, and let the troposphere be divided into three layers: C, the constant flux layer ($0 < z < 10^2$ m); B, the boundary layer ($10^2 < z < 10^3$ m); and A, the aloft layer ($10^3 < z < 10^4$ m). Then application of Eq. (38) to this case yields

$$\frac{1}{\tau} = \frac{1}{\tau_0(C/E)} + \frac{1}{\tau_0(A/S)} + \frac{1}{Q(T)} \left[\frac{Q(A)}{\tau_R(A)} + \frac{Q(B)}{\tau_R(B)} + \frac{Q(C)}{\tau_R(C)} \right] \quad (39)$$

in which $\tau_0(C/E)$ represent outflow from the C-layer to the earth's surface; $\tau_0(A/S)$ represents outflow to the stratosphere, and $Q(T)$ is the total amount of the pollutant in the troposphere. Thus, in Eq. (39), there appears no explicit influence, on the overall residence time, from mixing between the individual layers. However, mixing definitely influences τ because the amount of mixing dictates the magnitude of Q_n , i.e., the amount of pollution

in each subreservoir. Notice, too, that if the outflow from the entire reservoir is zero (i.e., $\tau_0 \rightarrow \infty$) then the overall residence time is just the weighted sum of the removal times (*not* the residence times) for each subreservoir.

Although Eq. (38) is an informative result, it does not appear to have much practical value. Notice that, to arrive at Eq. (38), only the steady-state assumption was used. However, the purpose of subdividing the large reservoir was to permit treating the removal processes as constants in each subreservoir. We now pursue this purpose and introduce appropriate assumptions about the removal processes.

INHOMOGENEOUS, FIRST-ORDER REMOVAL

The internally inhomogeneous case of most practical interest is when the loss rate per unit volume is first order in χ , i.e., $L = \lambda\chi$ or $L = \sum \lambda_i \chi$, with the L rate coefficients, λ_i , dependent upon position in the reservoir. To treat this case, we first divide the reservoir into n subreservoirs, small enough so that the $\lambda_{i,n}$ can be treated as constants in each. For constant $\lambda_{i,n}$ in each subreservoir, it is recalled that even for poorly mixed subreservoirs [cf., Eq. (12)],

$$\frac{1}{\tau_{R,n}} = \sum_{i=1}^n \lambda_{i,n} \equiv \sum_{i=1}^n \frac{1}{\tau_{r,i,n}} \quad (40)$$

Consequently, from Eq. (38) the residence time in the original, large reservoir becomes

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \sum_{n=1}^N \sum_{i=1}^n \frac{Q_i}{Q} \frac{1}{\tau_{r,i,n}} \quad (41)$$

Unfortunately, Eq. (41) cannot be evaluated unless the Q_n are known.

The simplest case of Eq. (41) occurs when the mixing ratio is constant throughout the original, large reservoir. Then Eq. (41) becomes

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \sum_{n=1}^N \sum_{i=1}^I \frac{m_n}{M} \frac{1}{\tau_{r,i,n}} \quad (42)$$

where M_n is the mass of air in the n th reservoir and $M = \sum M_n$ is the total mass in the large reservoir. For example, suppose that dry deposition of SO_2 can be ignored, and ignore the flux of SO_2 to the stratosphere (i.e., take $\tau_0 \rightarrow \infty$). Further, suppose that the dominant removal is by first order chemical transformations with rate constants: $\tau_{ch}^{-1}(M)$ in the mixed layer, and $\tau_{ch}^{-1}(F)$ in the free troposphere, above the mixed layer. Then, if the mixing ratio for SO_2 were uniform throughout the troposphere (generally, this is a poor assumption) Eq. (42) would yield

$$\frac{1}{\tau} = \frac{1}{M} \left[\frac{m(M)}{\tau_{ch}(M)} + \frac{m(F)}{\tau_{ch}(F)} \right] \approx \frac{0.1}{\tau_{ch}(M)} + \frac{0.9}{\tau_{ch}(F)} \quad (43)$$

In reality, this estimate for $\tau(SO_2)$ is expected to be poor since the SO_2 mixing ratio is not uniform in the troposphere, especially over the continents.

The case of more practical interest is when the mixing ratio is constant in each subreservoir, but different constants for different subreservoirs. Then, as was seen for the development of Eq. (26), each Q_n can be determined since the outflow from (and inflow to) each subreservoir can be described. Thus, in practice, what is needed is to *choose the subreservoirs* for which: (a) there is uniform mixing, and (b) the removal rates can be approximated to be constants. One or the other of these two requirements may be more stringent. Thus, in summary, the practical method for evaluating the overall residence

time in a large reservoir, is to divide the reservoir into subreservoirs small enough so that *both* the conditions (a) and (b) described above, are satisfied. Then use Eq. (41) for those pollutants with first-order removal or Eq. (38) for more complicated removal terms. When each subreservoir is well-mixed, then each Q_n can be determined.

It may be worthwhile to demonstrate details of the determination of each Q_n for the case that each subreservoir is well mixed. For steady-state conditions in each subreservoir, then

$$\frac{Q_n}{P_n + I_n} = \tau_{G,n} = \tau_{D,n} = \frac{Q_n}{R_n + O_n} \quad (44)$$

For first-order removal with constant rate coefficients in each subreservoir, then

$$R_n = \sum_{i=1}^I \lambda_{i,n} Q_n \equiv \sum_{i=1}^I Q_n / \tau_{r,i,n} \quad (45)$$

For uniform mixing ratio in each subreservoir, then, from Eq. (26),

$$O_n / Q_n = \sum_{j=1}^J \tau_{d,j,n}^{-1} + \sum_{k=1}^K \tau_{t,k,n}^{-1} \quad (46)$$

where τ_d^{-1} and τ_t^{-1} are the characteristic dry transfer rates defined in conjunction with Eq. (26). Now, if Eqs. (45) and (46) are substituted into Eq. (44), there results

$$Q_n = (I_n + P_n) \tau_n \quad (47)$$

where

$$\frac{1}{\tau_n} = \sum_{i=1}^I \frac{1}{\tau_{r,i,n}} + \sum_{j=1}^J \frac{1}{\tau_{d,j,n}} + \sum_{k=1}^K \frac{1}{\tau_{t,k,n}} \quad (48)$$

Eq. (47) obviously represents a set of N coupled equations for the N , Q_n 's.

Solving these equations, and substituting the results into Eq. (41) completes the proposed solution for the practical problem with inhomogeneous boundary conditions and inhomogeneous, first-order removal processes.

EXAMPLE: THE TROPOSPHERIC RESIDENCE TIME OF ACCUMULATION-MODE AEROSOL PARTICLES

The aerosol particles considered are those with radii, a , in the range $0.1 \leq a \leq 1 \mu\text{m}$. To illustrate the results in the previous section, the troposphere is considered to be subdivided into two layers: a mixed layer, M , and an F -layer, representing the free troposphere above the mixed layer. The symbol E will represent the earth's surface. For illustrative purposes, the following characteristic heights [cf. Eqs. (23) and (28)] will be assumed: $h(M/E) = 1 \text{ km} = h(M/F)$; $h(F/M) = 10 \text{ km}$. The mixing velocity for air at the M/F interface $v_t(M/F) = v_t(F/M)$ will be taken to be 1 cm/sec . Mixing at the tropopause will be ignored and the dry deposition velocity $v_d(M/E)$ will be taken to be 0.1 cm/sec . For the wet removal time constants, we choose, for illustrative purposes: $\tau_w(M) = 1 \text{ mo} \approx 2.6 \times 10^6 \text{ sec}$ and $\tau_w(F) = 1 \text{ wk} \approx 6 \times 10^5 \text{ sec}$. The additional time constants in Eq. (48) are then calculated to be $\tau_d(M/E) = 10^3 \text{ m} / (10^{-3} \text{ m/s}) = 10^6 \text{ sec}$; $\tau_t(M/F) = 10^3 \text{ m} / (10^{-2} \text{ m/s}) = 10^5 \text{ sec} \approx 30 \text{ hrs}$; $\tau_t(F/M) = 10^4 \text{ m} / (10^{-2} \text{ m/s}) = 10^6 \text{ sec}$.

Although the objective of this example is to calculate the residence time of these particles in the entire troposphere, it is informative to examine the residence time in each subreservoir. From Eq. (48)

$$\frac{1}{\tau(M)} = \frac{1}{\tau_w(M)} + \frac{1}{\tau_d(M/E)} + \frac{1}{\tau_t(M/F)} \quad (49)$$

Substituting the numerical values from the previous paragraph into Eq. (49), and retaining the order for the terms displayed in Eq. (49), yields

$$\frac{1}{\tau(M)} = \frac{1}{2.6 \times 10^6 \text{ s}} + \frac{1}{10^6 \text{ s}} + \frac{1}{10^5 \text{ s}} \Rightarrow \tau(M) \approx 1 \text{ day} \quad (50)$$

The details in Eq. (50) are interesting in that they display that the dominant influence on the particles' residence time in the mixed layer is *not* from dry deposition but from what might be called *dry ascension*; i.e., the ascension of the particles to the free troposphere. If correct, this is an important result. As a minimum, it suggests that much greater effort should be expended, ascertaining realistic values for the mixing velocity at the mixed-layer/free-layer interface.

In a similar manner, the residence time for these particles in the free layer is given by

$$\frac{1}{\tau(F)} = \frac{1}{\tau_w(F)} + \frac{1}{\tau_t(F/M)} + \frac{1}{\tau_t(F/S)} \quad (51)$$

although we will take the troposphere/stratosphere mixing rate, $\tau_t^{-1}(F/S)$, to be negligible. Substituting the numerical values into Eq. (51) yields

$$\frac{1}{\tau(F)} = \frac{1}{6 \times 10^5 \text{ s}} + \frac{1}{10^6 \text{ s}} \Rightarrow \tau(F) \approx 4 \text{ days} \quad (52)$$

It is noted that wet removal appears to be the most important factor determining the residence time, for these particles, in the upper troposphere. Also, it should be noted that if vertical mixing in the upper troposphere

proceeds with a characteristic mixing time $\tau_{M,z} \sim 1$ week, then the condition for uniform mixing, $\tau_{M,z} \ll \tau$ has not been satisfied. In reality, though, the assumption that the F- layer is well mixed may not be so poor as might at first be thought. The reason is because, in reality, the conditions of significant vertical ascent also activates the dominant removal process (i.e., precipitation scavenging). Therefore, the incidents of large intrusions of more polluted air, from the mixed layer, may not result in such nonuniform concentrations as would otherwise occur.

To estimate the residence time for these particles, in the entire troposphere, we apply Eq. (41) with $\tau_0 = \tau_d(T/E)$:

$$\frac{1}{\tau(T)} = \frac{1}{\tau_d(T/E)} + \frac{Q(M)}{Q(T)} \frac{1}{\tau_w(M)} + \frac{Q(F)}{Q(T)} \frac{1}{\tau_w(F)}, \quad (53)$$

where T symbolizes troposphere. In the general case, described earlier, the amount of the pollutant in each subreservoir could be evaluated using Eq. (47), assuming each subreservoir is well mixed. However, to evaluate Q_n from Eq. (47), the production in each reservoir, P_n , is needed. For accumulation mode aerosol particles, though, the P_n are not known: the rate of production appears to depend on a host of gas-to-particle conversion reactions, including homogeneous, heterogeneous and aqueous phase reactions. Therefore, for the present illustration, the following mixing ratios will be assumed: $m(M) \approx 50$ ppb

($\chi(M) \approx 50 \mu\text{g}/\text{m}^3$); $m(F) \approx 5$ ppb. Then $Q(M)/M(T) \approx m(M)M(M)/M(T) \approx 50 \times 10^{-9} \times 0.1 \approx 5 \times 10^{-9}$, $Q(F)/M(T) = 5 \times 10^{-9} \times 0.9 \approx 4.5 \times 10^{-9}$, and $Q(T)/M(T) = 9.5 \times 10^{-9}$.

These assumed mixing ratios allow an estimate for the characteristic height:

$$h(T/E) = \int \chi dV / \int \chi(T/E) dS = [m(M) \int \rho dz_M + m(F) \int \rho dz_F] / [m(M) \rho_0] \approx 2 \text{ km. Then}$$

$$\tau_d(T/E) = h(T/E) / v_d(T/E) \approx 2 \times 10^3 \text{ m} / (10^{-3} \text{ m/s}) \approx 2 \times 10^6 \text{ sec. Substituting}$$

these numerical values into Eq. (53) yields

$$\frac{1}{\tau(T)} = \frac{1}{2 \times 10^6 \text{ s}} + \frac{5}{9.5} \left(\frac{1}{2.6 \times 10^6 \text{ s}} \right) + \frac{4.5}{9.5} \left(\frac{1}{6 \times 10^5 \text{ s}} \right) \quad (54)$$

i.e., $\tau(T) = 6.7 \times 10^5 \text{ s} \approx 1 \text{ week}$. The details in Eq. (54) demonstrate that wet removal of particles from the free troposphere dominates the removal of these particles from the entire troposphere.

Although the calculations in this section were presented mainly to illustrate the method of analysis and do not claim to describe reality too accurately, nevertheless some important general conclusions seem to be permissible:

1. It appears that dry deposition of accumulation-mode aerosol particles is not so important to their residence time in the mixed layer as is the dry ascension of the particles into the free troposphere. More accurate estimates of this ascension velocity should be obtained.
2. Because of this ascension, the (average) residence time of these aerosol particles in the mixed layer is quite short, of the order of 1 day. However, this estimate is for average conditions. Obviously, when there is synoptic-scale subsidence, the ascension velocity essentially vanishes, and the residence time in the lowest layer of the atmosphere increases to a value dictated by the dry deposition velocity.
3. If the total mass of accumulation mode aerosol particles is about the same in the mixed layer as in the free-layer, aloft, i.e., $\chi(M) \approx 10 \chi(F)$, then the residence time of these particles in the troposphere is approximately equal to the wet removal time for scavenging from aloft, i.e., $\sim 1 \text{ week}$ during winter months and $\sim 2 \text{ weeks}$ during the summer.

The final point we wish to make about this example is that it illustrates

another difficulty yet to be overcome. Namely, to calculate $\tau(T)$, it was necessary to assume $Q(M)$ and $Q(F)$ because the production rates were unknown.

SOME COMMENTS ABOUT CO_2

As a final illustration, consider CO_2 . The first reservoir to be considered will be the entire atmosphere. At the outset, this reservoir will be assumed to be well mixed. The adequacy of this assumption can be checked after τ is calculated; for a uniform mixing ratio, it is required that $\tau \gg \tau_{M,i}$. For the case under consideration, Eq. (48) simplifies to

$$\frac{1}{\tau} = \frac{1}{\tau_w} + \frac{1}{\tau_{ch}} + \frac{1}{\tau_d(A/O)} + \frac{1}{\tau_d(A/B)} \quad (55)$$

in which we have already assumed that dominant dry deposition is from the atmosphere to the oceans, $\tau_d(A/O)$, and to the biosphere, $\tau_d(A/B)$.

Actually, there are many complicating features of the CO_2 residence time problem (e.g., see Junge, 1963; Machta, 1971; Woodwell, 1978). Here, to simplify the analysis, we propose to ignore interactions of CO_2 with the biosphere. This interaction creates the familiar annual cycle in measured values of the CO_2 concentration in the troposphere. Chemical transformations of CO_2 in the atmosphere are negligible (Junge, 1963). Finally, although CO_2 does dissolve in rain water, it can be seen that wet removal's contribution to CO_2 's residence time in the atmosphere is negligible (e.g., see Slinn *et al.*, 1978). With these assumptions and approximations, then Eq. (55) yields the simple result

$$\tau \approx \tau_d(A/O) = h(A/O) / v_d(A/O) = H / v_d(A/O) \quad (56)$$

where H is the scale height for the atmosphere which we will take to be 10 km; cf., Eq. (29).

Earlier in this report, it was frequently repeated that O was the *total* outflow of the trace constituent from the reservoir, not the *net* outflow. Consequently, the corresponding deposition velocity in Eq. (56) should not contain any inflow *from* the oceans *to* the atmosphere. From various methods, it can be estimated that $v_d \approx 1$ cm/sec (e.g., see Slinn *et al.*, 1978). Consequently, from Eq. (56), the residence time of CO_2 in the entire atmosphere

$$\tau \approx 10^4 \text{ m} / (10^{-2} \text{ m/s}) \approx 10 \text{ days} . \quad (57)$$

It is noted that this result is drastically different from the familiar result that the residence time of CO_2 "in the atmosphere" is 1-10 years (e.g., see Slinn, 1978); nevertheless the essence of Eq. (57) is correct.

To improve on the estimate for CO_2 's lifetime in the atmosphere, it is noted that it may be incorrect to assume that the entire atmosphere is well mixed since the answer yields $\tau \ll \tau_{M,i}$. It is true that the *majority* of the CO_2 is well-mixed in the atmosphere, but the *majority* of the CO_2 has had eons to reach equilibrium in the various geospheres. To improve the basis of the result given by Eq. (57), we take the reservoir, instead, to be the troposphere. Then, with the same assumptions as before, including $h = 10$ km, and assuming transfer to the stratosphere is relatively slow, there results $\tau \approx 10$ days, in the troposphere. This residence time is approximately the same as the time for vertical mixing in the troposphere. Thus, there appears to be little point in belaboring the question of adequate mixing; it will not reveal the main source of the discrepancy between the result given by Eq. (57)

and the usual result that CO_2 's residence time "in the atmosphere" is 1-10 years.

The source of the discrepancy is, of course, that most authors use the *net* outflow of CO_2 to the oceans, rather than the *total* outflow. The net outflow is very small: almost as much CO_2 is resuspended from the oceans as is deposited on the oceans (e.g., see Slinn *et al.*, 1978). However, in reality, the residence time of CO_2 in the troposphere is nearer 10 days than 1 - 10 years. That is, the average time required for an individual CO_2 molecule to leave the troposphere and enter the oceans is about 10 days. That the molecule subsequently re-enters the atmosphere is a separate matter, of interest if it is desired to know CO_2 's residence time in the oceans. Of course, the value for the oceanic residence time of CO_2 depends on the size of the oceanic reservoir chosen; this follows because $\tau = Q/R$ depends on Q .

To reconcile the differences displayed in the previous paragraphs, it is useful to consider the residence time of CO_2 in other geospheres. These considerations will be quite crude. They are presented not so much to contribute to solving some of the important questions about atmospheric CO_2 , as to illustrate the importance of proper choices for the reservoirs. For simplicity, we shall continue to ignore the biosphere. The following choices of reservoirs are considered:

(a) Carbon Dioxide in the Troposphere

This is the case considered already; the result for the residence time is $\tau = 10$ days.

(b) Carbon Dioxide in the Mixed Layer of the Oceans

The concentration of dissolved CO_2 in the oceans is quite small: $C = \alpha x$ where $\alpha = 1$ is the solubility coefficient. If the top ~100 m of the oceans were chosen as the CO_2 reservoir, then it would be seen that transfer across

the thermocline, to the deep oceans, is negligible compared with CO₂ resuspension into the atmosphere. The resuspension velocity is about 1 cm/sec, essentially the same as the velocity of CO₂ deposition from the atmosphere to the oceans. Then, ignoring chemical transformation of CO₂ in the mixed layer of the oceans, a first estimate of CO₂'s residence time in this reservoir is: $100 \text{ m} / (1 \text{ cm/sec}) \approx 3 \text{ hours}$. This result demonstrates a poor choice for a reservoir: the mixing time in the mixed layer of the oceans, $\tau_{M,z} \gg 3 \text{ hours}$. Consequently, different reservoirs should be considered.

(c) CO₂ in the Atmosphere Plus the Oceans' Viscous Sublayer

The depth of the viscous sublayer of the oceans, just below the air/sea interface, is about 1 cm. Therefore, there is negligible CO₂ in this sublayer compared to the amount of CO₂ in the atmosphere. The transfer velocity past the sublayer, deeper into the mixed layer, is about 10^{-2} cm/sec (e.g., see Slinn *et al.*, 1978). Consequently, the residence time for CO₂ in this coupled reservoir is about $10 \text{ km} / (10^{-2} \text{ cm/sec}) \approx 1 - 10 \text{ years}$. However, mixing into the stratosphere does not occur on a time scale short compared with 1 - 10 years and therefore this case again illustrates a poor choice for a reservoir.

(d) CO₂ in the Troposphere Plus the Oceans' Viscous Sublayer

For this choice, an estimate for transport into the stratosphere is also needed. This estimate can be determined as in the case for halogenated hydrocarbons described earlier in this report. However, in the present example, mixing throughout the entire stratosphere ($\sim 40 \text{ km}$) is needed. Therefore, $\tau_t(T/S) \sim 10 \text{ years}$. With this estimate and the estimate in the previous paragraph for the transfer rate to the rest of the oceans' mixed layer, then there results the estimate for CO₂ residence time in this reservoir: 1 - 10 years. On this time scale, the troposphere can be considered to be well mixed.

It is this reservoir, the troposphere plus the oceans' viscous sublayer, that presumably is meant when it is stated that the residence time of CO_2 "in the atmosphere" is 1 - 10 years.

As stated earlier, the purpose of these examples was not to contribute to solving important problems about atmospheric CO_2 , but to illustrate the importance of proper choices for the reservoirs. However, these examples do provide an opportunity to suggest a possible solution to one of the current questions about atmospheric CO_2 . In his recent article, Woodwell (1978) states:

If the biota has not been a sink for atmospheric carbon dioxide, and if the absorption of CO_2 by the oceans of the world is no greater than we have thought, then the amount of CO_2 in the atmosphere should be increasing even faster than the observations show. Obviously the estimates are wrong. But where does the error lie?

Based on the cases just considered, the first question that arises is: what is meant by "in the atmosphere"? Presumably it means "in the troposphere" since this is where (all?) the CO_2 measurements have been taken. Further, in the case of CO_2 in the troposphere plus the viscous sublayer of the oceans, it should be appreciated that the stratosphere will act as a sink of CO_2 for about 50 years ($\tau_{M,z} \approx (40 \text{ km})^2 / (1 \text{ m}^2/\text{s}) \approx 50 \text{ years}$) until the mixing ratio becomes uniform throughout the atmosphere. That is, with every anthropogenic increment of CO_2 , then during the first ~ 10 - 100 years, the stratosphere acts as a sink for a quarter of the increment. The factor of 1/4 follows from the relative masses of air in the stratosphere and troposphere. Whether or not this outflow of CO_2 is sufficient to make up for the "missing CO_2 " may be examined in a later report.

To test the hypothesis that some of the missing CO_2 is still mixing into the stratosphere, it would be useful to measure CO_2 concentrations in the stratosphere, up to heights of about 40 km. Such measurements could also yield useful information about stratospheric mixing if the data could reveal

the height to which annual CO_2 concentration variations penetrate into the stratosphere. Certainly, obtaining information about K_z is important; for example, the estimate $\tau_{M,z} \approx 50$ years depends directly on the assumed value for K_z ($= 1 \text{ m}^2/\text{sec}$). This value for K_z is only an order-of-magnitude estimate.

CLOSING COMMENTS

The objective of this report has been to formulate methods for improving estimates of the residence times for atmospheric trace constituents. To improve these estimates, the essential first step is the careful choice of reservoirs.

For the practical evaluation of a pollutant's residence time in a reservoir, the first feature required of the reservoir is that approximately steady-state conditions prevail; i.e., $\tau_G = \tau_D \ll \sigma$. Only for steady-state conditions is the residence time defined. To evaluate the residence time via

$$\frac{1}{\tau} = \frac{1}{\tau_D} = \frac{R}{Q} + \frac{O}{Q} \equiv \frac{1}{\tau_R} + \frac{1}{\tau_O}$$

it is necessary to evaluate both the removal rate, τ_R^{-1} , and the outflow rate, τ_O^{-1} .

To evaluate the outflow rate, the second feature required of the reservoir is that the pollutant's concentration (or mixing ratio) be known both at the reservoir's boundaries and within the reservoir. Thus, as in Eq. (26),

$$\frac{1}{\tau_O} = \sum_{j=1}^J \frac{1}{\tau_{d,j}} + \sum_{k=1}^K \frac{1}{\tau_{t,k}}$$

where $\tau_{d,j} = h_j/v_{d,j}$ and $\tau_{t,k} = h_k/v_{t,k}$ and the scale heights h are given by

$$h = \int \chi dV / \int \chi dS .$$

The practical method to meet the requirement that χ be known is to choose the reservoir so that the mixing ratio is constant throughout the reservoir or constant in various subreservoirs. This requires that the mixing time in the reservoir or subreservoir, $\tau_{M,i}$ be short compared with the appropriate residence time. In either case, it is essential, too, that the total outflow (and inflow) be used in the formulation, not the net outflow.

To evaluate the removal rate, τ_R^{-1} , in the important practical case that removal processes depend on location within the reservoir, it is necessary to divide the original reservoir into subreservoirs, small enough so that the removal processes can be treated as constants in each. Then the residence time for the original reservoir is given by

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \sum_{n=1}^N \frac{Q_n}{Q} \frac{1}{\tau_{R,n}}$$

where $\tau_{R,n}^{-1}$ is the removal rate for the n'th subreservoir but τ_0 is the outflow from the original, large reservoir.

A simple but important case that has been considered in this report is when the loss rate per unit volume, L , is first order in the pollutant's concentration, i.e., $L = \sum \tau_{R,i}^{-1} \chi$. In this case, and for uniform mixing in each subreservoir, then Q_n in each subreservoir can be determined from the coupled set of equations

$$Q_n = (I_n + P_n) \tau_n$$

where

$$\frac{1}{\tau_n} = \sum_{i=1}^I \frac{1}{\tau_{r,i,n}} + \sum_{j=1}^J \frac{1}{\tau_{d,j,n}} + \sum_{k=1}^K \frac{1}{\tau_{t,k,n}} .$$

However, although the mass inflow to the n'th subreservoir is just the sum of the outflows from neighboring reservoirs, solving for Q_n requires that the

production in each subreservoir, P_n , be known.

When the reservoir and subreservoirs have been chosen to satisfy all the features described above, then improvements in estimates for the residence time rely on improved description of the various rates contained in the formalism. When seeking these improvements, it is most important to focus attention on the fastest rates. For example, for improving estimates of the residence time of tropospheric aerosol particles, it appears to be more important to improve estimates for the transfer velocity at the top of the mixed layer (i.e., what we have called the dry ascension velocity) than to improve estimates for the dry deposition velocity. For the case of aerosol particles in the troposphere, it is also important to improve estimates for the production rate, P_n , and/or Q_n .

In this report, a number of illustrative examples have been considered. One example was for CO_2 . It was shown that the residence time of CO_2 in the troposphere, alone, is about 10 days. The residence time for CO_2 in a combined reservoir that includes both the troposphere and the viscous sublayer of the oceans, may be in the range 1 - 10 years. It was also suggested that the "case of the missing CO_2 " may be solved by recognizing that about 1/4 of the anthropogenic CO_2 released during the past 50 years may still be mixing into the stratosphere. In a subsequent report (Slinn, 1979), the general analysis will be developed further and applied to the dramatically inhomogeneous $\text{SO}_2/\text{SO}_4^-$ problem.

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NOTATION

The following is a list of frequently used symbols, subscripts, and special notation. The dimensions M, L and T represent mass, length, and time, respectively. Sometimes it is more convenient to use dimensions other than mass to characterize the amount of an atmospheric trace constituent (e.g., number of particles, or disintegrations per minute for radioactivity) but, for simplicity, the symbol M will be used. Also, although a more appropriate term is (atmospheric) trace constituent, the word pollution will be used. The list of symbols follows.

a = particle radius (L)

A = magnitude of the mass flux of air ($ML^{-2}T^{-1}$)

\vec{F} = pollutant flux ($ML^{-2}T^{-1}$)

G = volumetric gain rate ($ML^{-3}T^{-1}$)

h = $\int \chi dV / \int \chi dS$, characteristic height scale (L)

I = total, mass inflow rate (MT^{-1})

K_z = vertical diffusivity (L^2T^{-1})

L = volumetric loss rate ($ML^{-3}T^{-1}$)

L_z = characteristic length in the vertical direction (L)

m = χ/ρ = mass mixing ratio (dimensionless)

M = total mass of air in the reservoir (M)

\hat{n} = unit outward normal vector (dimensionless)

O = total mass outflow rate (MT^{-1})

P = $\int G dV$ = mass production rate (MT^{-1})

Q = $\int \chi dV$ = total pollutant mass in the reservoir (M)

R = $\int L dV$ = mass removal rate (MT^{-1})

v_d = generalized, dry deposition velocity, i.e., transfer velocity at interfaces between the reservoir and other geospheres or the biosphere (LT^{-1})

v_t = transfer velocity at interfaces between the reservoir and other portions of the atmosphere (LT^{-1})

$\lambda = \tau_r^{-1}$ = first order removal rate coefficient (T^{-1})

ρ = mass density for air (ML^{-3})

$\sigma^{-1} = \tau_G^{-1} - \tau_D^{-1}$ = net growth rate (T^{-1})

$\tau = \tau_G = \tau_D$ = residence time (T)

$\tau_D^{-1} = (R + O)/Q \equiv \tau_R^{-1} + \tau_O^{-1}$ = decay rate (T^{-1})

$\tau_G^{-1} = (P + I)/Q \equiv \tau_P^{-1} + \tau_I^{-1}$ = growth rate (T^{-1})

$\tau_I^{-1} = I/Q$ = inflow rate (T^{-1})

$\tau_O^{-1} = O/Q$ = outflow rate (T^{-1})

$\tau_P^{-1} = P/Q$ = production rate (T^{-1})

$\tau_r^{-1} = \lambda$ = first order removal rate coefficient (T^{-1})

$\tau_R^{-1} = R/Q$ = removal rate (T^{-1})

τ_w^{-1} = wet removal rate (T^{-1})

τ_{ch}^{-1} = chemical transformation rate (T^{-1})

τ_{ph}^{-1} = physical transformation rate (T^{-1})

$\tau_{M,i}^{-1} = (\tau_{M,x}^{-1}, \tau_{M,y}^{-1}, \tau_{M,z}^{-1})$ = mixing rates (T^{-1})

x = pollutant concentration (ML^{-3})

Subscripts

d - dry

i - generally refers to I, different, first order removal rate coefficients

j - index for the J interfaces between the reservoir and other geospheres of the biosphere

k - index for the K interfaces between the reservoir and other portions of the atmosphere

n - index for the N subreservoirs

o - generally signifies that the subscripted variable is constant

r - removal

t - transfer

Other Notation

For further distinction of the various rates, notation such as $\tau_t(A/B)$ has been used. The letters in the parentheses are abbreviations as follows.

A = Atmosphere or Aloft layer

B = Biosphere or Boundary layer

C = Constant flux layer

E = Earth's surface

F = Free layer

M = Mixed layer

O = Ocean

S = Stratosphere

T = Troposphere or Total

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