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Title: Estimates for Wet and Dry Removals' Contribution to the Residence Time for Atmospheric Pollutants in the Eastern United States

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The length of time that atmospheric pollutants released from low-level sources in the midwestern United States can expect to remain in the atmosphere is discussed. The pollution is assumed to be removed from the atmosphere by dry deposition and precipitation scavenging. Layer-average trajectories originating from Kansas City, Missouri are used to determine the Lagrangian probability of dry and wet conditions. The residence time of these pollutants is estimated based on parameterizations for the effective scavenging rates during wet and dry conditions.

This investigation shows that, in summer, the probability that precipitation is being experienced by the pollutant is twice as great as the probability of precipitation at the origin of the pollution; this same ratio of probabilities is three in winter. Therefore, when precipitation scavenging is the more important removal mechanism, the statistics for the length of wet and dry periods at the source region overestimate the residence time by a factor of about two to three.

By taking into consideration the Lagrangian probability of wet and dry periods, the relative importance of dry deposition and precipitation

scavenging is discussed as a function of the wet and dry removal rates. It is seen that for a time- and vertical-average dry deposition velocity as large as 1 cm/sec, then dry deposition would normally be the more important removal process for the meteorological conditions in the mid-west to eastern United States.

Estimates for the expected atmospheric lifetimes of aerosol particles and trace gases are reported as functions of dry deposition velocities and collection efficiencies (or washout ratios). For example, lead particles of mass mean diameter ~0.5 μm, should have a residence time ~8 days in winter, and ~3 days in summer, based on available data for the dry deposition velocity and washout ratio. In general, the residence time can be expected to be about twice as long during the summer season than the winter.

The winter, monthly average distribution of pollutant mass is shown, based on the steady-state Gaussian approximation solution of the convective diffusion equation. The calculations are based on a statistical analysis of the 12 hourly positions of a series of trajectories. Thus, monthly average "diffusion" and removal are incorporated into the Gaussian model.

Estimates for Wet and Dry Removals' Contribution to the Residence Time for Atmospheric Pollutants in the Eastern United States

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I. INTRODUCTION

Aerosol particles and trace gases released into the atmosphere are eventually removed by natural cleansing processes. The major cleansing processes are precipitation scavenging, dry deposition, and physical-chemical transformations. Precipitation scavenging can be the result of many processes; e.g., the result of the material acting as condensation nuclei, attaching to cloud droplets by Brownian motion, transferring to droplets by the water vapor gradient or electrical field gradient, collecting of the material by falling raindrops, etc. Dry deposition refers to transfer of particles or gases to surfaces, and uptake of the material by surface elements. Physical-chemical transformations "remove" species by altering chemical compositions and physical characteristics. Meteorological conditions, and specific species properties, will determine how these individual mechanisms play a role in affecting overall residence times in the atmosphere.

This report investigates certain aspects of the influence of meteorological conditions on the relative contributions of wet and dry removal to the residence times of atmospheric pollutants. The purpose is to present improved estimates of the residence time for pollutants routinely released into the atmosphere. The method involves applying a probability model developed by Rodhe and Grandell (1972) to the Lagrangian frequency of wet and dry periods.

During the past twenty years a substantial amount of research has been directed towards determining residence times for various atmospheric

trace constituents. Several reports of interest are referenced in the bibliography. In the next section, a general review will be made of some relevant studies, as well as a more in-depth review of studies by Junge and Gustafson (1957), and Scriver and Fisher (1975). Following this review, the probability model reported by Rodhe and Grandell (1972) is presented. Following these reviews, a section describes the method used herein to apply Rodhe and Grandell's model to the eastern United States. After a brief review of available parameterizations used in describing precipitation scavenging and dry deposition, results are presented for the residence time if only dry deposition or precipitation scavenging are acting alone, and then for both processes acting together. In the conclusion, the present results for estimates of atmospheric residence times are summarized.

Appendix A demonstrates how the residence time is used in the time-averaged convective diffusion equation governing the concentration in air of trace contaminants. Appendix B shows a steady state distribution of pollutant mass released from Kansas City, Missouri based on the Gaussian approximation to describe the dispersion, and a time and space averaged removal rate; i.e., the inverse of the residence time.

II. REVIEW OF LITERATURE

A. General Review

There have been numerous studies concerned with tropospheric residence times of various species. Table 1, reprinted from Slinn (1978a), contains some estimates of these residence times. A great deal of work, particularly in Europe, has been recently devoted to determining the fate of sulfur dioxide in the atmosphere. We will now summarize some of these studies.

Scriven and Fisher (1975), using a method to be described in section IIC, estimated the residence time of sulfur dioxide to be around one day when no precipitation was occurring, and two hours in a moderate rain. Precipitation scavenging was parameterized in terms of the fraction removed per unit time, Λ. As suggested by Chamberlain (1960), this fraction was assumed to be

$$\Lambda = 10^{-4}\ s^{-1}\ [I_o/1\ mm\ hr^{-1}]^{1/2}$$

where I_o is the rainfall rate (in mm hr^{-1}).

Rodhe and Grandell (1972) estimated the turnover time caused by precipitation scavenging to be around six days in summer and two days in winter for aerosol particles. They used the model described in section III, but with the precipitation statistics evaluated at one Swedish station. Rodhe and Grandell's effective scavenging coefficient was .4 hr^{-1} and .25 hr^{-1} in summer and winter, respectively.

Henmi, Reiter, and Edson (1977) predicted the residence time of sulfur dioxide over the eastern United States to be one day in winter

Table 1. Estimates for average tropospheric residence times, reprinted from Slinn 1978a.

MATERIAL	VINYL CHLORIDE CH_3I	SO_2	0.1-1.0 μm PARTICLES (e.g. $SO_4^=$) and H_2O	DDT	HT PCB's	CH_4 CCl_3F	CO_2 N_2O	^{85}Kr	O_2
RESIDENCE TIME	~hrs	~1 d	~1 wk	~3 mo	~1 yr	1-10 yrs	~10 yrs	~10 yrs	~10^4 yrs

and 1.5 days in summer. The sulfur dioxide was assumed to be removed by dry deposition, precipitation scavenging, and chemical-physical transformation. The method of these authors was equivalent to the model proposed by Rodhe and Grandell, with the transformation rate added. The precipitation scavenging was parameterized in terms of a washout ratio, (assumed to be 5×10^4), a mean mixed layer height, and a mean precipitation rate. The fraction removed per unit time by dry deposition was assumed to be v_d/H, where the dry deposition velocity, v_d, is equal to 1 cm/s, and H is the mean mixed layer height.

Eliassen and Saltbones (1975) estimated the residence time of sulfur dioxide to be around 0.5 days in western Europe. The method involved a simple trajectory model with decay, caused by wet and dry removal processes, and transformation to particulate sulfate. The best fit of the model to observed air concentrations resulted in estimates for the decay and transformation rates. The results assume the source strength of SO_2 is known over the majority of western Europe.

In Slinn's (1978a) report, the atmospheric residence time, τ, is defined by integration of the time-average convective diffusion equation over a space volume. The result is

$$\frac{1}{\tau} \equiv -\frac{1}{q}\frac{\partial q}{\partial t} = \frac{1}{\tau_d} + \frac{1}{\tau_w} + \frac{1}{\tau_c} + \frac{1}{\tau_p}$$

where q is the total mass of pollutant, and τ_d, τ_w, τ_c, and τ_p are separate contributions to the overall residence time from dry, wet, chemical, and physical removal processes, respectively. This report by Slinn reviews many of the theoretical and experimental studies done to

determine the contribution to the residence time from wet removal. The work by Slinn (1978b) considers the assumptions and limitations of using a residence time to describe time and space average removal of pollutants. Estimates for the lifetimes of various atmospheric pollutants are presented, and the importance of determining the rate limiting removal process for a particular pollutant is described. The "well-mixed," and "steady-state" assumptions, are reviewed to assess their accuracy in various reservoirs.

In summary, even for sulfur dioxide for which the removal and transformation rates have been extensively studied, there remains considerable disagreement as to average lifetimes for pollutants in the atmosphere. In different regions with different climatologies, the relative importance of precipitation scavenging and dry deposition will vary, thus we cannot expect the residence time to be the same. Because of the highly variable rates of removal and atmospheric conditions over short time periods, it appears the best we can do is to present reasonable limits for the residence on an average basis.

B. Junge and Gustafson's Study

In Junge and Gustafson's (1957) pioneering work, a conceptual model to describe the precipitation scavenging of sea salt aerosol was developed. By estimating the daily fraction of material removed by in-cloud and below-cloud scavenging, they obtained the halflife of the material as a function of several variables. The model assumes a series of independent precipitation events with complete tropospheric mixing of the aerosol between each event.

The fraction of material removed via in-cloud processes is deduced in the following manner. Consider a vertical column of cross-sectional area A, which contains precipitating cloud elements. A conservation equation is written that relates the amount of water coming out of the clouds to the amount of condensed water that is present. Their model is deficient in that it suggests that clouds are static, rather than dynamic, and that the clouds occupy a fixed volume of space, removing particulates from within. With these assumptions, the authors' conservation equation is

$$\rho_w RA = LhA \tag{1}$$

where ρ_w is the density of water, R the average daily rainfall, A the cross-sectional area, h the thickness of the cloud layer, and L is the liquid water content of the cloud. Thus the "equivalent thickness" of cloud from which rain falls and aerosol particles can be removed is

$$h = \frac{\rho_w R}{L} \tag{2}$$

This equivalent thickness is used to define a volume fraction of the troposphere that is cleansed by precipitation:

$$\alpha = \frac{R\varepsilon}{LH} \tag{3}$$

where H is the depth of the troposphere, and where it is assumed that the cloud removes its water at 100% efficiency, but that the aerosol particles are removed with an efficiency $\varepsilon < 1$. By considering the

rainfall to occur in n independent events, interrupted by complete tropospheric mixing, then as n becomes large, the fraction of the aerosol removed becomes

$$a = 1 - e^{-\overline{\alpha}} \tag{4}$$

where $\overline{\alpha}$ represents an average of the meteorological variables over these storm events.

Junge and Gustafson also model removal from below cloud base. They propose that the daily fraction removed by this process is a function of the below-cloud volume fraction of the troposphere, the frequency of rainy days, and the collection efficiency. This fraction is

$$b = \frac{H_{CB}}{H} f\gamma \tag{5}$$

where H_{CB} is the cloud base height, f the frequency of days with rain, and γ the collection efficiency. Consequently, the daily total fraction removed by precipitation scavenging is c = a + b. Subjecting the aerosol to m consecutive days of scavenging, the fraction remaining on the mth day is

$$d = (1 - c)^m \quad . \tag{6}$$

This equation can be used to calculate the half life. Representative values are shown in Figure 1. For the case shown; $\varepsilon = 1$, $\gamma = 1$, $H = 10$ km, $H_{CB} = 2$ km, $f = .26$, and $L = 1.5$, 2.0, and 3.0 g/m^3.

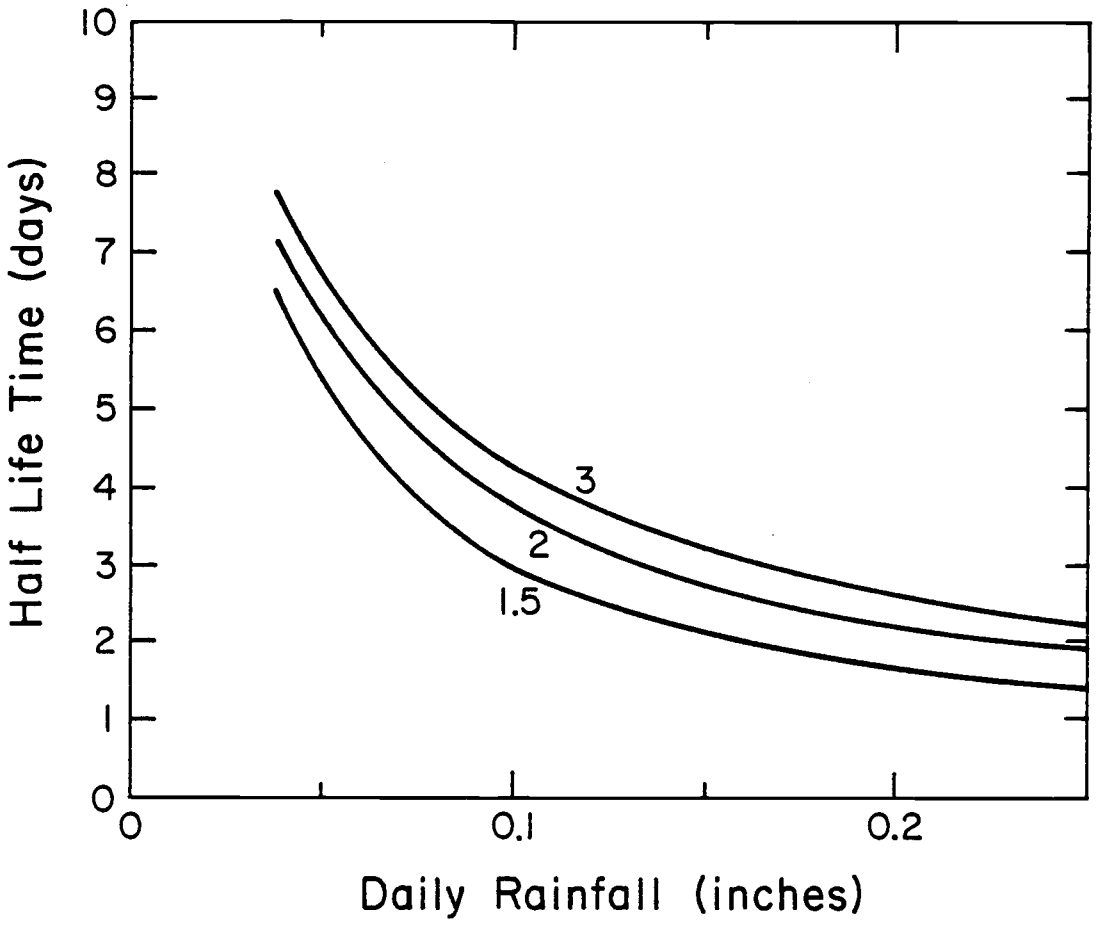

Figure 1. The half-life of sea salt aerosol as a function of daily rainfall at three values of the cloud liquid water content [g/m^3] (reprinted from Junge and Gustafson 1957).

C. Scriven and Fisher's Model

Scriven and Fisher's report (1975), investigates the e-fold travel distance by considering a steady state reservoir model. The mass conservation equation, when the concentration of the species is assumed constant in the crosswind and vertical, is

$$\bar{u}h \frac{dC}{dx} = -F \tag{7}$$

where F is the removal flux, C the concentration in air, $\bar{u}$ the wind speed, h the height of the reservoir, and x the downwind direction. Scriven and Fisher parameterize the flux in the following manner;

$$F = [v_d + h\lambda f]\ C$$

where v_d is the dry deposition velocity, λ is the fraction removed per unit time because of scavenging, and f is the fraction of distance over which rain is falling at a rate implicit in λ. Assuming v_d, h, λ, and f are downwind averaged values, the expression for the concentration integrates to

$$C(x) = C_o \exp\left(-\frac{(v_d + h\lambda f)}{h} \frac{x}{\bar{u}}\right) \quad . \tag{8}$$

Consequently, according to these authors, the residence time is given by

$$\tau = h/(v_d + h\lambda f) \quad . \tag{9}$$

For example, if h ~ 1 km, v_d ~ 1 cm/s, $\lambda \sim 10^{-4}\ s^{-1}$ and f = 1, then the residence time is three hours. If it is not raining during the

travel time, then $\tau \sim 1$ day, which corresponds to a travel distance of 400-800 km. This result suggests that wet removal is roughly an order of magnitude more effective than dry removal when it is raining. Thus, according to these authors' results, wet and dry processes will contribute to τ equally if it is raining for approximately ten percent of the travel time.

Their report also investigates the effect of allowing the vertical eddy diffusivity to be finite. The result is that the residence time caused by dry deposition is increased because it takes time for the pollutant to reach the surface. If the pollutant is released at an effective height s, the residence time when no precipitation is falling is

$$\tau = \frac{h}{v_d} + \frac{sh}{K} - \frac{s^2}{2K} \qquad (10)$$

where K is the eddy diffusivity. For $s \sim 100$ m and $K \sim 5$ m^2/s, the dry removal residence time is approximately 1.2 days, or an increase of 20 percent over the case of an infinite vertical eddy diffusivity. Even for species with an infinite dry deposition velocity, the residence time remains nonzero since K is finite.

Scriven and Fisher also investigated the consequences of allowing the diffusivity to vary with height. In particular, K was taken to be a constant K_o at the height of the roughness elements z_o, then to increase linearly throughout the surface layer up to a height z_1, and then a

constant K_1 above the surface layer. They introduced an effective deposition velocity, v_d^*, such that

$$\frac{1}{v_d^*} = \frac{1}{v_d} + \frac{z_1}{K_1} \ln(z_1/z_o) \quad . \tag{11}$$

For purely mechanical turbulence, in which case $K(z) = ku_*z$ and $u(z) = (u_*/k) \ln(z/z_o)$, where u_* is the friction velocity and k the Kármán constant, the expression becomes

$$\frac{1}{v_d^*} = \frac{1}{v_d} + \frac{u(z_1)}{u_*^2} \quad . \tag{12}$$

Thus the effective resistance to dry removal is the sum of the resistance to uptake of the material by the surface elements and resistance to transfer through the surface layer. Letting $z_1 \sim 100$ m, $z_o \sim .1$ m, and $u(z_1) = 5$ m/s, then $u_* = 30$ cm/s. For the often quoted value of $v_d = 1$ cm/s for sulfur dioxide, most of the resistance is accounted for by the uptake of SO_2 by surface elements. Since 1 cm/s is a large dry deposition velocity for the majority of atmospheric pollutants of anthropogenic origin, in most cases the dry removal process is rate limited by the interaction of the pollutant with the surface, not by the transfer through the surface layer. The upper limit for the effective deposition velocity (i.e., for negligible surface resistance), is roughly 2 cm/s for average meteorological conditions (i.e., average u_* and $\bar{u}$).

D. Summary

This section will discuss some of the limitations of the reviewed works. Junge and Gustafson's model assumes the aerosol is well mixed

throughout the troposphere. This appears reasonable for a large source such as the oceans, but not for a point or small area anthropogenic source of aerosol. The model also assumes the aerosol is exposed to a series of days with the average daily rainfall assumed to occur each day. This is misleading since, in their model, a fraction of the aerosol will be scavenged every day whether it actually rained or not. Also, the model as it stands provides no information on the distribution of the residence time. The values which are in Figure 1 may represent mean values, but they may occur only a small fraction of the time.

Scriven and Fisher's model contains two variables that present problems: the height of the reservoir, h, and the fraction of distance over which precipitation occurs, f. The height of the reservoir in which the material is assumed well mixed will be different in wet and dry conditions; in fact, the well mixed assumption can be expected to be quite poor during a storm. The assumption of a lid on the mixing, thus confining the pollutant to a layer ~1 km, is reasonable during sustained dry conditions; thus, parameterizing dry deposition in terms of h is reasonable. However, during precipitation periods when well organized updrafts and downdrafts may exist, it is highly unlikely the concentration will be uniform with height. Even if the pollutant were well mixed, the level up to which the pollutant would be dispersed would not be the mixed layer height, but rather the cloud layer height. In this case we should write the flux caused by scavenging, F_w, as $F_w = h_w \lambda f C$, where $h_w \neq h$.

When we are dealing with reservoir models in which the well mixed assumption is critical, we must be sure a well mixed argument is reasonable.

For the case of vertical mixing governed by an average diffusivity, K_z, it is required (Slinn 1978b) that

$$\frac{L_z^2}{K_z} = \tau_{Mz} << (\tau_{dry}, \tau_{wet}) = \left(\frac{L_z}{v_d}, \frac{L_z}{v_w}\right) \tag{13}$$

where L_z is a characteristic vertical length scale and τ_{dry} and τ_{wet} are average dry and wet removal time scales, respectively. Thus, the characteristic time for the mixing must be less than the times which create nonuniformities by wet and dry removal. By putting reasonable values into the above it is seen that for dry deposition, the well mixed assumption is reasonable under certain conditions, but wet removal proceeds at a rate so much faster than the mixing that we cannot assume well mixed during precipitation.

Another problem with Scriven and Fisher's model is f, the fraction of distance over which rain is falling. The expression for the e-fold travel distance contains f, which is a function of the travel distance itself; therefore, determining appropriate values for f becomes somewhat ambiguous. Also, similar to the aerosol scavenging model of Junge and Gustafson, this model provides no clues as to the distribution of the residence time as a result of the probability of various meteorological conditions.

In view of these difficulties, a model which explicitly examines the distribution of dry and wet periods is desired. Assuming we can adequately parameterize the scavenging rates during dry and wet periods, such a model will give us the distribution of the tropospheric residence time. Because of the highly random nature of atmospheric conditions, it is only reasonable to treat the residence time as a random variable and proceed accordingly.

III. STATISTICAL METHOD

A. Introduction

We now consider a method to estimate lifetimes in the atmosphere based on the exponential failure law of probability; for example see Gaver (1963). In our case, the time to failure is the time until removal. If a species is released into the atmosphere at time zero, and in subsequent time intervals $(t, t + \Delta)$ experiences a probability $\lambda\Delta$ of being removed, then the probability the species survives t time units in the atmosphere is $P(t) = \exp(-\lambda t)$, as Δ is made small. This assumes that λ is independent of previous history and absolute time. If we now let the removal rate be a function of exposure time (see Rodhe and Grandell 1972)

$$\lambda(t) = \left\{ \begin{array}{l} \lambda_d \text{ if dry at time } t \\ \lambda_w \text{ if wet at time } t \end{array} \right\} \tag{14}$$

then

$$P(t) = E\left[\exp\left(-\int_o^t \lambda(\tau)d\tau\right)\right] \tag{15}$$

provided that $\lambda(t)$ can be represented as a Markov process with stationary transition probabilities. In Equation 15, E[ ] denotes the expected value. The scavenging coefficient λ is defined by

$$\lambda = \lim_{\Delta \to o} \frac{\text{Probability of removal during time interval } \Delta}{\Delta} \tag{16}$$

By determining the transition probabilities of $\lambda(t)$, and estimating the values of λ_d and λ_w, the model may be used to estimate the expected residence time as well as the distribution function of the residence time.

Rodhe and Grandell (1972) first used this exponential distribution assumption and applied their predictive equations to the precipitation record at a Swedish station. Gaver (1963) presented the same basic model but with an entirely different development.

B. Markov Assumption

The assumption that $\lambda(t)$ obeys a Markov process means that $\lambda(t + \Delta)$ is independent of $\lambda(t - \Delta)$, where $\Delta > 0$. The validity of this assumption obviously depends on the value of Δ, which is a measure of the time required between our definition of past and future such that the future is independent of the past. In our case, the scavenging coefficient, λ, is a function of whether it is raining or not, so our assumption is that we can describe sequences of wet and dry periods using a Markov chain probability model. A few studies relevant to this question will now be discussed.

Gabriel and Neumann (1962) observed sequences of wet and dry days at Tel Aviv, and compared these to those predicted by a Markov chain model. The study, which included 27 different seasons, found excellent fit to the data. A study by Weiss (1964) found equally good agreement. The model involves two conditional probabilities, P_0 and $(1 - P_1)$, the probability of a wet day given the previous day was dry, and the probability of a dry day given the previous day was wet, respectively:

$$\begin{aligned} P_0 &= \Pr\{W|D\} & 1 - P_1 &= \Pr\{D|W\} \\ 1 - P_0 &= \Pr\{D|D\} & P_1 &= \Pr\{W|W\} \quad . \end{aligned} \tag{17}$$

Consequently, by this model, the probability of a dry sequence of n days is

$$P_0(1 - P_0)^{n-1} \quad , \tag{18}$$

and the probability of a wet sequence of n days is

$$(1 - P_1)P_1^{n-1} \quad . \tag{19}$$

The observed sequences of dry days, and those computed with Equation 18, for 50 years of precipitation data at Kansas City, Missouri, are shown in Table 2. The agreement is seen to be very good. In Table 2 a wet day is defined as one with >.01 inches of precipitation. Making this requirement more strict, for example >.10 inches, did not affect the fit of the model. These results indicate that the Markov assumption is reasonable when $\Delta \sim 1$ day.

For the case of an air parcel moving through the atmosphere along a trajectory, we expect the lower limit of Δ to be less than 1 day. This means that conditions in the future, as experienced by the moving parcel, will change faster than conditions at a fixed location. Since there is appreciable flow of air through storm systems, we can expect that the conditions the air parcel is subject to will change so rapidly that a value of ~12 hours for Δ seems reasonable. This corresponds to (using an average wind velocity of 8 m/s) a change in position of approximately 350 km.

TABLE 2. Comparison of sequences of dry days observed at Kansas City (1912-1961) and those computed by a Markov chain probability model (reprinted from Weiss 1964). A dry day is defined as one with <0.01 inches of precipitation. In the Markov model it is assumed that conditions on day n+1 are independent of conditions on day n-1, thus Δ = 1 day.

Length of Dry Period	January p_0=0.192		April p_0=0.300		July p_0=0.221		October p_0=0.185	
	Comp.	Obs.	Comp.	Obs.	Comp.	Obs.	Comp.	Obs.
1	41	45	79	74	55	51	39	40
2	33	33	55	62	43	42	32	31
3	27	31	39	30	34	30	26	27
4	22	26	27	35	26	32	21	20
5	18	13	19	14	20	28	17	13
6	14	9	13	16	16	10	14	17
7	11	7	9	11	13	13	11	10
8	9	8	6	6	10	11	9	9
9	8	3	5	6	8	8	8	4
10	6	5	3	2	6	4	6	8
11	5	4	2	4	5	5	5	3
12	4	6	2	1	4	3	4	5
13	3	4	1	1	3	1	3	2
14	3	1	1	1	2	2	3	3
15	2	6	1	1	2	4	2	4
16	2	4		0	1	2	2	1
17	1	1			1	1	2	2
18	1	3			1	1	1	2
19	1	3			1	0	1	1
20	1	0				0	1	1
21	1	0				1	1	0
22		0				1	1	0
23		0				0		1
24		0				0		2
25		0				0		0
26		0				1		1
27		0						1
28		1						0
29		1						0
30								0
31								1
Total		214		264		251		209

C. Stationarity Assumption

The assumption that $\lambda(t)$ has stationary transition probabilities presents some problems. Semi-permanent low pressure regions and areas where orographic precipitation is common may result in different transition probabilities for $\lambda(t)$ as the species approaches these regions. Because of our uncertainty of the trajectory calculations around a storm, and the fact that a large fraction of the material is probably removed in the first storm encounter, we have only recorded the first transitional probability and have assumed all subsequent transitions to be equally probable. The uncertainties in the total analysis are such that the possible variations in the transitional probabilities of $\lambda(t)$ will be ignored.

D. Model Equations

The subsequent development is after Rodhe and Grandell (1972). The relationship between the length of dry and wet periods and the transitional probabilities of $\lambda(t)$ is

$$\lim_{\Delta \to o} \frac{1}{\Delta} \Pr\{\lambda(t + \Delta) = \lambda_d \mid \lambda(t) = \lambda_w\} = \frac{1}{\tau_w} \tag{20}$$

$$\lim_{\Delta \to o} \frac{1}{\Delta} \Pr\{\lambda(t + \Delta) = \lambda_w \mid \lambda(t) = \lambda_d\} = \frac{1}{\tau_d} \tag{21}$$

where τ_w is the length of time the species experiences precipitation, and τ_d the length of time that dry conditions prevail.

Let T be the time required for removal of an aerosol particle or gas molecule from the atmosphere because of precipitation scavenging and dry

deposition. Thus in the previous notation,

$$\Pr\{T > t\} = E\left[\exp\left(-\int_o^t \lambda(\tau)d\tau\right)\right] \quad . \tag{22}$$

Let us call this probability G(t), and partition it according to conditions at the time the species is released into the atmosphere.

$$G(t) = P_d G_d(t) + P_w G_w(t) \tag{23}$$

where

$$G_d(t) = \Pr\{T > t | \lambda(o) = \lambda_d\} \tag{24}$$

$$G_w(t) = \Pr\{T > t \mid \lambda(o) = \lambda_w\} \tag{25}$$

$$P_d = \Pr\{\lambda(o) = \lambda_d\} \tag{26}$$

$$P_w = 1 - P_d \quad . \tag{27}$$

By considering the changes $\lambda(t)$ can make in the interval $t\varepsilon(o,\Delta)$, where the probability of such transitions is expressed in terms of τ_d and τ_w, we obtain the following set of linear differential equations.

$$\dot{G}_d(t) = -\left(\frac{1}{\tau_d} + \lambda_d\right) G_d(t) + \frac{1}{\tau_d} G_w(t) \tag{28}$$

$$\dot{G}_w(t) = \frac{1}{\tau_w} G_d(t) - \left(\frac{1}{\tau_w} + \lambda_w\right) G_w(t) \quad . \tag{29}$$

The reasoning behind Equation 28 is as follows: $G_d(t + \Delta) = \Pr\{T > t + \Delta \mid \lambda(t) = \lambda_d\}$; thus after time Δ, $\lambda(t) = \lambda_d$, so either it was dry at

t = o and it continued to be dry, or it was wet at t = o and it changed to the dry state. Hence

$$G_d(t + \Delta) = \Pr\{\lambda(t + \Delta) = \lambda_d \mid \lambda(t) = \lambda_d\} \times \Pr\{T > \Delta \mid \lambda = \lambda_d\} \times \Pr\{T > t \mid \lambda(o) = \lambda_d\}$$

$$+$$

$$\Pr\{\lambda(t + \Delta) = \lambda_w \mid \lambda(t) = \lambda_d\} \times \Pr\{T > \Delta \mid \lambda = \bar{\lambda}\} \times \Pr\{T > t \mid \lambda(o) = \lambda_w\} \quad (30)$$

or

$$G_d(t + \Delta) = \left(1 - \frac{\Delta}{\tau_d}\right) e^{-\Delta\lambda_d} G_d(t) + \frac{\Delta}{\tau_d} e^{-\Delta\bar{\lambda}} G_w(t) \quad (31)$$

where $\bar{\lambda} = \frac{\lambda_d + \lambda_w}{2}$, and we have ignored the possibility of more than one jump in interval Δ. Writing $e^{-\Delta\lambda}$ as $1 - \Delta\lambda + o(\Delta\lambda)$, and letting $\Delta \to o$, we obtain Equation 28.

It follows that $G(t) = \alpha e^{tr_1} + \beta e^{tr_2}$, where r_1 and r_2 are the eigenvalues of the coefficient matrix in Equations 28 and 29. Since $G(o) = 1$, $\beta = 1 - \alpha$, and because the residence time is finite, $G(\infty) = o$. Integrating Equations 28 and 29 we obtain two equations for $\int_o^\infty G_d(t)dt$ and $\int_o^\infty G_w(t)dt$. Solving, and substituting into Equation 23, gives us the integral time scale of G(t)

$$\int_o^\infty G(t)dt = \frac{\tau_d + \tau_w + \tau_d\tau_w(P_d\lambda_w + P_w\lambda_d)}{\tau_d\lambda_d + \tau_w\lambda_w + \tau_d\tau_w\lambda_w\lambda_d} \quad (32)$$

This is the expected value of our random variable T, which will be denoted as E(T).

Integrating the equation $G(t) = \alpha e^{tr_1} + (1 - \alpha)e^{tr_2}$, and equating with Equation 32, gives an expression for α, and now the equations are solved. The distribution function $F(t) = 1 - G(t)$ = the probability that the aerosol particle is removed from the atmosphere in a time less than or equal to t, is

$$F(t) = 1 - \alpha e^{r_1 t} - e^{r_2 t} + \alpha e^{r_2 t} \tag{33}$$

where

$$\alpha = r_1 + \tau_d^{-1} + \tau_w^{-1} + P_d\lambda_w + P_w\lambda_d \tag{34}$$

and

$$r_{1,2} = -\frac{1}{2}\left(\tau_d^{-1} + \tau_w^{-1} + \lambda_d + \lambda_w\right) \mp \left(\frac{1}{4}\left(\tau_d^{-1} + \tau_w^{-1} + \lambda_d + \lambda_w\right)^2 - \lambda_d\lambda_w - \lambda_d\tau_w^{-1} - \lambda_w\tau_d^{-1}\right)^{1/2} \tag{35}$$

The parameters in Equation 32 must now be estimated from data. The probabilities, P_d and P_w, can be determined from the precipitation record at a fixed location. The length of dry and wet periods, τ_d and τ_w, refer to conditions as experienced by the pollutant, and thus can be determined by examination of wet and dry periods along a trajectory. The trajectory model and method of analysis are described in Section IV.

IV. APPLICATION OF STATISTICAL MODEL

A. Trajectory Technique

The computerized trajectory model used in this study was provided by Dale Coventry at Research Triangle Park, North Carolina, and was developed at the Air Resources Lab, NOAA, Silver Springs, Maryland as explained in Heffter and Taylor (1975). The observed winds at reporting pibal and rawinsonde stations are used as input to the model. The trajectory is composed of a series of three-hour segments, each computed assuming persistence of the winds reported closest to the segment time. The winds used in the computation are averaged throughout a desired layer above the average terrain. The wind is weighted linearly according to the amount of vertical distance it is representative of, as in Figure 2.

Each trajectory segment is computed by

$$TS = \frac{\sum^{R} DW_i \; AW_i \; TS_i}{\sum^{R} DW_i \; AW_i} \qquad (36)$$

$\sum^{R}$ indicates summation over all reported winds within a distance R of segment origin (R = 300 nautical miles)

$TS_i = (V_i)\Delta t$ is the contribution to the trajectory segment from wind V_i, and Δt is the segment time interval

DW_i = the distance weighting factor = $1/dW_i^2$

AW_i = the alignment factor = a function of θ_i, the angle between TS_i and the line from the segment origin to the reporting station. In the model, $AW_i = 1 - .5 \mid \sin \theta_i \mid$. See Figure 3.

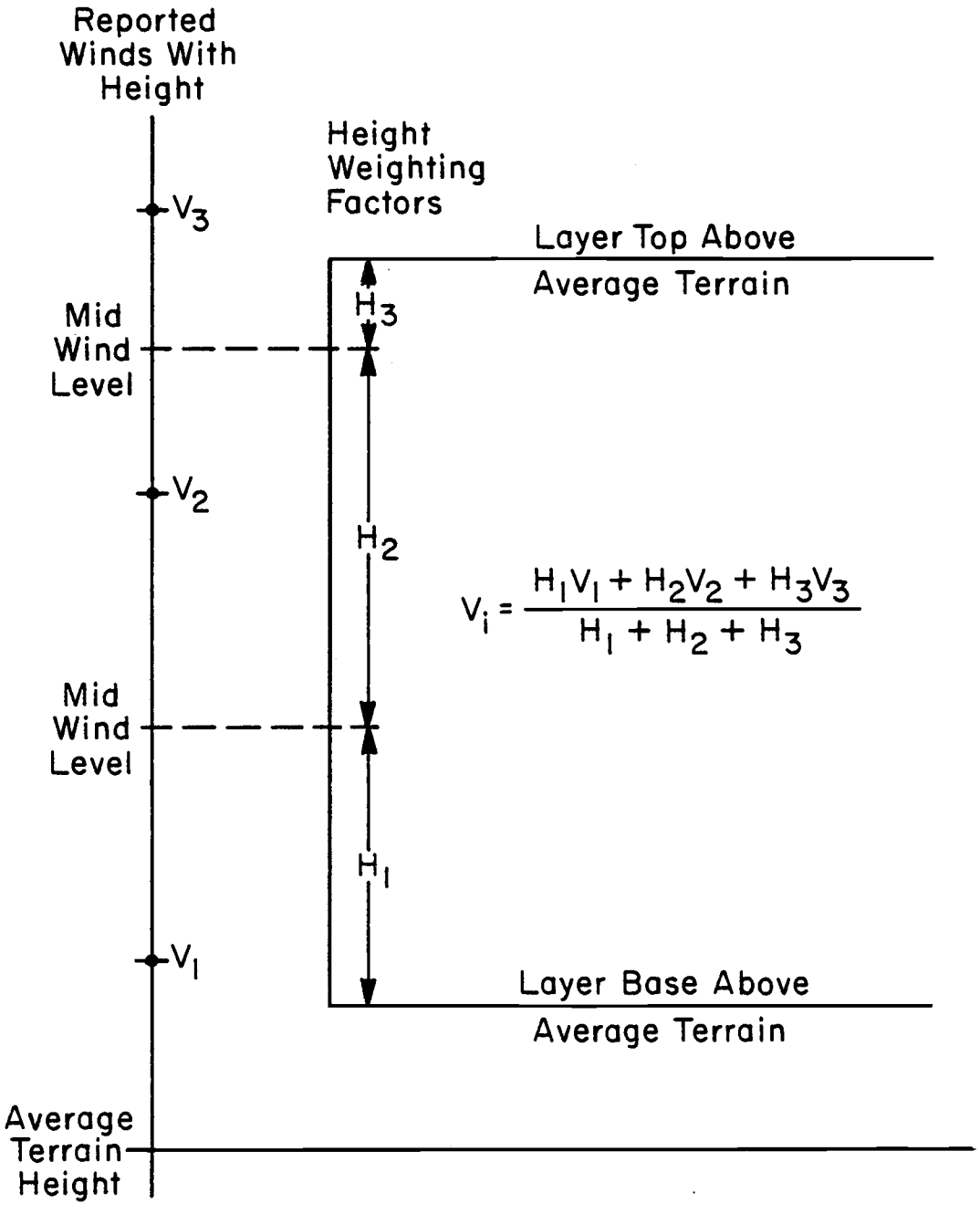

Figure 2. Vertical averaging technique of wind velocity (reprinted from Heffter and Taylor 1975).

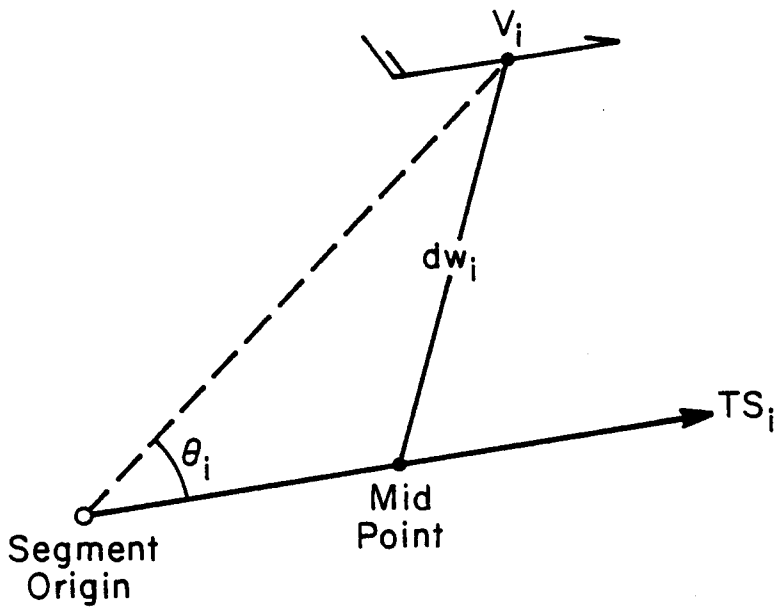

Figure 3. Method of trajectory construction (reprinted from Heffter and Taylor 1975).

In this work, trajectories were started from Kansas City, Missouri four times per day for each day in January and July 1975. The trajectories were run for five days or until the criteria for reported wind data was met. The layers in which the observed winds were averaged were 200-1000 m above average terrain in January, and 300-2000 m in July, chosen to approximate the seasonal average afternoon mixed heights for the region (Holzworth 1972). Figure 4 shows an example of the model output for three trajectories.

For a discussion of the accuracy of various boundary-layer trajectory techniques, including the layer average model described above, see Hoecker (1977). The results of the tetroon release experiment conducted in the fall of 1971 at Oklahoma City indicate the above layer average model performs fairly well in a variety of flow patterns. Hoecker suggests, on the basis of 13 examples, that the layer average trajectory requires no adjustment in northerly flow, 10° backing in southerly, and 20° backing in westerly flow. These estimates for westerly flow are based on three tetroon recoveries.

B. Precipitation Data

The hourly precipitation data for the Local Climatological Data Stations in the continuous United States, for the periods January and July 1975, were obtained from the National Climatic Center.

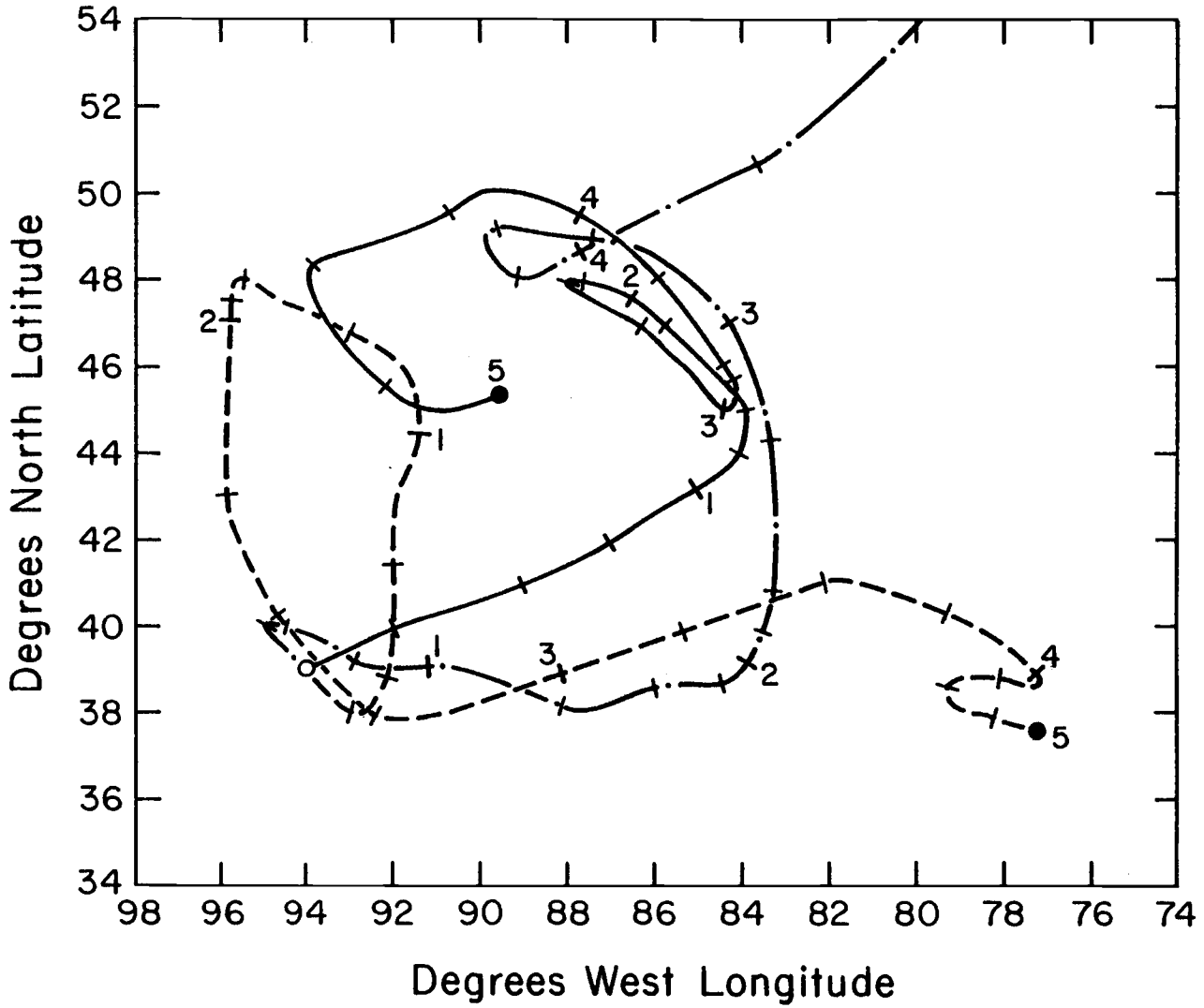

Figure 4. Example of three trajectories. Six hourly positions marked and daily positions numbered.

C. Method

Previous studies to estimate the residence time of various species have used average wet and dry deposition velocities without considering the times over which wet and dry deposition can occur. In other studies, Rodhe and Grandell's model was used but with the distribution of wet and dry periods at a fixed location used to determine τ_d and τ_w. Other authors have calculated mean residence times based on a detailed emission inventory and the steady state concentration in the atmosphere of the species. What we have done in this study is obtain the frequency function of the tropospheric residence time based on the Lagrangian distribution of wet and dry periods and the precipitation rates that the species encounters along its path through the atmosphere. This information, coupled with the conditions at the time of release of the pollution and the assumptions we have made about $\lambda(t)$, enables us to calculate the distribution of the tropospheric residence time.

The method of obtaining the frequency functions involved determining the hourly position of the trajectory end point and the precipitation for that time and position. The positions of the Local Climatological Data Stations (there are approximately 115 stations in the United States east of 95°W longitude) were plotted on a latitude longitude grid equivalent to the grid on which the trajectories were plotted. Starting from Kansas City, the data station closest to each hourly trajectory end point was determined. In the case that the distances of two or more stations were within 20 percent of each other from the end point, all such stations were recorded. Thus a time series of the trajectory position in terms of precipitation data points was made for each trajectory.

With the time series list of stations, the next step was to determine when, how long, and at what rate the precipitation occurred. The list was followed until a station was reached that indicated precipitation ≥.01 inches per hour was occurring at the time the trajectory was over the station. The travel time of the trajectory until the first precipitation was encountered was recorded as s. Carrying out this procedure for each month gave the frequency function, $N_d(s)$, where the expected time until a wet period is encountered, τ_d, is given by

$$\tau_d = \int_o^\infty sN_d(s)ds \quad . \tag{37}$$

Once precipitation was identified as occurring along the trajectory, the list was followed until a station was reached which recorded <.01 inches of precipitation per hour at the time the trajectory was over the station. The time in which precipitation was occurring was recorded and denoted as s'. The frequency function $N_w(s')$, which equals the frequency of occurrence for each month of a wet period of length s', contains the expected length of a wet period, τ_w, via

$$\tau_w = \int_o^\infty s'N_w(s')ds' \quad . \tag{38}$$

Each trajectory's encounter with precipitation produced precipitation rates which were averaged by encounter, and then by month. Starting with the first hour of precipitation, each hourly rate was recorded. The hourly rates for the storm were averaged over the duration of the storm. Thus, each trajectory produced an average rate, which was then averaged over all trajectories for that month.

For the case of more than one station being representative of the hourly trajectory position, the precipitation rates at all representative stations were considered. If precipitation was recorded at any of the stations at the time of trajectory passage, the trajectory was taken to be in a wet period. In most cases, precipitation was or was not occurring at all stations listed as being representative of the trajectory position. The hourly precipitation rate in these cases was taken to be an average of the rates at the individual stations.

Before we began the analysis we were concerned that a significant number of the trajectories would not encounter precipitation before they left our precipitation data grid. This would infer that τ_d was greater than around four days, and would prohibit us from obtaining the distribution functions (in general, the trajectory end points were over the Atlantic after four to five days). However, we found only two cases in winter, and four in summer, where precipitation was not encountered before passage out of the data area. Thus, our selection of Kansas City, because of the central location it has, proved to be useful in this respect.

In the cases where the trajectory passed through the hourly precipitation data area without experiencing precipitation, the Daily Weather Map series was consulted. The position was plotted on the surface synoptic map closest in time to the trajectory time. The determination of whether or not precipitation was occurring at that time and position was obtained by consideration of 24-hour precipitation amounts, over Canada, and surface fronts over the Atlantic. The 500 mb heights were also considered when determining general areas of the Atlantic where precipitation was or was not likely to occur.

D. Summary

In conclusion, we have attempted to determine the functions, N_d and N_w, which are required for application of Rodhe and Grandell's probability model. A great deal of the validity of our results rests with the accuracy with which the layer average wind trajectory model estimates the path of pollutants released into the mixed layer. It is because of our interest in near surface sources of pollution that our trajectories may be suspect. Since at least the first part of the transport will be within the mixed layer, isentropic trajectories (see Danielsen 1961) are not possible, because the potential temperature surfaces are vertical. Although the trajectories calculated with the model exhibit many realistic phenomena such as inertial loops and accelerations and decelerations, it is possible that they may differ from the true trajectories significantly. For a review of trajectory methods see Danielsen (1961).

V. RESULTS

A. Probability of Wet and Dry Periods

The Lagrangian frequency functions that we observed, N_d and N_w, were found to be exponential functions. Thus the distribution functions are of the form

$$D(t) = 1 - \exp(-t/\tau_d) \tag{39}$$

$$W(t) = 1 - \exp(-t/\tau_w) \tag{40}$$

where D(t) is the probability that the length of a dry period is less than or equal to t. Linear least-squares regression of $|\ell n(1 - D)|$ on t gave τ_d equal to 38 hrs in January and 54 hrs in July. Regression of $|\ell n(1 - W)|$ on t gave τ_w equal to 12 hrs in January and 2 hrs in July. The coefficient of determination, R^2, for all four of these regressions was ~.97, which means the total variation in $|\ell n(1 - D,W)|$ was reduced by 97 percent when t was introduced.

As a comparison, the Eulerian precipitation statistics at the source region were also calculated. We denote the first moment of these functions by E_d and E_w, where E_d is the expected length of a dry period at the source region. We found the Eulerian data overestimates the length of dry periods by roughly a factor of two, while the length of wet periods is about the same. Table 3 summarizes the observations.

The mean value of N_d, τ_d as shown in Equation 37, is nearly 5 percent larger than the mean value of the exponential distribution. This is

Table 3. Observational data determined by method described in text. $\tau_{d,w}$ is the mean length of a dry, wet period, I the precipitation rate, $P_{d,w}$ the probability of a dry, wet condition at time and location of pollutant release, and $E_{d,w}$ the mean length of dry, wet periods at the source region.

	τ_d	τ_w	I	P_d	P_w	E_d	E_w
JANUARY	38	12	.76	.92	.08	96	8
JULY	54	2	3.28	.98	.02	106	2
	hours		mm/hr	probability		hours	

because the frequency functions were not exact exponentials, and in fact, had slightly larger values at large s. Thus the mean was shifted higher in the actual functions than in the fitted exponential functions. This slight difference (with $\chi^2 = 2.05$ on 13 degrees of freedom) is insignificant in view of some other assumptions we have made.

The mean length of a dry period we found for the source region, 106 hours in July, agrees with results from Henmi, Reiter, and Edson (1977), and Weiss (1964). In Table 2 we have shown the observed and computed sequences of dry periods from Weiss's work. With $P_o = .221$, 106 hours occurs at the 63 percentile of the cumulative distribution given by the Markov chain model, which is where the mean value of an exponential distribution occurs.

B. Precipitation Rates

The distribution of rainfall rates (rainwater equivalent in the winter) was found to be normal. The first moment is denoted as I, and is shown in Table 3. The differences between the rainfall rates observed at the source and those found along the trajectories showed wide variation on particular days, but had no significant spread for the month overall. Our results show a strong seasonal variation in average rainfall intensity, with summer storms precipitating at a rate more than four times as great as winter storms.

VI. DRY DEPOSITION

A. Parameterization

The scavenging rate λ_d is often expressed in terms of a dry deposition velocity, v_d, which is the ratio of the deposition rate to the immediate ground-level air concentration. Use of a deposition velocity is convenient for reporting experimental data but avoids an explanation of details of the deposition process. These details can be exceedingly complex (e.g., see Slinn, 1978c).

One facet of the dry removal process involves turbulent transfer of the species to the surface and then the uptake of the material by surface elements. In this case, the two rates involved are the rate of transfer through the surface layer and the rate at which the surface accepts the material. Some studies done on dry deposition of particles and gases suggest that the rate limiting stage of the process may be the rate at which the surface accepts the pollutant, but this will depend on the particular pollutant and surface. For example, Wesely and Hicks' (1977) experiments in Illinois found that the dry deposition velocities for particles in the size range .05-.1 μm were about 50% less than that for momentum and for a passive surface reactive gas. They used the eddy-correlation method, which gives for the deposition velocity

$$v_d = \overline{w'c'}/\overline{c} \tag{41}$$

where $\overline{w'c'}$ is the covariance of the vertical wind velocity and the particulate concentration, and $\bar{c}$ is the mean concentration. Their results show v_d for these particles to be in the range .1-1 cm/s. A more recent paper by Hicks and Wesely (1978) suggests that a deposition velocity of .5 cm/s for particulate sulfur is appropriate on a daily average basis over a pine forest.

Prahm, Torp, and Stern (1976) found the average dry deposition velocity for particulate sulfur to be .4 cm/s over the North Sea. Gradient studies, as well as studies by the eddy-correlation techniques, have found that in some cases the appropriate deposition velocities for use in modeling studies may be as large as the limiting value dictated by the turbulence level, $u_*^2/\bar{u}$. For "typical" atmospheric conditions, this velocity is near 2 cm/s. In summary, for small particles a deposition velocity of .1 to 1 cm/s appears reasonable.

The relationship between the dry deposition velocity and the dry scavenging coefficient is now discussed. In the steady state case with the wind velocity in the x direction, the crosswind integrated concentration of the species in air must satisfy

$$u(z)\,\frac{\partial C}{\partial x} = -\,\frac{\partial F}{\partial z} \tag{42}$$

where C(x,z) is the concentration, and F is the net upward flux. Integrating over the mixed layer, which is assumed to be capped by an impenetrable inversion,

$$\frac{d}{dx}\int_o^h u(z)C(x,z)\,dz = -v_d C(x,o) \tag{43}$$

where $F\big|_{z=o} = -v_d C(x,o)$, and $F\big|_{z=h} = o$ (for example, see Scriven and Fisher 1975). If we can assume an exponential dependence in x for C(x,z), then the e-fold distance is

$$x_e = \frac{\int_o^h u(z)C(x,z)dz}{v_d C(x,o)} \quad . \tag{44}$$

It is seen from Equation 44 that

$$x_e \simeq \frac{\overline{uh}}{v_d} \tag{45}$$

since C and u are approximately constant with height in the mixed layer. Thus the scavenging rate is v_d/h. When conditions are such that we do not have a quasi-steady mixed layer capped by an inversion, we cannot obtain a closed form for the scavenging rate. In this case, numerical models may be used to solve the equations. For long-term average models, the simple parameterization in Equation 45 is probably accurate enough.

B. Residence Time

The model equation for the expected residence time if there is only dry removal ($\lambda_w = o$) is

$$E(T_d) = P_w \tau_w + \frac{\tau_d + \tau_w}{\tau_d} \frac{1}{\lambda_d} \simeq \frac{\tau_d + \tau_w}{\tau_d \lambda_d} \quad . \tag{46}$$

This assumes that the material is not available for dry deposition during precipitation. This assumption will depend on the type of the precipitation. If rain falls through a pollutant-laden layer near the surface which is trapped by an inversion above, then the scavenging rate during

precipitation is $\lambda_w + \lambda_d$, so that

$$E(T_d) = \frac{1}{\lambda_d} \quad . \tag{47}$$

For precipitation in which the low level polluted air is lifted into cloud systems, for example summertime convective storms, we expect the former expression.

Figure 5 shows $E(T_d)$ as a function of the dry deposition velocity with the well mixed assumption. The height of the mixing is set equal to the monthly average mixed layer height. See Holzworth (1972).

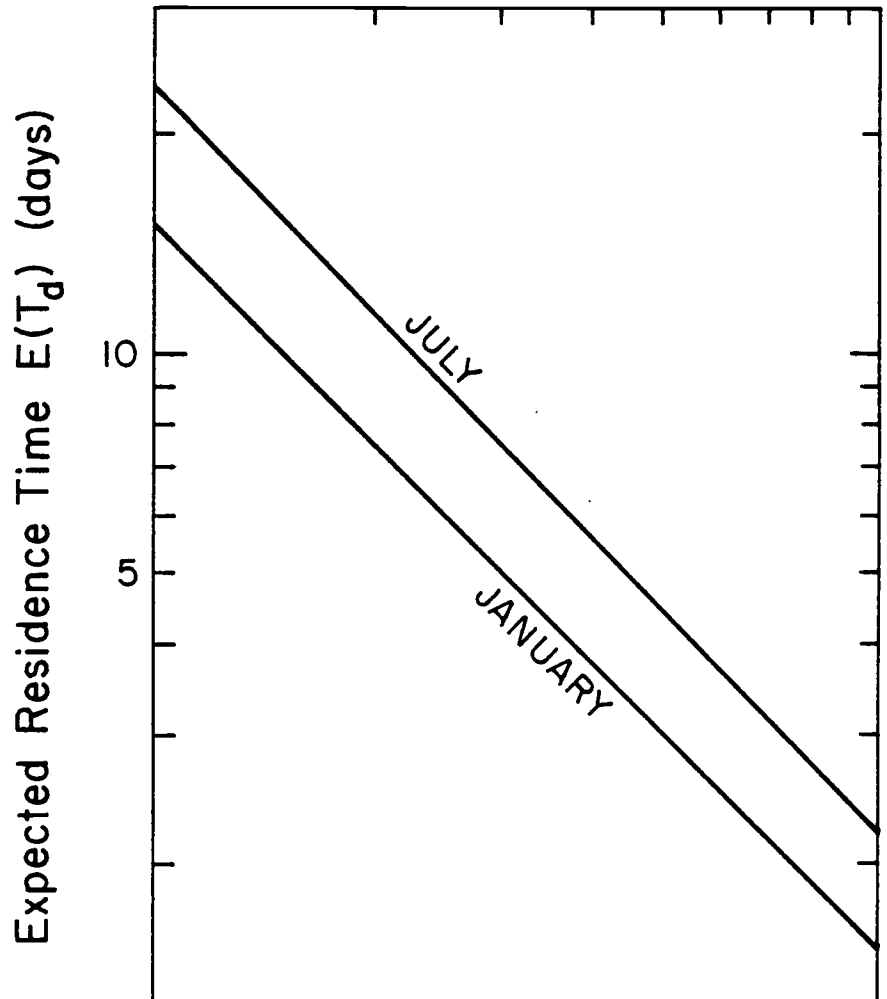

Figure 5. Residence time caused by dry removal only as a function of the effective dry deposition velocity.

VII. PRECIPITATION SCAVENGING

A. Parameterization

Much work has been done on parameterizing precipitation scavenging. See Slinn (1977, 1978a-c) and Slinn *et al.* (1978). In this section we will briefly summarize the results of these investigations. The important thing to realize is that great variability (three orders of magnitude) exists in the scavenging rate during individual storms. Thus, as the time resolution we desire shortens, the accuracy of our parameterization for the scavenging rate gets poorer. Slinn suggests that annual average values for the wet deposition velocity may be correct within a factor of two, but for submicron particles, the uncertainty increases to an order of magnitude.

For irreversible scavenging of aerosol particles of radii a by rain of intensity I, and mass-mean drop size R_m, the rain scavenging rate suggested for both in-cloud and below-cloud scavenging is

$$\lambda_w \simeq \frac{cI}{R_m} \bar{E} \tag{48}$$

where c is a numerical factor ~.5 and $\bar{E}$ is the collection efficiency for the mean drop size. Semi-empirical expressions for $\bar{E}$ as well as available data are discussed in Slinn (1977). This is an approximate expression of a complex integral over all drop sizes, and should be viewed as an order of magnitude estimate. Since R_m goes as $I^{1/4}$ for steady frontal rain, Mason (1971), the scavenging rate goes as $I^{3/4}$. This result has been observed experimentally by Dana and Wolf (1968, 1969, 1970), and Burtsev *et al.* (1970).

The contributions to the particle-drop collection efficiency by Brownian diffusion ($a \lesssim 0.1$ μm), and inertial impaction ($a \gtrsim 2$ μm), are well known (see Slinn 1978a). For the case of particles in the size range 0.1-2 μm, the collision efficiency (assumed to equal the collection efficiency) is not well known. Recent studies, which can be found in Slinn (1978a), suggest that particles in the range 0.1-1 μm may grow by water vapor condensation, thus realizing a collection efficiency ~1. For particles smaller than ~0.01 μm, it is suggested that Brownian diffusional coagulation will result in these particles readily attaching to cloud droplets. Thus, after the particles have been in clouds for a short time, it is suggested that only those particles originally in the size range $0.01 < a < 0.1$ μm will have an effective collection efficiency less than ~1. For below cloud scavenging, submicron particles may have a collection efficiency much less than 1, since particle growth by water vapor condensation can be expected to be less than for particles in the cloud.

An alternative formulation for describing washout of both particles and gases is available, Slinn (1978a). The wet flux of particles is given by

$$W \simeq \int_0^\infty L(\vec{r},t;a)\,dz = \int_0^\infty \lambda_w C\,dz \tag{49}$$

where the loss rate per unit volume, L, is assumed linearly dependent on the air concentration C. Using the previous expression for λ_w we find

$$W = w_r I_o C_o \tag{50}$$

where subscript o refers to surface level, and w_r is the washout ratio given by

$$w_r = c\int_o^\infty \frac{I(z)}{I_o}\frac{C}{C_o}\frac{E(a,R_m)}{R_m}\,dz \quad . \tag{51}$$

For gases which form simple solutions the washout ratio is given by

$$w_r = \frac{K_{eq}}{C_o} = \alpha \tag{52}$$

where K_{eq} is the equilibrium concentration of the dissolved gas in the drop and α the solubility coefficient. Thus,

$$W = \alpha I_o C_o \tag{53}$$

and the wet deposition velocity is defined via

$$v_w = \frac{W}{C_o} = \alpha I_o \quad . \tag{54}$$

For particles

$$v_w = w_r I_o \quad . \tag{55}$$

A scavenging rate may be attained by defining a wet deposition height scale

$$h_w = \int \frac{C(z)}{C_o}\frac{I(z)}{I_o}\,dz \quad . \tag{56}$$

If the pollutant is nearly uniform in concentration from the surface to the top of the scavenging layer, then h_w is just the cloud layer height,

and the scavenging coefficient is

$$\lambda_w = \frac{v_w}{h_w} = \begin{cases} \dfrac{\alpha I_o}{h_w} & \text{for gases} \\ \dfrac{w_r I_o}{h_w} & \text{for particles} \end{cases} \quad . \tag{57}$$

In our subsequent investigations we will assume a monthly average scavenging coefficient for aerosol particles of

$$\lambda_w = \frac{\overline{I}\,\overline{E}}{2R_m} \quad . \tag{58}$$

For $\overline{E}$ as a function of particle size and drop size see Slinn (1977). Our estimates are within the range 10^{-5} to 10^{-3} s^{-1} observed experimentally for the effective mass scavenging rate. The results for submicron particles are very approximate because of our lack of knowledge of $\overline{E}$ in this range. Using an average of Mason's (1971) and Bests' (1950) results for drop size as a function of precipitation rate, we have calculated the residence time caused by washout as a function of $\overline{E}$.

B. Residence Time

The expression for the residence time for only wet removal ($\lambda_d = o$) is

$$E(T_w) = P_d\tau_d + \frac{\tau_d + \tau_w}{\tau_w}\,\frac{1}{\lambda_w} \quad . \tag{59}$$

If the pollutant were released during a storm ($P_d = o$) the residence time would be similar to $(\varepsilon\nu)^{-1}$, where ε is the fraction scavenged during storms and ν the frequency of storms. In this case an infinite

scavenging rate would result in a residence time of zero. Equation 59 allows for a nonzero residence time even in the case of an infinite scavenging rate.

Figure 6 shows the expected residence time caused by precipitation scavenging as a function of the average collection efficiency. The associated travel distances for winter and summer months are included. It may be seen from the figure that two orders of magnitude variation in $\bar{E}$ results in one order of magnitude change in $E(T_w)$. The mean atmospheric lifetimes are around twice as long in summer than in winter.

Also shown in Figure 6 is the expected residence time calculated with Equation 59 using the precipitation statistics at the origin of the trajectories. These values overestimate the residence time by a factor of two in July, and 2.5 in January. Thus, in July, the fact that the Lagrangian probability for the material to be experiencing precipitation is twice as great as the probability of precipitation at the source of the material, results in an expected lifetime one-half as long as that predicted by the Eulerian precipitation data.

The distribution function $F(t)$, and the frequency function $f(t) = \dot{F}(t)$, for the length of time an aerosol particle can expect to remain in the atmosphere after having been released from Kansas City and subjected to only precipitation scavenging, are shown in Figures 7 and 8. A value of the scavenging coefficient must be assumed to find these functions; thus, each curve is shown for two values of the collection efficiency. Although the expressions for these functions are

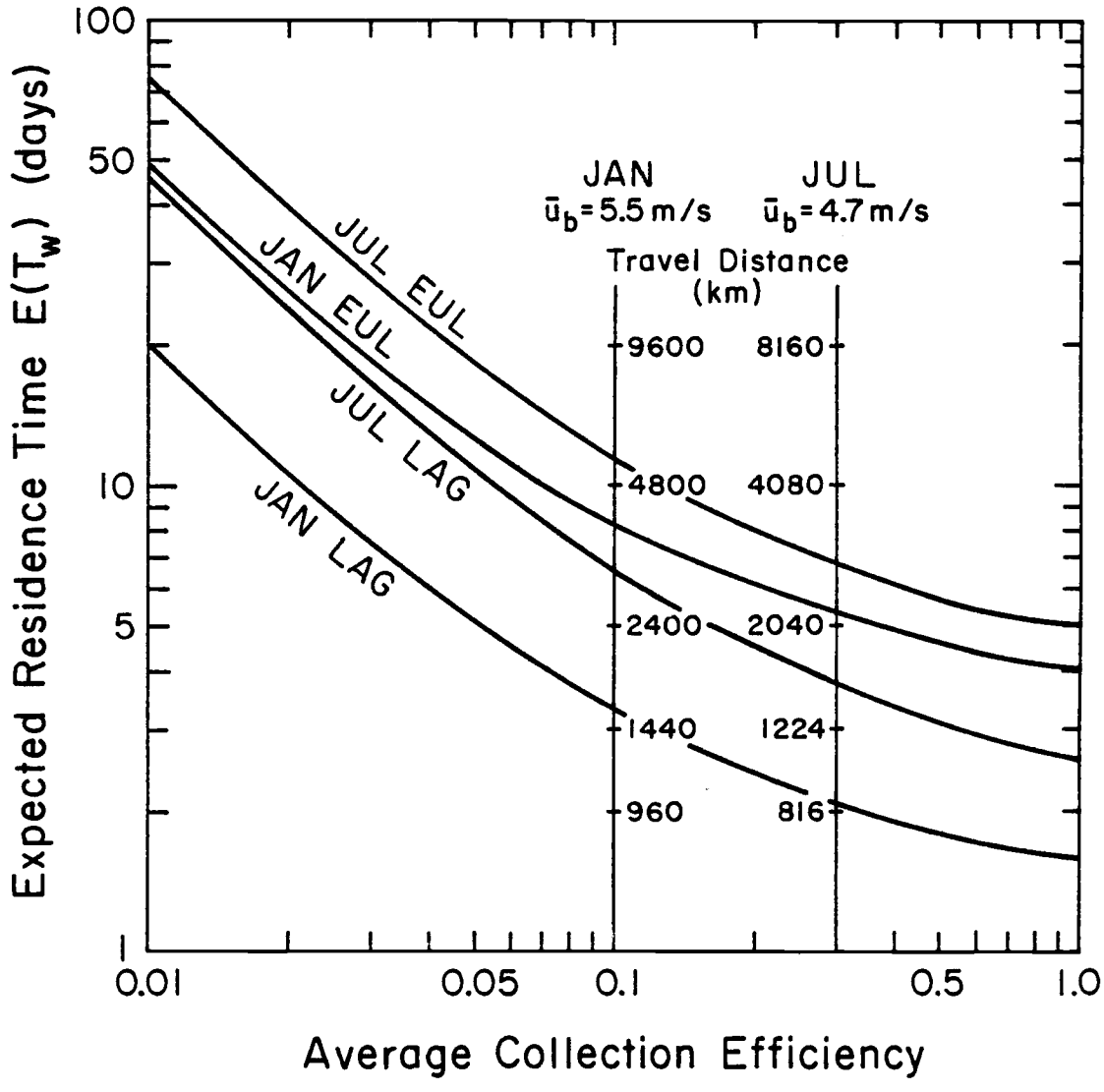

Figure 6. Residence time and associated travel distance caused by precipitation scavenging only as a function of the average collection efficiency. Abbreviations are: JAN = January; JUL = July; EUL = Eulerian; LAG = Lagrangian.

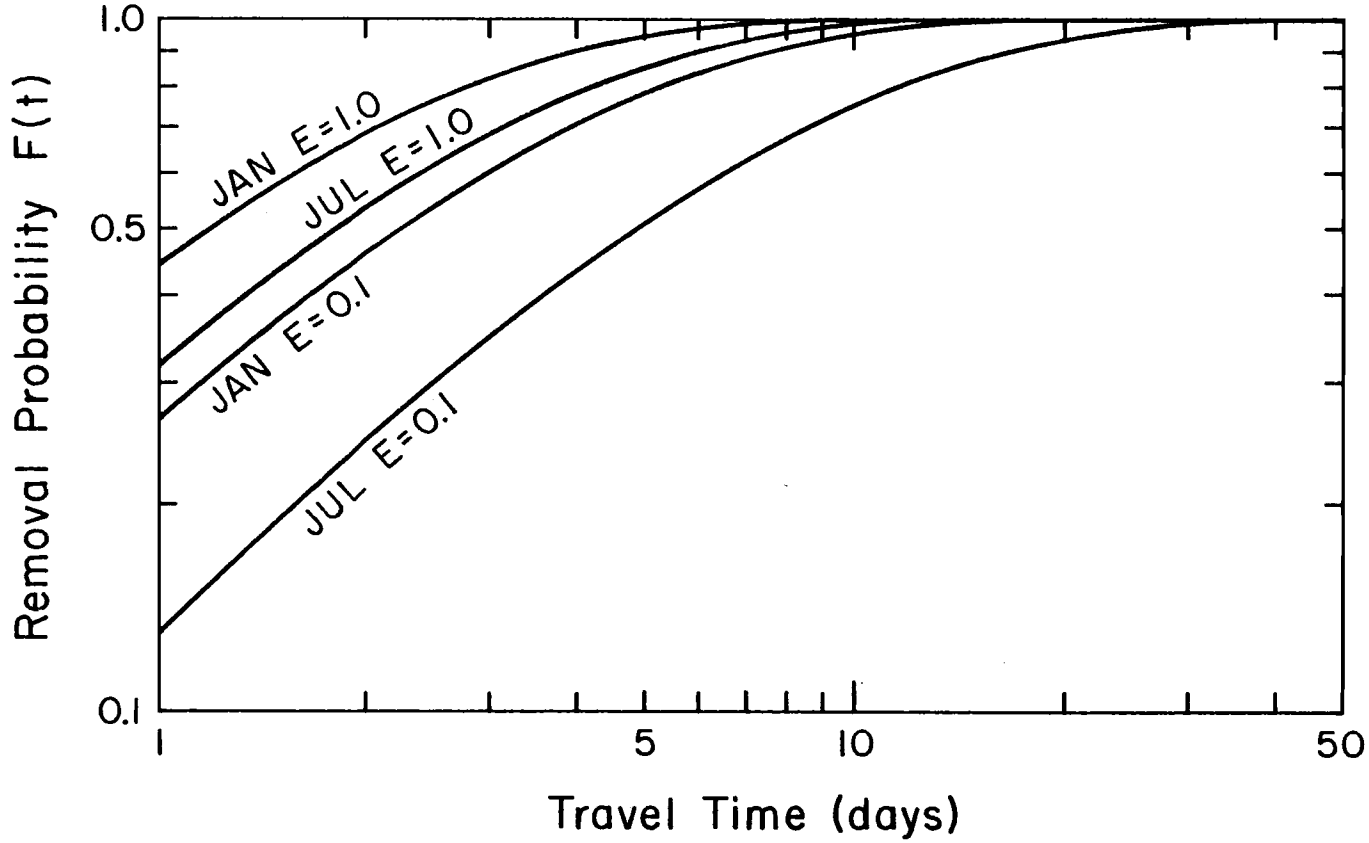

Figure 7. Distribution function of the residence time caused by precipitation scavenging only for two values of the average collection efficiency, E = 0.1 and E = 1.0.

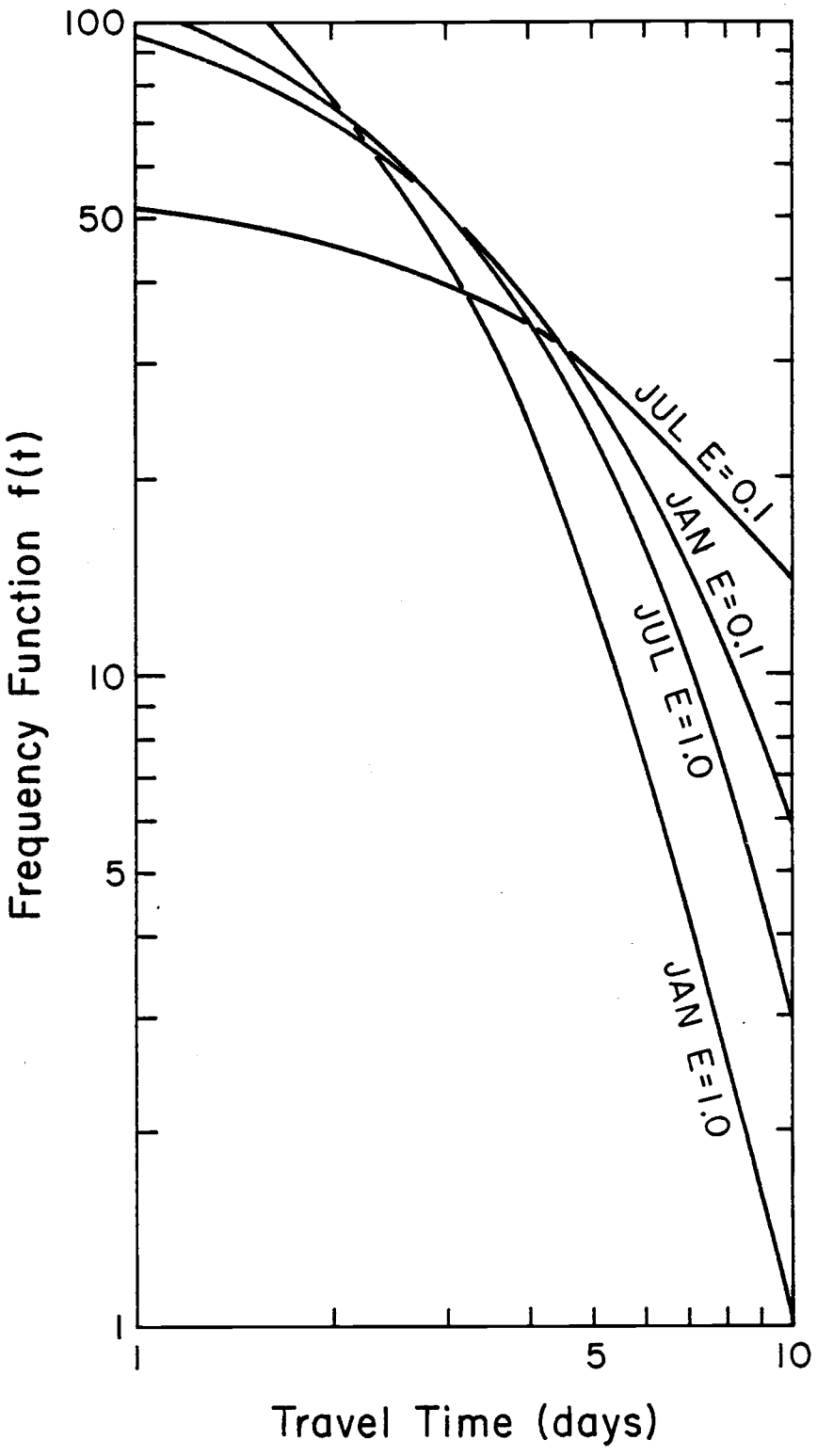

Figure 8. Frequency function of the residence time caused by precipitation scavenging only for two values of the average collection efficiency.

complex, in every case one term dominates such that

$$F(t) \simeq 1 - e^{r_2 t} \tag{60}$$

$$f(t) \simeq -r_2 e^{r_2 t} \tag{61}$$

where $r_2 < o$ in all cases. The mean value $f(t)$ is then

$$\int_o^\infty tf(t)dt = -\frac{1}{r_2} \quad . \tag{62}$$

Thus $E(T_w) = -1/r_2$.

So that the travel times in the figures may be associated with locations, for the case of a release from Kansas City, Figure 9 shows the trajectory end points after three days travel. Because the trajectories exhibit strong curvature and rapid acceleration, the positions at times other than three days should not be extrapolated from the figure. In fact, an attempt to categorize the trajectories according to general travel direction from Kansas City was abandoned because in many cases a trajectory that headed in one direction would reverse to another direction several times before the trajectory was terminated after five days.

The mean positions and standard deviations of the trajectory endpoints at 12 hour time intervals are discussed in Appendix B. The mean transport velocity, as determined by the mean endpoint locations, is much less than typical mean instantaneous wind speeds. Therefore, we suggest the mean wind speed used in steady state, long-term average models to predict air quality, should be less than typical instantaneous wind speeds.

Figure 8 may be interpreted in terms of relative probabilities. Reading from the figure, the residence time caused by wet removal in

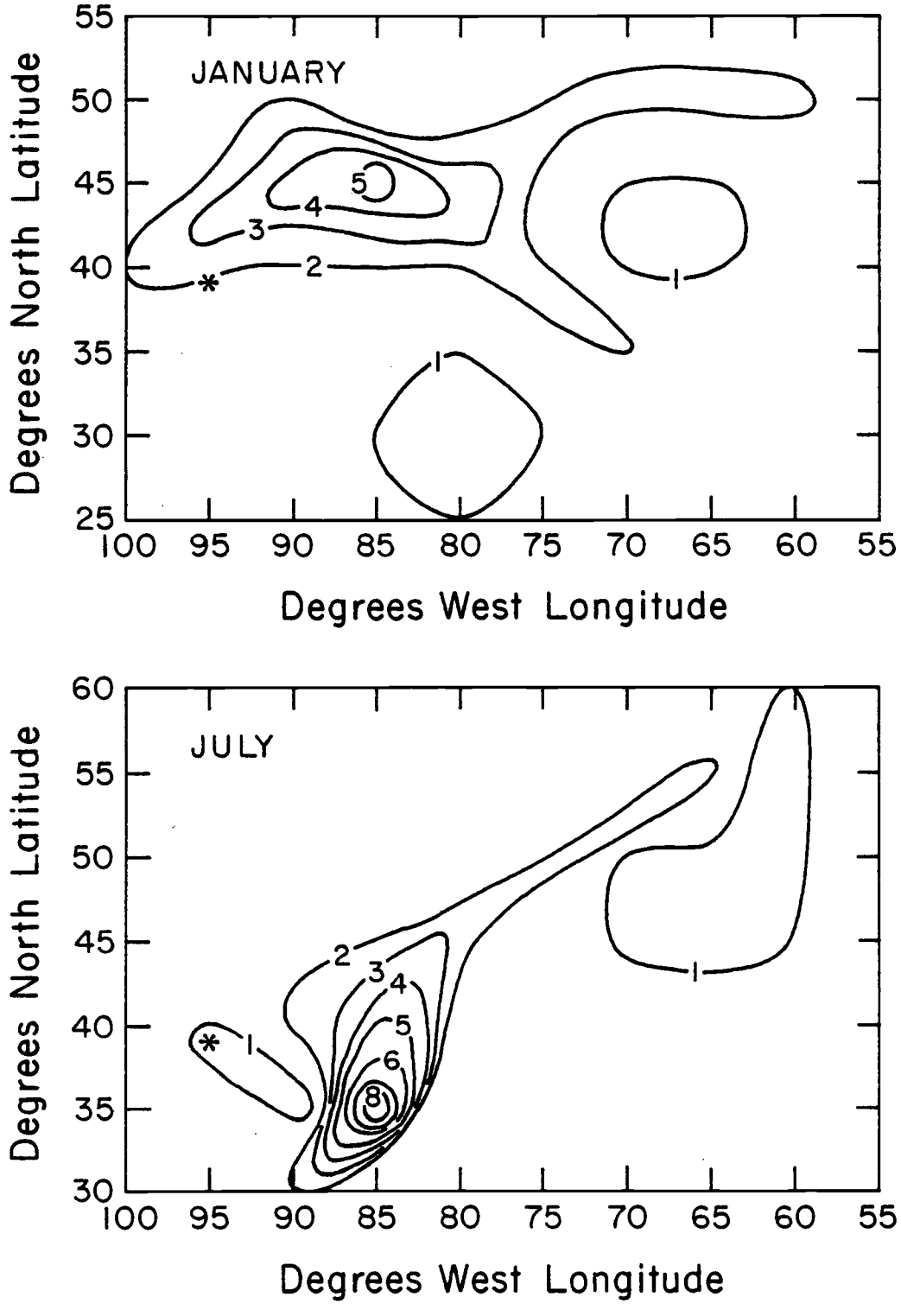

Figure 9. Distribution of trajectory endpoints after three days travel time from Kansas City, Missouri. Isopleths indicate positions where equal number of trajectory endpoints occurred. The values of the isopleths indicate the number of endpoints.

winter with $\bar{E}$ = 1.0, is 100 times more likely to be 1.5 days than ten days. The mean values of f(t) for the four cases are

	JAN. E=.1	JULY E=.1	JAN. E=1.0	JULY E=1.0	
$E(T_w)$	3.2	6.9	1.7	2.6	days

Of course, the lifetime can be expected to be less than or equal to these values 63 percent of the time. Figure 7 indicates that the upper limit to the residence time (90th percentile in July and E=.1) is near two weeks. The lower limit for the above cases (50th percentile in January and E=1.0) is near 29 hours, so the range of lifetimes covers an order of magnitude over winter and summer when the collection efficiency varies between .1 and 1.

VIII. WET AND DRY DEPOSITION

A. Residence Time

Our results for the expected value of the residence time (for pollutant subject to wet and dry removal) are shown in Figure 10. These results are applicable to aerosol particles or trace gases released from the midwestern United States in summer and winter. The pollution is assumed to remain below a height of 1 km in January and 2 km in July, unless it enters a region of precipitation, in which case it is washed out at a rate proportional to $EI^{3/4}$. In dry conditions, the pollutant is removed at a rate proportional to the dry deposition velocity. Using the rainfall rates observed, and the assumed heights for vertical mixing based on the climatological mean mixing heights, the length of time material may be expected to remain in the atmosphere is shown as a function of the average collection efficiency for five values of the dry deposition velocity.

Although the dry deposition velocity and washout ratio of specific pollutants are known only approximately, we will now consider some examples for estimates of particular pollutants. The dependence of these estimates for the residence time on the particular wet and dry removal rates we deem appropriate, should be kept in mind. The available data and theoretical considerations upon which we will base our estimates of the dry deposition velocity and the washout ratio (or effective collection efficiency) can be found in Slinn *et al.* (1978), and Slinn (1978b, 1978c).

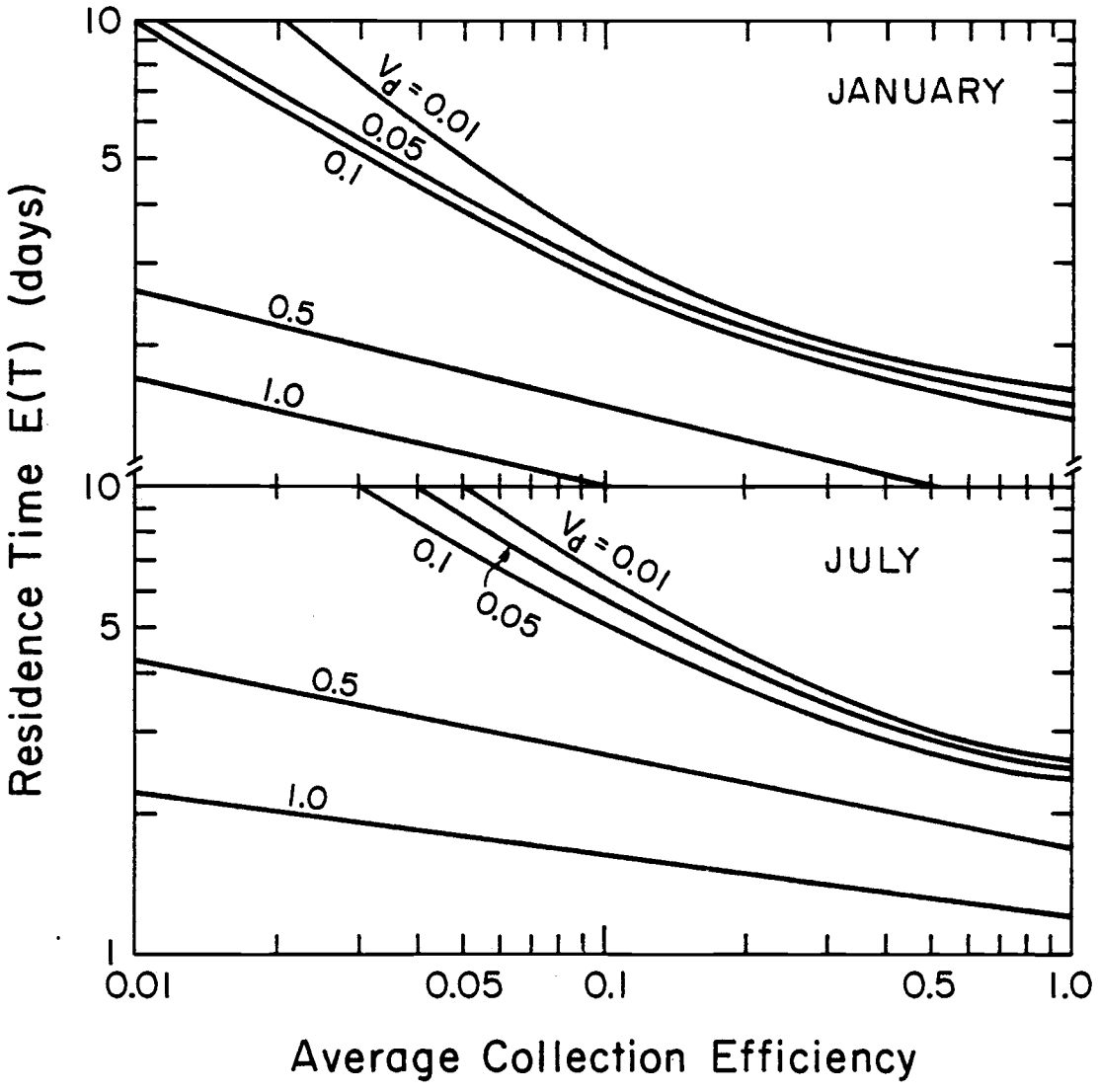

Figure 10. Residence time caused by precipitation scavenging and dry deposition as a function of the average collection efficiency for five values of the effective dry deposition velocity (v_d in cm/s).

First, consider lead particles of mass mean diameter ~.5 μm. For convective storms, $w_r \sim 0.06 \times 10^6$. The average dry deposition velocity is near .25 cm/s. If the lead is removed by precipitation scavenging from a characteristic height ~5 km, then the residence time is near nine days in the summer. (See Figure 10 with $v_d = .25$ and $\overline{E} = .01$). For the case of frontal precipitation $w_r \sim .24 \times 10^6$ (it has been suggested that w_r may be larger for frontal precipitation since the particles have a larger time to grow by water vapor condensation, and more time to attach to cloud droplets by Brownian diffusion, than for convective type precipitation). When the vertical extent of the precipitation is ~1 km, the residence time is approximately two days, which represents a winter-time estimate.

For convective type precipitation of gaseous SO_2, $w_r \sim 0.1 \times 10^6$. Many reports have suggested $v_d \sim 1$ cm/s for SO_2. Thus, during the summer when convective precipitation is common, the residence time of SO_2 caused by precipitation scavenging and dry deposition is approximately two days. The actual lifetime of SO_2 will be less than two days since SO_2 is usually converted to H_2SO_4 aerosol.

For a host of radionuclides (^{125}Sb, ^{89}Sr, ^{106}Ru, ^{137}Cs, ^{140}Ba, ^{90}Sr, ^{95}Zr) monthly average washout ratios appear to be ~.3 x 10^6 (see Slinn 1978a). Available data for submicron aerosol particles indicate $v_d \sim 0.1$ cm/s although there is much debate on this value. Using these inputs, the residence time is approximately two days in winter, and four days in summer.

In these examples, washout ratios have been used since many data studies report washout ratios. The relationship between w_r and $\overline{E}$ is

approximately

$$w_r \simeq \frac{h_w \bar{E}}{2 R_m} \quad . \tag{63}$$

See Slinn (1978a). The scale height, h_w, has been defined in Equation 56. If $h_w \sim 1$ km and $2 R_m \sim 1$ mm, then $w_r \sim 10^6 \bar{E}$. All experimentally observed washout ratios are typically near 10^6 in nondimensionalized form.

As one final example, consider magnesium aerosol particles of mass mean diameter 5.7 μm. For midwestern convective storms, w_r of approximately 0.4×10^6 has been reported (Gatz, 1976). If the dry deposition velocity for these particles is ~.5 cm/s, then the residence time in summer is approximately three days. If the dry deposition velocity is ~1 cm/s, the residence time reduces to slightly less than two days.

A recent experimental investigation of below-cloud plume washout reported by Radke, Elgroth, and Hobbs (1978), suggests the collection efficiency may vary from .1 to 1 over a particle size range of .1 to 10 μm. These results indicate small particles may grow rapidly in a humid environment, and thus be scavenged at a rate much higher than anticipated. The consequences of these results indicate precipitation scavenging is very important even for submicron particles.

After reviewing reported dry deposition velocities and washout ratios, it is safe to say the range shown in Figure 10 contains the correct combination of practically any pollutant in any meteorological conditions. Of course, it is possible that $\bar{E} > 1$ if electrical forces are important. Also, if submicron particles are such that they do not grow

by water vapor condensation, then it is possible that $\overline{E} < .01$. Many more experimental results will be needed before we can unequivocally say the residence time of some species is x number of days.

B. Contributions from Wet and Dry Removal

It is easily shown that the total resistance to removal of a species from the atmosphere is obtained by adding the resistance of individual processes like adding electrical resistances in parallel. For the case that dry deposition and precipitation scavenging are the only removal processes, this means

$$\frac{1}{E(T)} = \frac{1}{E(T_d)} + \frac{1}{E(T_w)} \quad . \tag{64}$$

Thus, the overall residence time will always be less than the residence time associated with the fastest removal process. From Equation 64 it is seen that if one removal mechanism proceeds at a rate ~10 times faster than the other, then the total residence time is approximately the residence time of this faster individual removal process.

The relative contributions of wet and dry removal will depend on the physical-chemical characteristics of the pollutant (v_d and $\overline{E}$), and on the meteorological conditions. Our investigation of the Lagrangian distribution of wet and dry periods enables us to determine the relative contributions only as a function of the specific pollutant. Figure 11 shows the regions in the v_d - $\overline{E}$ plane where dry deposition is more important, and where precipitation scavenging dominates the total removal process.

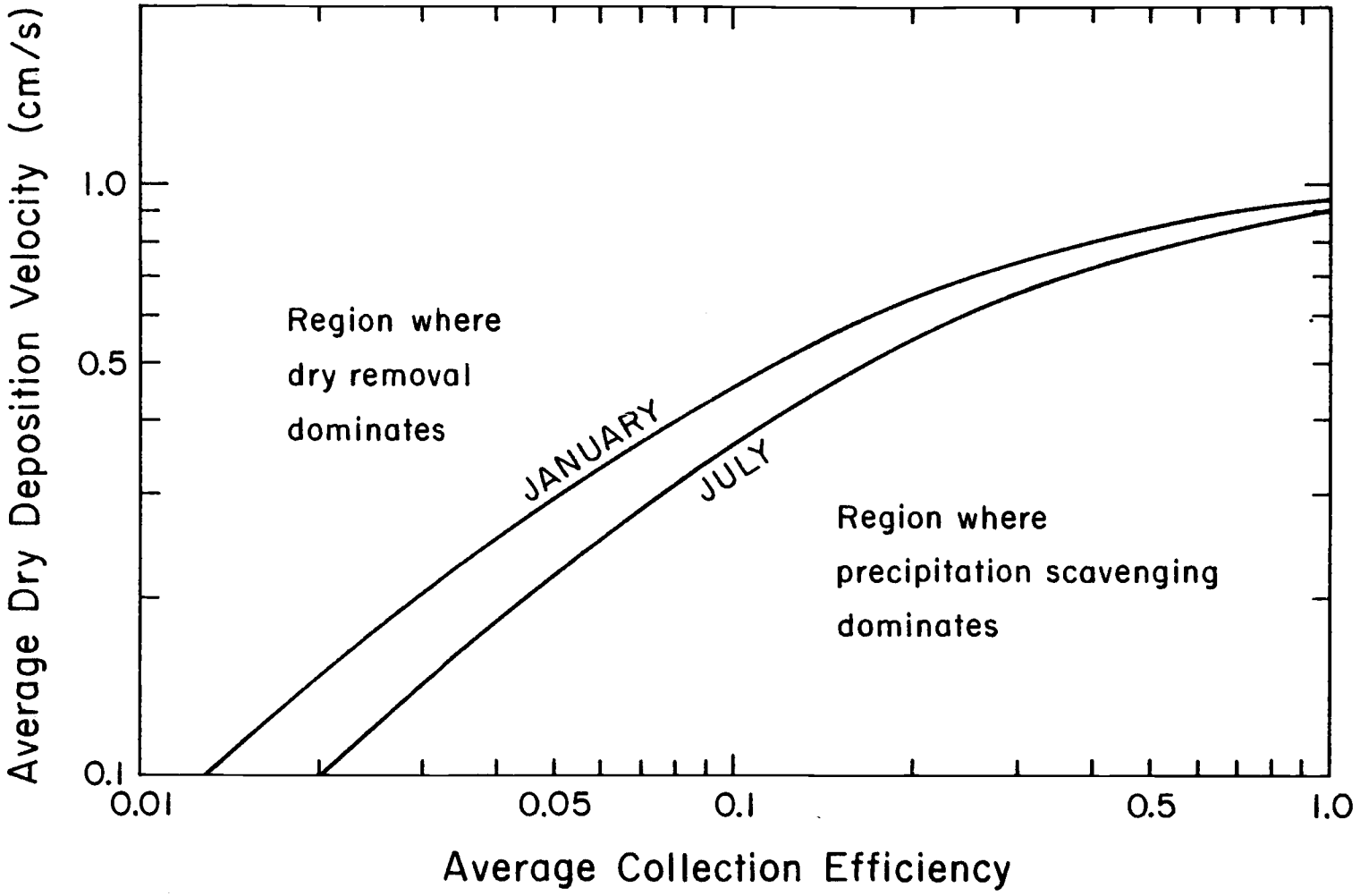

Figure 11. The relative importance of wet and dry removal to the overall residence time.

The figure indicates that if v_d = 1 cm/s, dry removal will always be the faster removal process unless $\overline{E} > 1$. Thus, we can conclude that for SO_2, dry removal appears to be much more efficient than precipitation scavenging year round. On the other hand, for small aerosol particles with $v_d \sim .1$ cm/s, scavenging will be the dominant removal mechanism. It is seen from the figure that dry deposition is more important in the summer months, even though the scavenging coefficient ($\lambda_d = v_d/h$) is less than in winter. This, of course, is caused by the more frequent occurrence of sustained dry periods in the summer.

IX. SUMMARY

We believe the results of this study present improved estimates of the atmospheric residence time of pollutants subjected to precipitation scavenging and dry deposition. Our results have been left general because of uncertainties in the removal rates during dry and wet periods. The dry deposition velocity and effective collection efficiency (or washout ratio) are not known well for any particular pollutant, and will certainly vary for different pollutants of interest. The dry and wet removal height scales, h_d and h_w, are also uncertain, although probably less so that $\bar{E}$ and v_d. Notwithstanding the uncertainties we have referred to, such as the validity of the trajectories and the parameterizations for wet and dry removal, the residence times we have reported represent our best estimates.

In general, the results show that the expected residence time is nearly a factor of two longer in summer than in winter. While the mean precipitation rate is four times higher in summer, the higher probability of rain, nearly seven times as great, in the winter, more than compensates for the lower precipitation rate. Thus, in the winter months, we can expect material released into the atmosphere to be deposited on the ground close to the source region, while in summer, the deposition pattern will be shifted downwind by roughly a factor of two.

Figure 12 shows the distribution function for the residence time. We conclude that for aerosol particles with monthly average dry deposition velocities ~.1 cm/s, and collection efficiencies ~.2, 90 percent of the time (representative of an ensemble average) the residence time

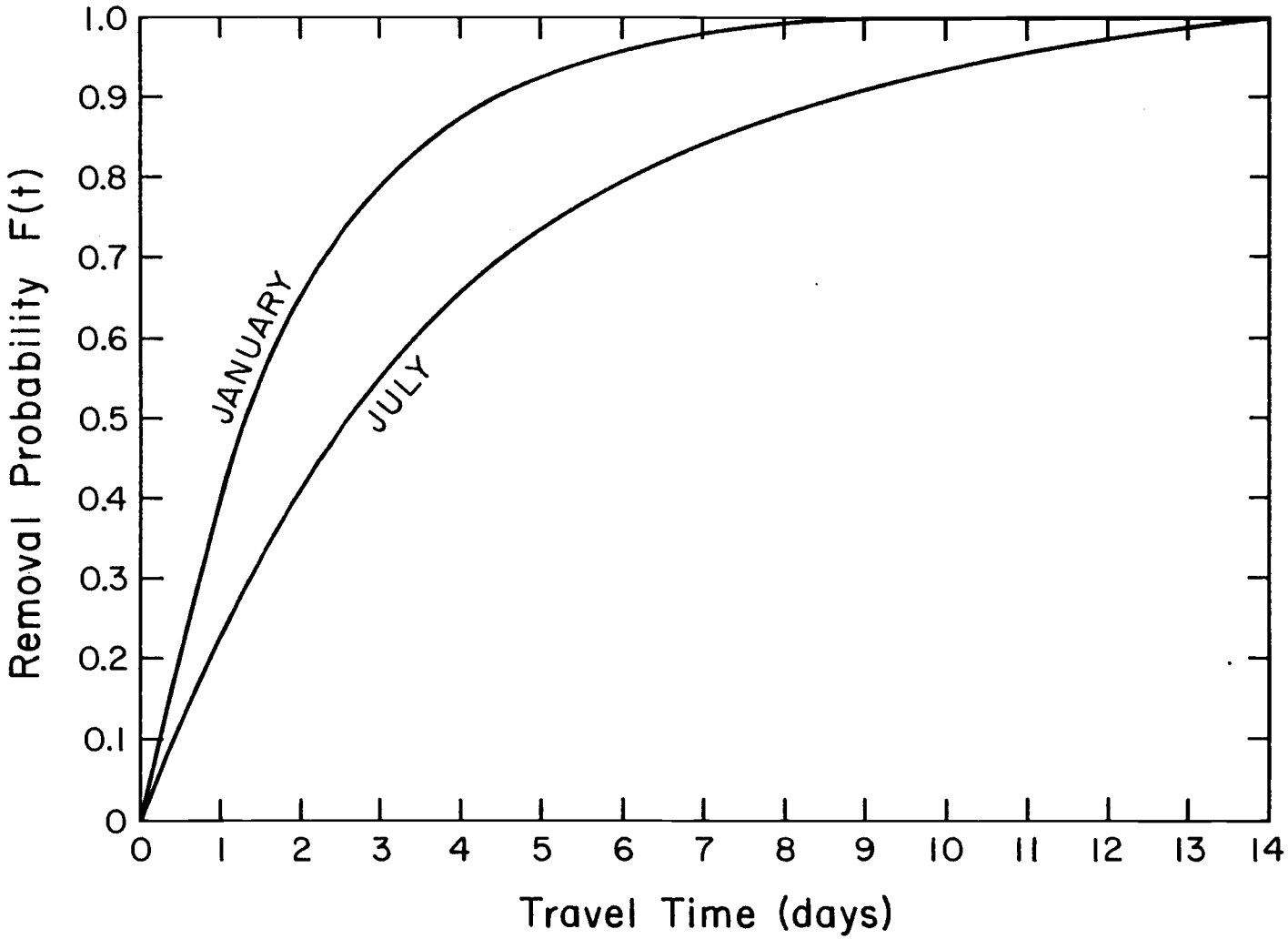

Figure 12. Distribution function of the overall residence time for v_d = 0.1 cm/s and $\bar{E}$ = 0.2.

in the atmosphere will be $\leq$4.5 days in winter, and $\leq$8.5 days in summer. The corresponding expected values are two and four days in January and July, respectively.

A monthly average transport speed of 5 m/s in winter and 4 m/s in summer, results in an e-fold travel distance of 860 km and 1400 km in winter and summer, respectively, when we have specified v_d and $\overline{E}$ as above. These travel distances correspond to the following locations from Kansas City: in 65 percent of the winter trajectories the position is near Toledo, Ohio; in 75 percent of the summer trajectories the location is near Buffalo, New York. Thus, for $v_d \sim .1$ cm/s and $\overline{E} \sim .2$, approximately 60 percent (fraction traveling in this direction times the fraction removed, .70 x .85) of the aerosol particles or trace gas molecules released from Kansas City, will be deposited about a line extending from Kansas City to Portland, Maine.

BIBLIOGRAPHY

Angell, J. K., 1962: On the use of tetroons for the estimation of atmospheric dispersion on the mesoscale. Monthly Weather Rev., 90, 263-270.

Best, A. C., 1950: The size distribution of raindrops. Quart. J. Roy. Meteor. Soc., 76, 16-36.

Bolin, B., G. Aspling, and C. Persson, 1974: Residence time of atmospheric pollutants as dependent on source characteristics, atmospheric diffusion processes and sink mechanisms. Tellus, 26, 185-195.

Burtsev, I. I., V. A. Burtseva, and S. G. Malakov, 1970: in B. Styra et al. (eds.), Atmospheric Scavenging of Radioisotopes, available as TT 69-55099 from NTIS, Springfield, VA.

Chamberlain, A. C., 1960: Aspects of the deposition of radioactive and other gases and particles. In Aerodynamic Capture of Particles, E. G. Richardson (ed.), Pergammon Press, Oxford. Also in Int. J. Air Pollution, 3, 63-88.

Dana, M. T., and M. A. Wolf, 1968: P.N.L. Annual Report for 1968 to the U.S. A.E.C. D.B.E.R., BNWL-1051, pt. 1, 77-81.

Dana, M. T., and M. A. Wolf, 1969: P.N.L. Annual Report for 1968 to the U.S. A.E.C. D.B.E.R., BNWL-1051, pt. 1, 18-25.

Dana, M. T., and M. A. Wolf, 1970: P.N.L. Annual Report for 1969 to the U.S. A.E.C. D.B.E.R., BNWL-1307, pt. 1, 77-81.

Danielsen, E. F., 1961: Trajectories: isobaric, isentropic, and actual. J. Meteor., 18, 479-486.

Durst, C. S., A. F. Crossley, and N. E. Davis, 1959: Horizontal diffusion in the atmosphere as determined by geostrophic trajectories. J. Fluid Mech., 6, 401-422.

Eliassen, A., and J. Saltbones, 1975: Decay and transformation rates of SO_2 as estimated from emission data, trajectories, and measured air concentrations. Atmos. Env., 9, 425-429.

Gabriel, K. R., and J. Neumann, 1962: A Markov chain model for daily rainfall occurrence at Tel Aviv. Quart. J. Roy. Meteor. Soc., 88, 90-95.

Gatz, D. F., 1976: Scavenging ratio measurements in METROMEX. Ph.D. Thesis and USAEC Rept. COO-1407-6, University of Michigan, Ann Arbor, MI.

Gaver, D. P., Jr., 1963: Random hazard in reliability problems. Technometrics, 5, 211-225.

Gifford, F. A., Jr., 1968: An outline of theories of diffusion in the lower layers of the atmosphere, in D. H. Slade (ed.), Meteorology and Atomic Energy, 1968, available as TID-24190 from NTIS, Springfield, VA.

Heffter, J. L., 1965: The variation of horizontal diffusion parameters with time for travel periods of one hour or longer. J. Appl. Meteor., 4, 153-156.

Heffter, J. L., and A. D. Taylor, 1975: A regional-continental scale transport, diffusion and deposition model. NOAA Technical Memorandum ERL ARL-50.

Henmi, T., E. R. Reiter, and R. Edson, 1977: Residence time of atmospheric pollutants and long-range transport. Env. Research Papers, 12, Colorado State University, Fort Collins, CO.

Hicks, B. B., and M. L. Wesely, 1978: Recent results for particle deposition obtained by the eddy-correlation method. A paper presented at AIChE meeting on June 7, 1978, in Philadelphia, PA.

Hoecker, W. H., 1977: Accuracy of various techniques for estimating boundary-layer trajectories. J. Appl. Meteor., 16, 374-383.

Holzworth, G. C., 1972: Mixing Heights, Wind Speeds, and Potential for Urban Air Pollution Throughout the Contiguous United States. Available as Office of Air Programs Publication No. AP-101, Research Triangle Park, NC.

Junge, C. E., and P. E. Gustafson, 1957: On the distribution of sea salt over the U.S. and its removal by precipitation. Tellus, 9, 164-173.

Lamb, R. G., 1973: Note on application of k-theory to turbulent diffusion problems involving chemical reactions. Atmos. Env., 7, 235.

Mason, B. J., 1971: The Physics of Clouds, 2nd Ed., Clarendon Press, Oxford, 659 pp.

Panofsky, H. A., and G. W. Brier, 1958: Some applications of statistics to meteorology. Pennsylvania State University, University Park, PA.

Pasquill, F., 1961: The estimation of the dispersion of windborne material. Meteor. Mag., 90 (1063), 33-49.

Prahm, L. P., U. Torp, and R. M. Stern, 1976: Deposition and transformation rates of sulphur oxides during atmospheric transport over the Atlantic. Tellus, 28, 355.

Radke, L. F., M. W. Eltgroth, and P. V. Hobbs, 1978: Precipitation scavenging of aerosol particles, in pp. 44-48 of Preprints, Conf. on Cloud Physics and Atmospheric Electricity, Issaquah, WA, July 31-August 4, 1978. Available from the Amer. Meteor. Soc., Boston, MA.

Roberts, O. F. T., 1923: The theoretical scattering of smoke in a turbulent atmosphere. Proc. Roy. Soc., London, Ser. A, 104, 640-654.

Rodhe, H., and J. Grandell, 1972: On the removal time of aerosol particles from the atmosphere by precipitation scavenging. Tellus, 24, 442-454.

Scriven, R. A., and B. E. A. Fisher, 1975: The long range transport of airborne material and its removal by deposition and washout. Atmos. Env., 9, 49-58.

Seinfeld, J. H., 1975: Air Pollution, Physical and Chemical Fundamentals, McGraw-Hill, Inc., pp. 260-342.

Slade, D. H., (Ed.), 1968: Meteorology and Atomic Energy 1968, available as TID-24190 from NTIS, Springfield, VA.

Slinn, W. G. N., 1977: Some approximations for the wet and dry removal of particles and gases from the atmosphere. Water, Air, and Soil Pollution, 7, 513-543.

Slinn, W. G. N., 1978a: Precipitation Scavenging, Chapter 11 of Atmospheric Sciences and Power Production - 1979, D. Randson (ed.), in press.

Slinn, W. G. N., 1978b: Relationships between removal processes and residence times for atmospheric pollutants. Env. International, in press.

Slinn, W. G. N., 1978c: Parameterizations for resuspension and for wet and dry deposition of particles and gases for use in radiation dose calculations. Nuclear Safety, 19, 205-219.

Slinn, W. G. N., L. Hasse, B. B. Hicks, A. W. Hogan, D. Lal, P. S. Liss, K. O. Munnich, G. A. Sehmel, and O. Vittori, 1978: Some aspects of the transfer of atmospheric trace constituents past the air-sea interface. Atmos. Env., 12, 2055-2087.

Tennekes, H., and J. L. Lumley, 1972: A First Course in Turbulence, MIT Press, Cambridge, MA, and London, England.

United States Environmental Protection Agency, 1976: 1973 National Emissions Report, National Air Data Branch, Monitoring and Data Analysis Division. Publication No. EPA-450/2-76-007. Available from Library Services Office (MD35), Research Triangle Park, NC.

Weiss, L. L., 1964: Sequences of wet or dry days described by a Markov chain probability model. Monthly Weather Rev., 92, 169-176.

Wesely, M. L., B. B. Hicks, W. P. Dannevik, S. Frisella, and R. B. Husar, 1977: An eddy-correlation measurement of particulate deposition from the atmosphere. Atmos. Env., 11, 561-563.

APPENDIX A

APPENDIX A

The purpose of this appendix is to demonstrate how the residence time may be used in the time averaged convective diffusion equation describing a pollutant's behavior in the atmosphere. The residence time (also called the e-fold time even though an exponential time dependence is not necessary) is a useful parameter when describing the distribution of a pollutant released into the atmosphere and subjected to a destruction or removal rate. Under certain conditions, to be discussed, the spatial distribution of pollutant mass can be described by a Gaussian function times an exponential term which contains the residence time.

To see how the residence time can appear in a formulation, consider the concentration in air of some species, $C(x,y,z,t)$. This concentration must satisfy the continuity equation

$$\frac{\partial C}{\partial t} + \nabla \cdot (\vec{V}C) = D\nabla^2 C + G - L \qquad \text{(A-1)}$$

where $\vec{V}$ is the three-dimensional fluid velocity, D the molecular diffusivity of the species in the fluid, and G and L represent gain and loss rates per unit volume, respectively. The gain rate may include generation of the species by physical-chemical reactions in the atmosphere (secondary sources), and direct generation by primary sources. The loss rate per unit volume is caused by destruction of the species via physical-chemical reactions, and precipitation scavenging. Dry deposition may be included in L, although it is more customary to include the effects of dry deposition through appropriate boundary conditions.

In addition to the species continuity equation, the fluid velocity and the temperature (in general the chemical reaction rates are temperature dependent) must satisfy the Navier-Stokes and energy equations. Also, the Navier-Stokes and energy equations are coupled, through the fluid velocity and temperature, with the fluid continuity equation and the equation of state. This means that in general it is necessary to simultaneously solve the coupled equations of mass, momentum, and energy conservation to account for the variation of fluid velocity, temperature, and air concentration of the species.

However, when C represents the concentration in air of some trace material, a simplification may be made. For most pollutants of interest C is a very small amount, typically a few parts per million. A reasonable assumption at this point, is to assume that the meteorological variables are not affected by the presence of the species. If this is the case, the continuity equation for the trace material may be solved independently of the fluid momentum and energy equations.

With this great simplification of the problem made, Equation A-1 completely describes the pollutant's atmospheric behavior. However, because the atmosphere often exhibits a turbulent nature, the fluid velocity must be recognized as a random variable. This in turn means the concentration is a random variable. Hence, we cannot solve Equation A-1 exactly.

Recognizing the randomness of $\vec{V}$ and C, a natural procedure is to partition the variables into mean and fluctuating components, and then solve for the mean states. Accordingly, let

$$\vec{V} = \bar{\vec{V}} + \vec{V}'$$
$$C = \bar{C} + C' \qquad \text{(A-2)}$$

where an overbar indicates a time average and a prime the fluctuating component. If we now substitute Equations A-2 into Equation A-1, and then time average the resulting equation, the result is

$$\frac{\partial \bar{C}}{\partial t} + \nabla \cdot (\bar{\vec{V}}\bar{C}) + \nabla \cdot \overline{(\vec{V}'C')} = D\nabla^2\bar{C} + \bar{G} - \bar{L} \quad . \qquad \text{(A-3)}$$

To obtain A-3 it has been assumed that G and L are linear in C.

Equation A-3 contains two dependent variables, $\bar{C}$ and $\overline{\vec{V}'C'}$. Separating our random variables into mean and fluctuating parts has resulted in a closure problem (we have one equation and two unknowns). This is the, as yet unsolved, closure problem of turbulence theory. A semi-empirical approach which solves the closure problem, but by no means is an exact representation of the real physical processes, is called K theory, or the mixing length model.

The K theory assumes the existence of an eddy diffusivity, analogous to molecular diffusivity, such that

$$\overline{\vec{V}'C'} = -K \cdot \nabla\bar{C} \qquad \text{(A-4)}$$

where K is the second order tensor, $\{K_{jk}\}$, turbulent diffusivity. Thus, in summation notation,

$$\overline{u_j'C'} = -\{K_{jk}\}\frac{\partial \bar{C}}{\partial x_k} \qquad j=1,2,3 \quad . \qquad \text{(A-5)}$$

Equation A-5 is nothing more than the definition of the proposed eddy diffusivity. In general $\{K_{jk}\}$ represents six unknowns since $K_{jk} = K_{kj}$. However, when the coordinate axis coincide with principal axes of $\{K_{jk}\}$, then $\{K_{jk}\} = o$ unless $j = k$. See Seinfeld (1975).

Thus, for the case that (x,y,z) are along the principal axes of K_{jk}, the parameters k_{xx}, k_{yy}, and k_{zz} are defined such that

$$\left.\begin{aligned} \overline{u'C'} &= -k_{xx}\frac{\partial \overline{C}}{\partial x} \\ \overline{v'C'} &= -k_{yy}\frac{\partial \overline{C}}{\partial y} \\ \overline{w'C'} &= -k_{zz}\frac{\partial \overline{C}}{\partial z} \end{aligned}\right\} \qquad \text{(A-6)}$$

For a discussion of the validity of using the K parameterization, see Lamb (1973). Very briefly, we conclude the K theory is reasonable if the gain and loss rates are "slow," and when the distribution of sources is "smooth." See Seinfeld (1975).

Substituting Equations A-4 into A-3, we obtain the often called "semi-empirical equation of atmospheric diffusion," given by

$$\frac{\partial \overline{C}}{\partial t} + \nabla \cdot (\overline{\vec{V}}\,\overline{C}) + \nabla \cdot (-\vec{K} \cdot \nabla \overline{C}) = D\nabla^2 \overline{C} + \overline{G} - \overline{L} \qquad \text{(A-7)}$$

where $\vec{K} = k_{xx}\hat{i} + k_{yy}\hat{j} + k_{zz}\hat{k}$. If we now assume incompressibility of the fluid, and ignore molecular diffusion compared to the "diffusion" caused by the eddy diffusivity (see Tennekes and Lumley 1972), A-7 reduces to

$$\frac{\partial \overline{C}}{\partial t} + \overline{\vec{V}} \cdot \nabla \overline{C} = \nabla \cdot (\vec{K} \cdot \nabla \overline{C}) + \overline{G} - \overline{L} \quad . \qquad \text{(A-8)}$$

At this point we will invoke a further simplification. If the eddy diffusivity is independent of the spatial coordinates, Equation A-8 is more readily solved. In particular, when k_{xx} is independent of x, and so forth, the diffusion is called Fickian, and the fundamental solutions are Gaussian functions. These solutions are possible when $\overline{G}$ and $\overline{L}$ are linearly dependent on $\overline{C}$.

Consider steady state Fickian diffusion of material from a continuous point source, with the mean wind in the x direction. When the eddy diffusion in the downwind direction is negligible compared to the mean transport, Equation A-8 becomes

$$\overline{u}\,\frac{\partial \overline{C}}{\partial x} = k_{yy}\,\frac{\partial^2 \overline{C}}{\partial y^2} + k_{zz}\,\frac{\partial^2 \overline{C}}{\partial z^2} + \overline{G} - \overline{L} \quad . \tag{A-9}$$

If the gain rate per unit volume from secondary sources is zero, and if the time averaged loss rate may be written as

$$\overline{L} = \overline{\Psi}\,\overline{C} \tag{A-10}$$

where $\overline{\Psi}$ is also independent of position (thus applicable to release of a particular species from a particular region), then the equation is easily solved. For the case of a time and space independent removal rate, the residence time is given by $E(T) = \Psi^{-1}$.

If we now make the substitution (Slinn 1978c)

$$B = \overline{C}\,\exp(\overline{\Psi}x/\overline{u}) \tag{A-11}$$

the expression for B is

$$\overline{u}\,\frac{\partial B}{\partial x} = k_{yy}\,\frac{\partial^2 B}{\partial y^2} + k_{zz}\,\frac{\partial^2 B}{\partial z^2} \quad . \tag{A-12}$$

Thus the air concentration is equal to B $\exp(-\overline{\Psi}x/\overline{u})$, where B is represented by a Gaussian function. See Gifford (1968).

For a continuous point source at height h above the surface, where we assume plume reflection by the surface, the expression for the concentration in air (under the same restrictions as already mentioned) becomes

$$\overline{C}(x,y,z) = \frac{\dot{Q}}{2\pi\overline{u}\sigma_y\sigma_z} \exp(-y^2/2\sigma_y^2) \left\{ \exp\left(-(z-h)^2/2\sigma_z^2\right) + \exp\left(-(z+h)^2/2\sigma_z^2\right) \right\} \exp\left(-x/\overline{u}E(T)\right) \quad . \tag{A-13}$$

In Equation A-13, $\dot{Q}$ is the source strength, and σ_y^2 and σ_z^2 are the variances of the distribution in the y and z directions, respectively. These variances are related to the eddy diffusivity and mean square velocity fluctuations via

$$\sigma_{y,z}^2 = 2K_{y,z}t = (\overline{v',w'})^2 \, t^2 \tag{A-14}$$

where $t = x/\overline{u}$, thus specifying the sigmas in terms of x.

As we have stated, Equation A-13 is semi-empirical. Many diffusion and transport experiments have been done to determine $\sigma_y(x)$ and $\sigma_z(x)$, for various atmospheric stability and turbulence level conditions. The work done on this problem is fairly well documented for $x \lesssim 100$ km (see Pasquill 1961). For long-range transport and diffusion we refer to Panofsky and Brier (1958), Angell (1962), and Durst *et al.* (1957). Slade (1968) summarizes the many experiments done in this area.

APPENDIX B

APPENDIX B

The following illustrates an example of how the semi-empirical equation of diffusion, Equation A-7 in Appendix A, can be applied. We will seek a solution for the monthly mean concentration in air of some pollutant. The concentrations predicted by the solution should be similar to the concentrations measured at air quality monitoring sites if: the instruments sample for long periods (~24 hours), the subsequent observations are averaged for the month, and if we have included all important sources (in our example only one source, located at Kansas City, Missouri, is considered).

One method of estimating the downwind concentration distribution from a source relies on a Gaussian puff description. If we start a trajectory every hour from the source for the whole month, and determine the distribution of the end points after successive time intervals, we have an estimate of the transport and dispersion. If at any particular travel time from the source, $(\bar{x},\bar{y},\bar{z})$ represents the mean location, and $(\sigma_x,\sigma_y,\sigma_z)$ represents the standard deviations of the end points in the respective directions, then the concentration at this particular time is

$$C(x,y,z,t) = \frac{Q}{(2\pi)^{3/2}\sigma_x\sigma_y\sigma_z} \exp\left\{-\left[\frac{(x-\bar{x})^2}{2\sigma_x^2} + \frac{(y-\bar{y})^2}{2\sigma_y^2} + \frac{(z-\bar{z})^2}{2\sigma_z^2}\right]\right\} \quad \text{(B-1)}$$

where Q is the total source strength, $Q = \int_o^T \dot{Q}dt$, T = 1 month. To obtain the monthly average concentration we integrate Equation B-1

$$\bar{C}(x,y,z,) = \frac{1}{T}\int_o^T C(x,y,z,t)\, dt \quad . \quad \text{(B-2)}$$

In practice, the concentration is calculated with Equation B-1 for each successive time step ($\Delta t \sim 1$ hour). Following this procedure until the pollutant has completely passed the location of interest, the contributions to $\overline{C}$ are then summed, and the result multiplied by dt/T. This technique is commonly referred to as a Gaussian puff model.

The puff model is useful in that a mean, steady wind velocity, $\overline{u}$, is not required. The mean wind velocity, as determined by the trajectory climatology, can go to zero, reverse direction, etc. This is in contrast to the plume model (an integrated form of the puff model), since in the steady state plume model the wind velocity, $\overline{u}$, appears explicitly, and must be a constant. The disadvantages of the puff model are the many calculations required for the numerical integration.

If the mean displacement velocity is constant, we can analytically integrate the puff model to obtain the steady-state plume (or spreading-disk) model. From Roberts' (1923) solution of the equation

$$\frac{\partial C}{\partial t} = K\nabla^2 C \tag{B-3}$$

where the coordinates are then stretched by introducing a mean wind, $\vec{\overline{V}} = \overline{u}\hat{i} + \overline{v}\hat{j} + \overline{w}\hat{k}$, the solution is

$$C(x,y,z,t) = \frac{Q}{8(\pi t)^{3/2}(K_x K_y K_z)^{1/2}} \exp\left\{-\frac{1}{t}\left[\frac{(x-\overline{u}t)^2}{4K_x} + \frac{(y-\overline{v}t)^2}{4K_y} + \frac{(z-\overline{w}t)^2}{4K_z}\right]\right\} \tag{B-4}$$

which is equivalent to Equation B-1 when

$$\sigma^2_{x,y,z} = 2K_{x,y,z}t \quad . \tag{B-5}$$

The right-hand side of Equation B-4 can be integrated by Laplace Transform techniques.

The result for the concentration at z = o, and $\overline{w}$ = o, including surface reflection, is

$$C(x,y,o) = \frac{\dot{Q}}{2\pi(K_h K_z)^{1/2}|R|} \exp - \left\{ \frac{|R||V|}{2K_h} (1-\cos\theta) \right\} \tag{B-6}$$

where $\vec{R} = x\hat{i} + y\hat{j}$, $K_h = K_x = K_y$, $\vec{V} = u\hat{i} + v\hat{j}$, and where θ equals the angle between $\vec{R}$ and $\vec{V}$. For example, if the location is directly downwind (θ = o), then

$$C(x,y,o) = \frac{\dot{Q}}{2\pi(K_h K_z)^{1/2}(x^2+y^2)^{1/2}} \quad . \tag{B-7}$$

We will now consider the monthly mean air concentration caused by a continuous release of pollutant from Kansas City, Missouri. The transport and dispersion is based on a series of 31 trajectories emanating from the source. The mean positions and one standard deviation around these central points, are shown in Figure 13. Surprisingly, the path is approximately a straight line! Also, the speeds of travel for each 12-hour segment are very nearly equal (they range from 13-20 km/hr). Thus, for this case, the plume model may be applied. The appropriate equation has been noted as Equation A-13 in Appendix A.

Figure 13. Average winter monthly dispersion of a series of trajectories emanating from Kansas City. Twelve hourly mean positions and one standard deviation around these positions are indicated. Trajectories are followed for four days.

It should be mentioned that the standard deviations, σ_x and σ_y, as determined by the distribution of end points at 12 hourly intervals, were not exactly equal as indicated by Figure 13. At each time interval, the variance in the north-south direction, σ_y^2, was slightly larger than σ_x^2. The difference, in terms of $(\sigma_y-\sigma_x)/\sigma_y$ was less than 10 percent until the travel time was 3.5 days. After four days the difference was 18 percent. Because of the approximate nature of our calculations we have let $\sigma_x = \sigma_y = (\sigma_x + \sigma_y)/2$.

Equation A-13 with z = o becomes

$$\overline{C}/\dot{Q} = (\pi \overline{u} \sigma_y \sigma_z)^{-1} \exp\left\{ - \left[\frac{y^2}{2\sigma_y^2} + \frac{h^2}{2\sigma_z^2} + \frac{x}{\overline{u}E(T)} \right] \right\} . \qquad \text{(B-8)}$$

The dispersion parameter, σ_y, was assumed to be of the form $\sigma_y = x^a$. Regression analysis gave a = 0.989. Thus, because of our long time-average, $\sigma_y \sim x$! The vertical dispersion parameter, σ_z, was set equal to one-half of the mean mixed layer height, H. Letting σ_z = 1/2 H at $x \leq 300$ km, and then 1/2 H_T at $x > 300$ km (H_T is the mean tropopause height) results in a factor of 5 reduction in the values of $\overline{C}/\dot{Q}$ obtained using σ_z = 1/2 H. The effective height of pollutant release was set equal to the base height of the layer in which the trajectories were calculated (h = 100 m). The average 12 hourly segment wind speed, $\overline{u}$, was 4.7 m/s. The residence time, E(T), was set equal to four days.

Using these inputs, we have shown in Figure 14 the air concentration distribution from a source at Kansas City. The values indicate January average values of the concentration. C has units of $\mu g/m^3$, and

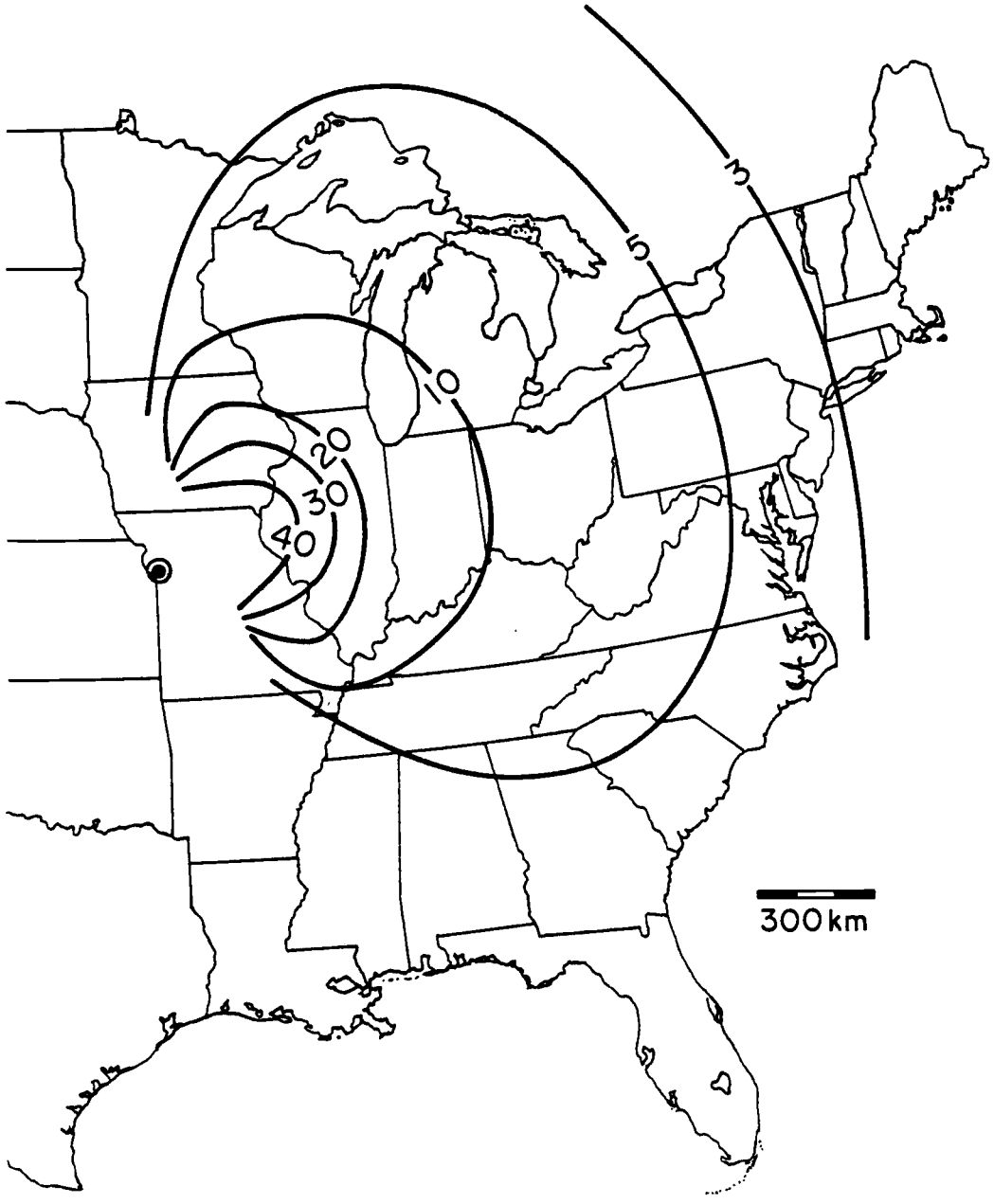

Figure 14. Steady-state winter monthly distribution of pollutant mass released from Kansas City. Values shown are $\bar{C}/\dot{Q}$ where $\bar{C}$ is in [$\mu g/m^3$] and $\dot{Q}$ is in [100 kg/s].

$\dot{Q}$ has units of 100 kg/s. Since the mean "wind" was steady, the distribution is simply symmetrical about the mean wind direction.

For example, if the particulate released from the metropolitan Kansas City area is 73,300 tons/year (see U.S. E.P.A. 1976, National Emissions Report), then $\dot{Q}$ = 0.02 [100 kg/s]. If the residence time of this particulate is ~4 days, then the average concentration over northern New York State is ~0.08 $\mu g/m^3$. Approximately 450 km downwind, over central Illinois, the concentration is ~0.6 $\mu g/m^3$. Of course, on any particular day, the concentration at a point in the northeastern United States, caused by a source at Kansas City, can be much greater than 0.08 $\mu g/m^3$. In order to demonstrate a calculation for a shorter time-averaged air concentration, consider the following.

If on any particular day a trajectory originating from Kansas City follows a path directly to a northeast location, the air concentration may be estimated as follows. Equation B-8 still holds, although now σ_y represents the diffusion of the material caused by fluctuations in the velocity components, and the vertical shear of these components. This is in contrast to our previous use of σ_y, which represented the dispersion of a series of trajectories. Heffter (1965) suggests for long-range transport, $\sigma_y[m] = 0.5t[s]$. If we use K_z = 5 m^2/s as an average value for the lower troposphere, then σ_z^2 = 10 m^2/s t. Using these values, with h = 100 m, $\bar{u}$ = 8 m/s (winter average wind speed in the afternoon mixed layer, from Holzworth 1972), and a residence time of four days, the air concentration at the surface may be calculated.

According to the plume model, the air concentration near Syracuse, New York, caused by a source of particulate at Kansas City of $\dot{Q}$ = 0.02[100 kg/s], would be ~0.3 $\mu g/m^3$. This value is for the values of the parameters given in the previous paragraph. If the residence time is increased by an order of magnitude (40 days), the concentration becomes ~.5 $\mu g/m^3$. These values may represent two day average values of the concentration (the wind is steady for the length of travel time, ~2.4 days).

It is impossible to calibrate the model because we have not included all the sources important to the air quality level at the location. For long-range transport studies, many sources become important, and adequately accounting for them all is beyond the scope of this work. However, using a detailed emission inventory, a trajectory climatology similar to what has been outlined, and appropriate values for the residence time as described in the text, air quality model results may be compared to observed air concentrations to test the accuracy of such dispersion and removal parameterizations.