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ATMOSPHERIC SOURCE-RECEPTOR  
RELATIONSHIPS: CONCEPTS AND  
TERMINOLOGY

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## SUMMARY

This report reviews a number of conceptual bases for the interpretation of atmospheric source-receptor phenomena, including spatial attributes, nonlinearity, and temporal attributes. Source-receptor properties are commonly expressed and interpreted in terms of statistical parameters. Definitions of these parameters often vary from one user to the next, however, and the resulting potential for confusion suggests the need for a standard and accepted set of terms for applied use.

Time-averaging is an important consideration in describing system linearity/nonlinearity as well as temporal and spatial variability. Unless expressed in terms of a conceptual model (such as a steady-state system) where time-averaging is implied, explicit statement of the averaging time, or period of observation, is necessary for satisfactory definition of pertinent statistical features. This plus a number of additional contributing factors tend to complicate the description of source-receptor phenomena and underline the need for consistent terminology.

This report provides a description of source-receptor linearity as well as several statistical measures of spatial and temporal variability in the source-receptor sequence. These are suggested for use as standard terminology in future source-receptor studies and in applied emission-control policy analyses.

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## CONTENTS

SUMMARY . . . . .	iii
ACKNOWLEDGMENTS . . . . .	v
1.0 INTRODUCTION . . . . .	1
2.0 SPATIAL ATTRIBUTES: SPATIAL DISTRIBUTIONS AND INFLUENCE REGIONS . . . . .	3
3.0 LINEARITY . . . . .	7
3.1 MACROSCOPIC SYSTEMS . . . . .	8
3.2 MICROSCOPIC SYSTEMS AND THEIR INFLUENCE ON MACROSCOPIC SOURCE-RECEPTOR BEHAVIOR . . . . .	14
3.3 SUMMARY COMMENTS ON LINEARITY . . . . .	24
4.0 TEMPORAL ATTRIBUTES: TEMPORAL DISTRIBUTIONS AND RESIDENCE TIMES . . . . .	27
4.1 ATMOSPHERIC RESIDENCE TIMES AND TRANSIENT RESPONSE . . . . .	27
4.1.1 Isolated Mechanisms . . . . .	27
4.1.2 Simultaneous Mechanisms . . . . .	29
4.1.3 Special Cases . . . . .	30
4.1.4 Extension to Continuous Systems . . . . .	32
4.2 ATMOSPHERIC RESIDENCE TIMES AND STEADY-STATE SYSTEMS . . . . .	34
4.2.1 Overview of Bolin-Rodhe Derivation . . . . .	34
4.2.2 Extension of Bolin-Rodhe Derivation to Describe Individual Removal Pathways . . . . .	37
4.2.3 Comparison of Transient-Puff and Steady-State Analyses . . . . .	38
4.2.4 Summary Comments on Temporal Distributions and Residence Times . . . . .	39

5.0 CONCLUSIONS . . . . .	41
6.0 REFERENCES . . . . .	43
APPENDIX - NOMENCLATURE . . . . .	A.1

## FIGURES

1 Hypothetical Spatial Probability-Density Functions for Exposure to a Pollutant Emitted at Center of Grid. . . . .	5
2 Examples of (a) Linear and (b) Nonlinear Source-Receptor Behavior for a Single Receptor Located at Point (x,y). . . . .	9
3 Hypothetical Plot of Measured Source Strength Versus Deposition Rate, Illustrating Conceptual Experiments for Linearity Assessment. . . . .	11
4 Schematic of an Idealized, One-Dimensional Linear System. . . . .	20
5 Schematic of a Continuous Stirred-Atmosphere Reaction System. . . . .	22
6 Linearity Plot for Example Reaction System. . . . .	23
7 Hypothetical Probability-Density Functions for Reactive, Dry-Deposition, and Wet-Deposition Removal Pathways in a Linearly Interactive System. . . . .	33
8 Time Series of Probability-Density Functions for a Series of Instantaneous Puffs. . . . .	35

indiscriminate application in cases where transients occur can lead to confusing, or even erroneous, results. The goal of this report is to review several of the most important of these source-receptor concepts and to provide a group of well-founded definitions and interpretations, which are suggested for standardized use by both the scientific and policy-analysis communities. In reflection of the three basic categories of questions posed above, general classes of these terms include spatial attributes, such as spatial distributions and influence regions, the concept of linearity, and temporal attributes, such as temporal distributions and residence times. These categories will be treated sequentially in the sections immediately following.

## 1.0 INTRODUCTION

The expression "source-receptor relationship" is commonly applied to describe the composite behavior exhibited by a pollutant, from the time that it is emitted to the atmosphere until the time it arrives at its ultimate point of reception. The term "reception" is used here to depict either deposition, or simply observation in the gaseous phase by some type of real or hypothetical monitoring device, at any specific location on the Earth's surface. Elements of source-receptor behavior can be illustrated best in terms of the following questions, which are often posed in the context of its discussion:

1. **Spatial attributes.** What is the spatial concentration (or deposition) pattern associated with a specific pollution source? What fraction of the pollutant molecules arriving at a specific receptor has originated from this source?
2. **Linearity.** What are the changes at a receptor that result from extended changes in source strength, and can this cause-effect relationship be expressed as a linear function?
3. **Temporal attributes.** How do pollutant fluctuations at a receptor relate to fluctuations of the source, and to fluctuations in the atmosphere? How long do pollutant molecules from a specific source reside in the atmosphere before exiting, either through deposition or through physicochemical transformation?

Each of these source-receptor questions is of central importance to emission-control strategy and policy analysis. Unfortunately, however, their interpretation is often clouded by substantial uncertainty; and at present the scientific community is working actively to elucidate interpretive aspects of these questions, and to reduce associated uncertainty levels. As a consequence of this combination of scientific and policy-analysis activity, these questions can be conveniently viewed as **interface points** between atmospheric scientists and policy makers. These interfaces have become especially active during the past several years, as regional/global issues such as ozone transport and acidic deposition have grown in importance.

Several concepts and terms are often encountered when dealing with source-receptor relationships. As is frequently the case with applied atmospheric analysis, the published literature contains a variety of definitions for and interpretations of these terms, which often depend on special conditions and/or modeling assumptions. As a consequence, substantial caution must be exercised when applying published results for the interpretation of particular situations. Quite often, for example, definitions applied in the literature are based on an assumed steady-state process, and



## 2.0 SPATIAL ATTRIBUTES: SPATIAL DISTRIBUTIONS AND INFLUENCE REGIONS

In assessing the effects of atmospheric processes, particularly those associated with pollutant deposition, one is generally concerned with fluxes and concentrations in the immediate vicinity of the Earth's surface. As a consequence we will confine this discussion to surface observations and neglect the distribution of pollutants aloft--a restriction that permits spatial distributions to be viewed simply as two-dimensional entities.

We begin by considering a single, specific source that is emitting a pollutant to its surroundings. If one were to measure the exposure of this pollutant (e.g., its concentration or its deposition flux) at all surface-level points surrounding the source at some instant in time, the resulting field could be represented by

$$\text{exposure}(x,y) = E(x,y) = E_0 f(x,y), \quad (2.1)$$

where  $x$  and  $y$  are coordinate positions relative to the source,  $E_0$  is a normalizing constant, and  $f(x,y)$  is an **instantaneous spatial probability-density function** for pollutant occurrence, which obeys the relationships

$$f(x,y) = \frac{1}{E_0} \frac{\partial^2 \Xi(x,y)}{\partial x \partial y} \quad (2.2)$$

and

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f(x,y) dx dy = 1 \quad (2.3)$$

where  $\Xi(x,y)$  represents a cumulative exposure across the  $(x,y)$  domain. Figure 1a provides a pictorial example of an instantaneous probability-density function corresponding to an arbitrary single source.

Similar density functions can be derived for other receptor attributes, such as wet- and dry-deposition flux fields, as well. All of these density functions have the mathematical properties characteristic of the usual density functions encountered in statistics. In particular the centroid coordinates and standard deviations  $\bar{x}$ ,  $\bar{y}$ ,  $\sigma_x$ , and  $\sigma_y$  of the spatial concentration (or deposition) pattern can be expressed as follows:

$$\bar{x} = \int \int x f(x,y) dx dy, \quad (2.4)$$

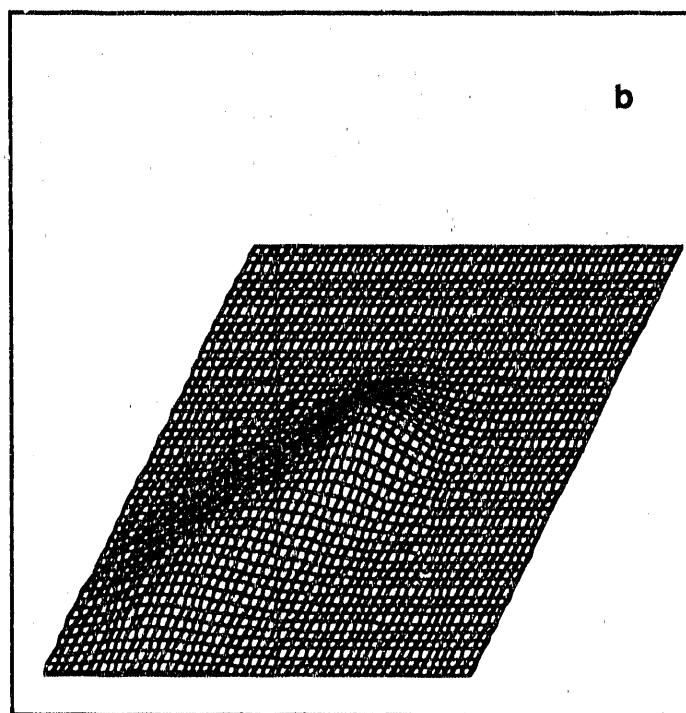
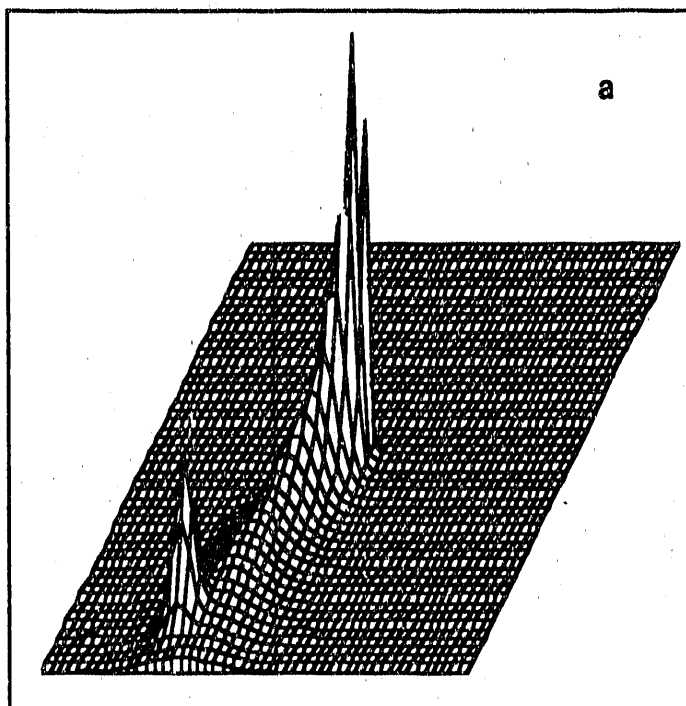
$$\bar{y} = \int \int y f(x,y) dx dy, \quad (2.5)$$

$$\sigma_x^2 = \int \int (x - \bar{x})^2 f(x,y) dx dy, \quad (2.6)$$

$$\sigma_y^2 = \int \int (y - \bar{y})^2 f(x,y) dx dy. \quad (2.7)$$

Parameters for higher moments of the distributions can be obtained using straightforward extensions of these forms. It is important to note the **instantaneous** nature of  $f(x,y)$  and to recognize that similar density functions can be defined that correspond to observations averaged over finite periods of time. In general, one can denote density functions corresponding to averaging times  $\theta$  as  $f_\theta(x,y)$ , where  $f_\theta$  conforms to the mathematical properties noted for  $f$  in Equations (2.2) and (2.3). Because of temporal variations in pollutant behavior, one would expect the field described by  $f_\theta$  to become progressively more smooth with increasing  $\theta$ , as indicated by the curve in Figure 1b. If the temporal variability of  $f$  is free from long-term trends, then for large  $\theta$ ,  $f_\theta(x,y)$  will converge to a limiting distribution, which can be taken to be the long-term average. The moment parameters also will change with averaging time, in reflection of changes of the density function; thus, time-averaged parameters  $\bar{x}_\theta$ ,  $\bar{y}_\theta$ ,  $\sigma_{x\theta}$ , and  $\sigma_{y\theta}$  may be derived, which correspond to the instantaneous parameters in Equations (2.4) through (2.7).

The **influence region** of a specific pollution source is the geographical domain where the source's contributions to pollutant concentration and/or deposition fluxes are considered to be "significant." Obviously this description is flexible, depending on the direct needs associated with the problem at hand. Typical criteria for the bounds of an influence region are **absolute** magnitude, such as the specification of a lower-limit value for  $f_\theta(x,y)$ , or **relative** magnitude, such as specification of a lower-limit ratio of  $f_\theta(x,y)$  to some background contribution. A moderate  $\text{SO}_2$  source in the polluted midwestern United States, for example, would not be expected to make a strong relative contribution to pollution fields at extended downwind distances and thus could be considered to have a limited relative influence region for most practical applications. The Chernobyl plume, on the other hand, could rightfully be stated to have an influence region encompassing the total northern



**FIGURE 1.** Hypothetical Spatial Probability-Density Functions for Exposure to a Pollutant Emitted at Center of Grid: a) Instantaneous Density Function; b) Time-Averaged Density Function.

hemisphere, both on a relative and an absolute basis. Consequently, the term "influence region" should be considered as a qualitative descriptor, unless an explicit quantitative definition has been given to describe some situation of immediate interest.

### 3.0 LINEARITY

The concept of linearity/nonlinearity represents a juncture between science and policy analysis that is a particularly important feature of the present international dialogue on acidic precipitation. In policy analysis, this concept is usually considered from a *macroscopic* viewpoint, that is, in the context of the total source-receptor sequence. Scientific analysis is often concerned with macroscopic manifestations of nonlinearity as well; in addition, however, scientific evaluations frequently deal directly with nonlinearity's causative mechanisms, which tend to be molecular-scale, or *microscopic* in nature. Moreover, a variety of observational scales, falling between these two extremes, is possible. Instead of considering the total source-receptor sequence, for example, one might choose to examine nonlinearities associated with a limited segment of this sequence, such as pollutant ingestion and precipitation scavenging by an isolated storm at some location that is remote from the pollutant's source.

Because of this wide range of analysis scales and also because of diverse terminology applied in associated scientific fields such as mathematics, engineering, and systems research, a variety of interpretations of linearity/nonlinearity have appeared in the atmospheric-sciences literature. In view of the possible confusion associated with these interpretations, there is a need for a standard characterization of linearity/nonlinearity that

- is sufficiently concise to be of practical use for strategic planning by the policy-analysis community
- is sufficiently well-posed to preclude any ambiguity of interpretation
- provides a consistent interpretation over all scales of application, ranging from microscopic systems to the macroscopic source-receptor sequence
- is consistent with (or at least reconcilable with) standard mathematical terminology.

The purpose of this section is to provide such a characterization. We approach this goal in the following subsections by first examining macroscopic aspects of nonlinearity, then scrutinizing microscopic features, and finally discussing the relationships between these two limiting situations.

### 3.1 MACROSCOPIC SYSTEMS

Linearity/nonlinearity in the total source-receptor sequence can be described superficially in relatively simple terms. Basically, if a percentage emission change of a particular pollutant from a specific source results in the same percentage change in exposure of that pollutant from that source--at all receptor points over the source's influence region--then the macroscopic source-receptor process is said to be "linear." That is, the source-receptor relationship can be represented by some equation of the form

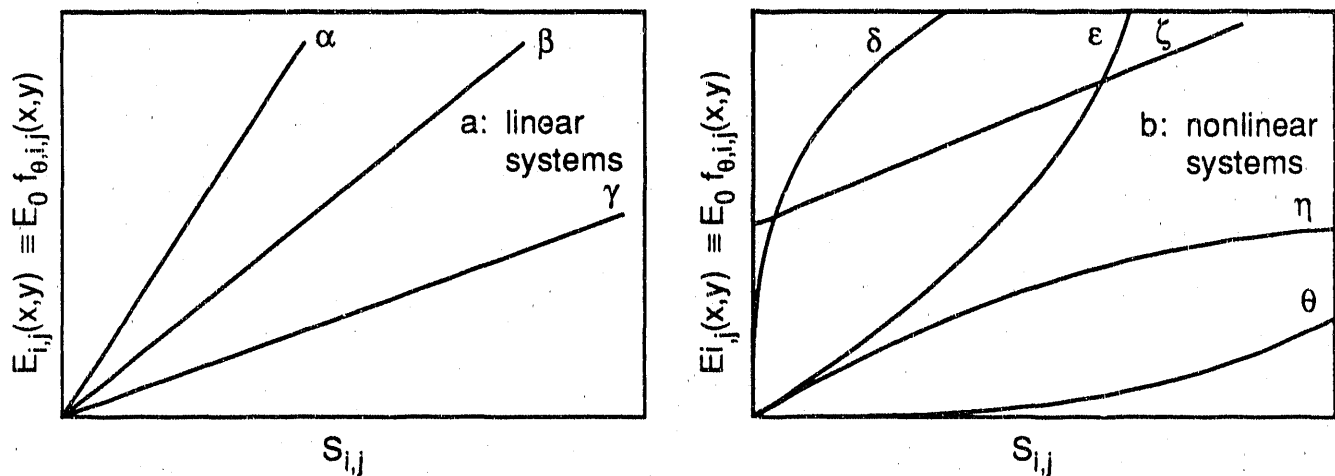
$$E_{\theta,i,j}(x,y) = A_{\theta}(x,y) S_{\theta,i,j} \quad (3.1)$$

where  $E_{\theta,i,j}(x,y)$  is the exposure (e.g., the concentration or deposition flux) of pollutant  $i$  at location  $(x,y)$  that is attributable to source-array  $j$ ,  $S_{\theta,i,j}$  represents the aggregate emission rate of the associated pollution source, and  $A_{\theta}(x,y)$  is a proportionality function. As indicated by the subscript  $\theta$ , a finite averaging time for the observations of  $E_{\theta,i,j}$  and  $S_{\theta,i,j}$  is implied.  $S_{\theta,i,j}$  can characterize a single point-source at some fixed position, or it can depict the combined strength of any chosen array of sources. The latter case is best visualized in terms of a spatial density function  $s_{\theta,i,j}(x,y,z)$  of pollutant emissions, where the source strength at any location,  $\Sigma_{\theta,i,j}(x,y,z)$ , is given by the product of  $S_{\theta,i,j}$  and  $s_{\theta,i,j}(x,y,z)$ .

The property characterized by Equation (3.1) implies that the spatial probability-density function  $f_{\theta,i,j}(x,y)$  for pollutant deposition (or concentration) is insensitive to changes in the aggregate source strength  $S_{\theta,i,j}$ ; in fact, a somewhat more revealing statement of the source-receptor linearity condition can be given as

$$E_{\theta,i,j}(x,y) \equiv E_0 f_{\theta,i,j}(x,y) = A_{\theta}(x,y) S_{\theta,i,j} \quad (3.2)$$

As will be indicated below, these equations do not constitute a complete *definition* of macroscopic linearity. They do suffice, however, to indicate this concept's importance in policy analysis. If the source-receptor behavior is indeed linear, then an acceptable control strategy can be designed in a relatively simple and straightforward manner. Furthermore, confidence in the strategy's ultimate success will be greatly enhanced, because one is assured that any incremental rollback in emissions will be directly reflected by a proportionate drop in exposure to the associated pollutants at the receptor. Several hypothetical examples of linear and nonlinear systems, as characterized in the context of this report, are shown in Figure 2.



**FIGURE 2.** Examples of (a) Linear and (b) Nonlinear Source-Receptor Behavior for a Single Receptor Located at Point  $(x,y)$ . The density function  $s_{ij}(x,y,z)$  characterizing the source distribution is stipulated to remain constant under these conditions, although the composite source strength  $S_{ij}$  is allowed to vary.

Equations (3.1) and (3.2) are potentially useful for evaluating the presence or absence of macroscopic linearity. One could, for example, observe a source-receptor system for two different time periods (say  $\theta_1$  and  $\theta_2$ ), each of which involves a different source strength ( $S_{\theta_1,i,j}$  and  $S_{\theta_2,i,j}$ ). Subsequent comparison of the resulting exposures  $E_{\theta_2,i,j}$  and  $E_{\theta_1,i,j}$  would allow direct evaluation of system conformance to Equation (3.1), and thus to linearity. Although this appears superficially to be a simple and straightforward process, a number of conditions must be satisfied for valid application of Equations (3.1) and (3.2). Explicit recognition of these conditions, summarized below, is essential for interpretation of system linearity.

1. Explicit designation of the source array (characterized by index  $j$  in Equations (3.1) and (3.2)), and distinction between pollutant that has originated from this array and that which has not, is critically important. Ignoring this requirement can lead to a serious misinterpretation of system linearity/nonlinearity. Definitive source attribution is a major problem in field measurements of source-receptor nonlinearity, because usually no convenient way exists to determine explicitly the sources responsible for specific contributions to the pollutant levels observed at a receptor site.
2. Equations (3.1) and (3.2) are valid characterizations of linearity only if the source density-function  $s_{\theta,i,j}(x,y,z)$  is invariant in time, or represents a stable time-average of a fluctuating source array. Because emission patterns are usually subject to change,  $s_{\theta,i,j}(x,y,z)$  is difficult to control in practice and often presents a substantial impediment to interpreting linearity/nonlinearity from field observations. Although temporal changes in  $s_{\theta,i,j}(x,y,z)$  may invalidate the application of Equations (3.1)

and (3.2) for linearity/nonlinearity analysis, this lack of applicability does *not* imply that the source-receptor system is nonlinear under transient conditions.

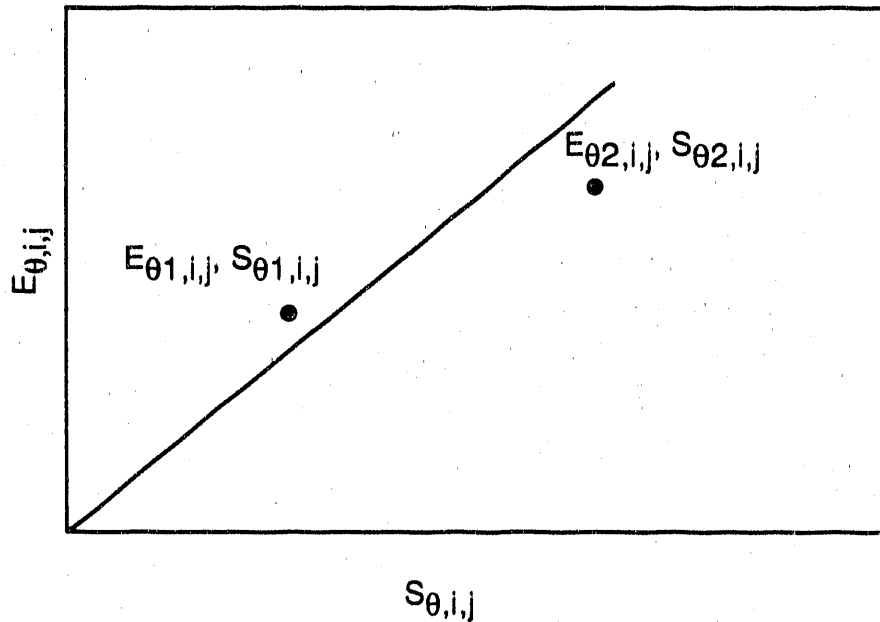
3. Application of Equations (3.1) or (3.2) for evaluating linearity/nonlinearity is valid only after sufficient time has elapsed to allow completion of transient responses to changes in  $S_{\theta,i,j}$ . One would not, for example, attempt to assess nonlinear behavior by doubling  $S_{\theta,i,j}$  at some instant in time, and then measuring  $E_{\theta,i,j}$  in the following few seconds at some (x,y) location several hundred kilometers downwind. This point is of limited practical concern for field assessments of nonlinearity but poses a potential basis for misinterpretation of modeling calculations.
4. The receptor density function  $f_{\theta,i,j}(x,y)$  depends on meteorology and thus will vary with time, even for a constant source strength and source configuration. The best one can hope for is that, for sufficiently large averaging time  $\theta$ , this function will converge to a stable state, which will be replicated by observations for subsequent sampling periods. Experimental determination of source-receptor linearity/nonlinearity by measuring  $E_{\theta,i,j}$  for some fixed  $S_{\theta,i,j}$ , and subsequently modifying  $S_{\theta,i,j}$  and measuring the corresponding change in  $E_{\theta,i,j}$ , depends on this ability to replicate  $f_{\theta,i,j}(x,y)$ .
5. Application of Equations (3.1) and (3.2) for linearity/nonlinearity analysis is based on the assumption that either a) the source-receptor relationship is not affected by other, co-existing pollutants or b) the emissions of these co-existing pollutants remain unchanged during the total period of observation.

Conditions 1 through 5 complicate the description and testing of macroscopic linearity appreciably. Moreover, they suggest a distinction between the **properties** of a linear system and the **conditions** that are necessary to test for its existence. Insofar as necessary test conditions are concerned, it is instructive to view such attributes in terms of conceptual experiments, which one might propose to evaluate linearity using either modeling or field-measurement techniques. Two possible conceptual experiments of this type are:

**Conceptual Experiment 1.** This experiment is essentially a formalization of the approach outlined at the beginning of this discussion. Select a source-receptor system of interest and observe this system for two different periods,  $\theta_1$  and  $\theta_2$ . Assume that the meteorological conditions, averaged for each of the two periods, are identical. Assume also that the source density functions are identical but that the aggregate source strengths  $S_{\theta_1,i,j}$  and  $S_{\theta_2,i,j}$  differ. Measure  $S_{\theta,i,j}$  and  $E_{\theta,i,j}(x,y)$  for each period, and assess deviations from linearity by plotting as shown in Figure 3.

**Conceptual Experiment 2.** Select a source-receptor system of interest, which exists in some well-defined initial state. Observe the system as a function of time for some defined, but not necessarily constant, values of  $S_{i,j}$  and  $s_{i,j}$ . Note values of





**FIGURE 3.** Hypothetical Plot of Measured Source Strength Versus Deposition Rate, Illustrating Conceptual Experiments for Linearity Assessment

$E_{i,j}(x,y)|_1$  at some elapsed time during this process. Repeat the observation, applying the same source density-function and the same meteorology, but for an amplified aggregate source strength  $S_{i,j}$ . Note the corresponding values of  $E_{i,j}(x,y)|_2$  at the same elapsed time. Assess linearity by plotting in the same manner as for Conceptual Experiment 1.

Consideration of these experiments provides insight regarding the importance of Conditions 1 through 5, and gives some indication of the difficulties involved in measuring linearity/nonlinearity in practice. Both experiments can be performed conveniently using model simulations, since in such cases the investigator has explicit control over both the source configuration and the meteorology. Under relatively ideal conditions one might expect to conduct Experiment 1 as a field study; because of the impossibility of repeating the instantaneous meteorological conditions in field experiments, Experiment 2 is practical only in a modeling context.

These experiments, in conjunction with Equations (3.1) and (3.2), also suggest the following quantitative measure of nonlinearity:

$$L^* = \frac{S_{i,j} \partial E_{i,j}}{E_{i,j} \partial S_{i,j}} \approx \frac{(E_{i,j}|_2 - E_{i,j}|_1) / (E_{i,j}|_2 + E_{i,j}|_1)}{(S_{i,j}|_2 - S_{i,j}|_1) / (S_{i,j}|_2 + S_{i,j}|_1)} \quad (3.3)$$

$L^*$  is essentially a normalized sensitivity coefficient and has been suggested as an appropriate measure of linearity/nonlinearity by previous authors (e.g., Easter and Luecken 1988). While  $L^*$  is certainly not the only measurement index that could be suggested, this parameter will suffice for the purposes of this report. As can be determined by inspection of Equation (3.3), an  $L^*$  value of 1 corresponds to linear behavior, as described by Equations (3.1) and (3.2).  $L^*$  values exceeding and less than 1 depict positive and negative deviations from linearity, as exemplified by curves  $\epsilon$  and  $\eta$ , respectively, in Figure 2.

Additional interpretive features of macroscopic linearity are not directly related to observational validity, but are nevertheless worthy of mention at this point. Equations (3.1) and (3.2), for example, can be applied directly for the linearity/nonlinearity analysis of reaction products as well as primary emitted species.  $S_{\theta,i,j}$  could be used to describe a source array of  $\text{SO}_2$  emissions, for example, with  $E_{\theta,i,j}(x,y)$  being applied to characterize the associated deposition flux of the  $\text{SO}_4$  reaction product. Moreover, Equations (3.1) and (3.2) can be generalized to describe linearity for sub-elements of the total source-receptor sequence, by allowing  $S_{\theta,i,j}$  and  $E_{\theta,i,j}$  to depict pollutant inflow and outflow, respectively, for the chosen sub-element.  $S_{\theta,i,j}$  could be used, for example, to depict the chemical input to a cloud system from the surrounding clear air, rather than the direct emission of a pollutant to the atmosphere.

"Global" linearity, that is, linearity of gross behavior across the total  $(x,y)$  domain, is implied by Equations (3.1) and (3.2). Integration of Equation (3.2) over the total  $(x,y)$  domain leads to the obviously linear form

$$E_0 = \bar{A} S_{\theta,i,j}, \quad (3.4)$$

where the constant  $\bar{A}$  is defined by

$$\bar{A} = \int \int A_{\theta}(x,y) dx dy. \quad (3.5)$$

Equations (3.4) and (3.5) demonstrate that the "normalization constant"  $E_0$  is equivalent to the area-integrated exposure.

As a final point in this review of macroscopic phenomena we note that linearity, as described by Equations (3.1) and (3.2), is at variance with some of the interpretations appearing elsewhere in the literature. This point is illustrated by curve  $\zeta$  in Figure 2b, which may be represented by the equation

$$E_{\theta,i,j}(x,y) = A_{\theta}(x,y) S_{\theta,i,j} + b \quad (3.6)$$

where  $b$  is some non-zero intercept, a form that is usually considered to be "linear" in an algebraic context. A more restrictive characterization of linearity (i.e., zero intercept) has been chosen for the purposes of this report for three major reasons. First, emission-control strategy is greatly simplified under conditions where curves such as those in Figure 2a prevail, a situation that definitely does not exist in the case of curve  $\zeta$ . Second, it is difficult to conceive of a situation where curve  $\zeta$  would be exhibited in nature, because its implication of non-zero pollutant deposition associated with sources that are emitting no pollution whatsoever is obviously absurd. Any indication of a source-receptor relationship similar to curve  $\zeta$  would immediately be suspected of either 1) having a radical but unmeasured downturn toward zero in the vicinity of the origin (and thus being highly nonlinear by both criteria (3.1) and (3.6)) or 2) being an artifact arising from background contributions from unaccounted sources. Third, as will be demonstrated below, Equation (3.6) is inconsistent with the mathematical definition of a "linear operator," a concept that will be used in relating macroscopic linearity to its microscopic origins. For these reasons we will continue with our more restrictive characterization of linearity for the purposes of this report and will refrain from using terms such as "proportional" and "linear-proportional," which have been applied elsewhere to distinguish between behavior exhibited by Equation (3.1) and Equation (3.6). In so doing we caution the reader to remember that the terms "linearity" and "nonlinearity" are defined in a variety of ways in the literature, and that due caution is mandatory to avoid confusion and erroneous interpretation of the source-receptor sequence.

### 3.2 MICROSCOPIC SYSTEMS AND THEIR INFLUENCE ON MACROSCOPIC SOURCE-RECEPTOR BEHAVIOR

As we have noted above, microscopic phenomena are important practical considerations because nonlinear molecular-scale processes generally form the mechanistic basis for macroscopic nonlinearity. The following equations, for example,<sup>(a)</sup> represent the rates of chemical reactions:

$$\text{rate of loss of species A} = -\partial c_A / \partial t |_{\text{reaction}} = k_A(x,y,z,t) c_A \quad (3.7)$$

$$\text{rate of loss of species B} = -\partial c_B / \partial t |_{\text{reaction}} = k_B(x,y,z,t) c_B^2 \quad (3.8)$$

$$\text{rate of loss of species C} = -\partial c_C / \partial t |_{\text{reaction}} = k_C(x,y,z,t) c_C c_D \quad (3.9)$$

The first of these is considered to be linear (because it depends on the first power of the concentration of A), and the second nonlinear (because it depends on something other than the first power of the concentration of B). The third reaction is also considered to be nonlinear in general because, although the rate appears superficially to be dependent on  $c_C$  to the first power, it also depends on the concentration of species D, which is presumed to vary with reaction progress in some manner that depends on  $c_C$ . If reactions represented by Equations (3.8) and (3.9) play large roles in affecting source-receptor behavior, then the total macroscopic manifestation can be expected to exhibit nonlinearity in the sense of Section 3.1.

Microscopic linearity is important from a modeling standpoint as well. If linear conditions are assumed to prevail, one frequently can obtain analytical solutions to model equations (or components of these equations), whereas with nonlinear systems numerical approximations are almost always mandatory. Moreover, under linear conditions it is possible to perform relatively simple calculations for individual source-receptor elements of a multiple-source composite and then derive the total composite's depiction by adding these contributions using linear superposition. Simple superposition is not permissible with nonlinear systems. Finally, linear systems allow greater model-application economy, in the sense that a single model execution can be applied to describe a variety of source-receptor scenarios. Quite often this multiple type of scenario analysis has been accomplished by subdividing the

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(a) We will use reaction kinetics as our primary illustration of microscopic linearity/nonlinearity in this report. The reader should note, however, that numerous additional microscopic interactions, such as solubility phenomena and cloud-physics interactions, are potential contributors to system nonlinearity.

source regions and receptor regions into grids, and allocating the emission-density and receptor magnitudes to corresponding two-dimensional matrices. A single execution of a linear model can be applied to create, in addition to a matrix of receptor values corresponding to the source matrix, a general transformation that permits direct evaluation of receptor patterns corresponding to any arbitrary emission array. This transformation, which is often referred to as a *transfer matrix*, thus can be applied for multiple scenario analyses without subsequent execution of the model's code. Again, the application of such techniques is not permissible under nonlinear conditions.

Any acceptable depiction of linearity must be sufficiently general to describe both its microscopic and macroscopic aspects, and to conform to the conditions noted above for model applications. In formulating such a description it is helpful to apply the mathematical concept of a *linear operator*,  $L$ , (cf. Sokolnikoff and Redineffer 1966) which satisfies the form

$$L(C_1 u + C_2 v) = C_1 L(u) + C_2 L(v), \quad (3.10)$$

where  $u$  and  $v$  are any two functions of the independent variables and the  $C_s$  are constants. Differentiation and integration are linear operations under this definition. For example, if one sets  $L(y) = dy/dx$ , then Equation (3.10) becomes

$$\frac{d}{dx}(C_1 u + C_2 v) = C_1 \frac{du}{dx} + C_2 \frac{dv}{dx}.$$

If, on the other hand, one attempts to define  $L$  in terms of a nonlinear operation, say  $L(y) = y^2$ , then similar introduction into Equation (3.10) results in

$$\begin{aligned} (C_1 u + C_2 v)^2 &= C_1^2 u^2 + C_2^2 v^2 + C_1 u C_2 v \\ &\neq C_1^2 u^2 + C_2^2 v^2. \end{aligned}$$

The operations (3.1), (3.2), (3.4) and (3.7) are linear according to the criterion (3.10), whereas (3.6), (3.8) and (3.9) are not; thus both microscopic and macroscopic characterizations of linear systems, as given in this report, conform with this description. Accordingly, we stipulate that a necessary condition for linearity is that both the macroscopic source-response equations and their microscopic root expressions satisfy the criterion stated by Equation (3.10).

Differential equations of the form

$$\mathcal{L}(c) - q(x,y,z,t) = 0 \quad (3.11)$$

where  $q$  is any (possibly) spatially and temporally variant function that is independent of the dependent variable  $c$ , are considered to be linear differential equations in a mathematical context. Although  $\mathcal{L}(c)$  is by definition a linear operator, the left-hand side of Equation (3.11) does not in general satisfy condition (3.10). Furthermore, solutions to differential equations of the form (3.11) do not, in general, lead to linear algebraic expressions of the form (3.1).

More restricted forms of Equation (3.11), which do lead to algebraic solutions that are linear in the sense of Equation (3.1), can be stated. In particular, the pollutant-species conservation equation

$$\frac{\partial c_{i,j}}{\partial t} + \nabla \cdot (\mathbf{v}_{i,j} c_{i,j}) - r_{i,j} = \Sigma_{i,j}(x,y,z,t) = \tilde{S}_{i,j} \tilde{s}_{i,j}(x,y,z,t) \quad (3.12)$$

is considered to be a linear differential equation as long as the divergence and reaction terms [ $\nabla \cdot (\mathbf{v}_{i,j} c_{i,j})$  and  $r_{i,j}$ , respectively], satisfy condition (3.10). This requirement will be fulfilled if the pollutant velocity vector  $\mathbf{v}_{i,j}$  is independent of  $c_{i,j}$ , and the reaction rate  $r_{i,j}$  depends on  $c_{i,j}$  to the first power only. If the problem's boundary conditions satisfy certain restrictions to be discussed below, solutions to this equation can be expressed in terms of Equation (3.1).

Because macroscopic linearity is usually assessed by time-averaged observations, it is often convenient to consider a time-smoothed form of Equation (3.12). Such an equation can be derived in principle by separating the instantaneous variables into time-smoothed and fluctuating terms; i.e.,

$$c_{i,j} = c_{\theta,i,j} + c'_{i,j} \quad (3.13)$$

$$r_{i,j} = r_{\theta,i,j} + r'_{i,j} \quad (3.14)$$

$$\Sigma_{i,j} = \Sigma_{\theta,i,j} + \Sigma'_{i,j} \quad (3.15)$$

$$\mathbf{v}_{i,j} = \mathbf{v}_{\theta,i,j} + \mathbf{v}'_{i,j}, \quad (3.16)$$

and time-averaging on a term-by-term basis with the formula

$$\xi_{\theta} = \frac{1}{\theta} \int_t^{t+\theta} \xi \, dt \quad (3.17)$$

to obtain the result

$$\frac{\partial c_{\theta,i,j}}{\partial t} + \nabla \cdot (\mathbf{v}_{i,j} c_{i,j})_{\theta} - r_{\theta,i,j} = \Sigma_{\theta,i,j}(x,y,z). \quad (3.18)$$

We will not dwell on this time-smoothing procedure here except to note that several rather subtle features are associated with this process, which have been treated at length in the field of general fluid mechanics. These include the turbulent-transport "closure" problem associated with the second term in Equation (3.18) and the question of nonlinear reaction phenomena in fluctuating concentration fields (cf., Bird, Stewart, and Lightfoot 1960, Donaldson and Hilst 1972).<sup>(a)</sup> If  $\theta$  is sufficiently large, then the time derivative will become negligible compared to other terms. This behavior is directly associated with the condition demanded by Condition 3 above, regarding the absence of transients induced by changes in source strength.

Equations (3.12) and (3.18) provide the mathematical link between microscopic and macroscopic linearity/nonlinearity, and their representation is useful for elaborating on Conditions 1 through 5 as well as the additional conditions noted at the conclusion of Section 3.1. First, Equation (3.12) represents only one pollutant, and

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(a) Time-smoothing of the source term can lead to cross-products between the instantaneous aggregate source strength and the instantaneous source density function, if dependences exist in the time-variability of these terms. As a consequence the source strength and density function associated with a time-smoothed  $\Sigma$  are not necessarily the same as the source strength and density function obtained from time-smoothing  $\tilde{S}$  and  $\tilde{s}$  directly. This distinction is reflected in the mathematical notation by the tildes above the instantaneous  $\tilde{S}$  and  $\tilde{s}$  in Equation (3.12). The reader can verify this by performing a simple time-smoothing of the relevant terms using the procedure described above.

similar, simultaneous equations can be set forth for other atmospheric constituents. Because these multiple pollutants react with each other in numerous ways, the equations are often coupled [usually through reaction terms such as Equation (3.9)], possibly creating secondary sources of nonlinearity. As a consequence, any realistic investigation of linear/nonlinear behavior must consider these possible interactions, and observations of one species (say sulfur deposition) must be examined and reported in the context of its concurrently existing pollutants. Such microscopic behavior leads to Condition 5, regarding assumptions pertaining to co-existing pollutants in the context of macroscopic linearity.

It is also important to re-examine the constraints placed on the source density function  $s_{\theta,i,j}(x,y,z,t)$  by Conceptual Experiments 1 and 2. Experiment 1 demands that  $s_{\theta,i,j}$  remain constant, or at least that its average value remain stable from one observation period to the next. Experiment 2 allows  $s_{\theta,i,j}$  to vary with time, but demands that this time-history be replicated between observation periods. Attempts to apply these experiments for other types of  $s_{i,j}$  behavior will result in modifications to the spatial distribution pattern  $f_{\theta,i,j}(x,y)$ , which have little to do with nonlinearity, and thus defeat any possibility of examining linear/nonlinear effects. If the behavior of some particular source or source area is in question, it is possible in principle to tag this source with a unique tracer, vary the  $S_{\theta,i,j}$  corresponding to just this source, and ascertain the extent of its nonlinear behavior.<sup>(a)</sup> Radioactive isotopes such as  $^{35}\text{S}$  have been suggested as experimental tracers for this purpose, and models can conveniently simulate virtual tracers simply by incorporating an additional equation of the form (3.12) with the original equation set. It is extremely important to note, however, that any modeling or experimental investigation of nonlinearity must exercise care to eliminate the possible confusion of spatial/temporal distortions in  $s_{\theta,i,j}$  with true nonlinearity.

A final point relates to the variability of the meteorological field, which is reflected in Equation (3.12) by the velocity vector  $v_{i,j}(x,y,z,t)$  and has direct bearing on Condition 4 of our characterization of macroscopic linearity. Straightforward model realizations of Conceptual Experiment 1 can be conducted, where an initial code execution is performed for some value of  $S_{\theta,i,j}$ , using a prescribed  $v_{i,j}(x,y,z,t)$  (in addition to other meteorological features). The code is then re-executed for some

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<sup>(a)</sup> There is, however, a danger of misinterpreting the results of such studies and arriving at inappropriate measures of nonlinearity. This issue and its underlying causes will be illustrated by Example 2.

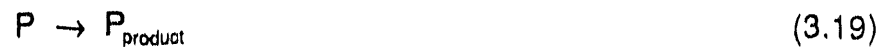


other value of  $S_{\theta,i,j}$ , using a meteorological description that is identical to that for the first execution. Unfortunately one cannot mimic this type of experiment in the real world. At best one can observe  $f_{\theta,i,j}(x,y)$  fields experimentally for some value of  $\Sigma_{\theta,i,j}$ , for the meteorology that occurs during this experiment period (of length  $\theta$ ). Subsequently, one can repeat the experiment, accepting whatever meteorology that occurs during this second period, with the hope that the two meteorological records will be sufficiently similar so as to contribute insignificantly to observed differences in  $f_{\theta,i,j}(x,y)$ . Based on observed natural variability in annual wet-deposition patterns (Finkelstein and Seilkop 1986), such an assumption requires substantial evaluation before any conclusions regarding linearity from experiments of this type can be made.

Some additional important features of linearity/nonlinearity are most conveniently described using reduced forms of Equations (3.12) and (3.18), which are sufficiently simple for clear illustration but can be extended to the more general cases encompassed by the complete equations. We present here two simple case examples to illustrate the significance of boundary conditions and the application of tracer techniques for nonlinearity analysis.

Example 1: One-Dimensional Linear Systems: Illustration of the Importance of Boundary Conditions.

Figure 4 is a schematic of an idealized atmosphere, which exhibits a one-dimensional, constant flow in the x-direction. A constant source strength  $S_p$  is distributed evenly throughout the system's domain, and advection in the x-direction is the sole mechanism for pollutant transport. A first-order chemical reaction of pollutant P proceeds kinetically as



with a reaction rate described by

$$\partial c_p / \partial t |_{\text{reaction}} = -k c_p \quad (3.20)$$

Under these conditions Equation (3.12) reduces to

$$U \frac{\partial c_p}{\partial x} + k c_p = S_p \quad (3.21)$$

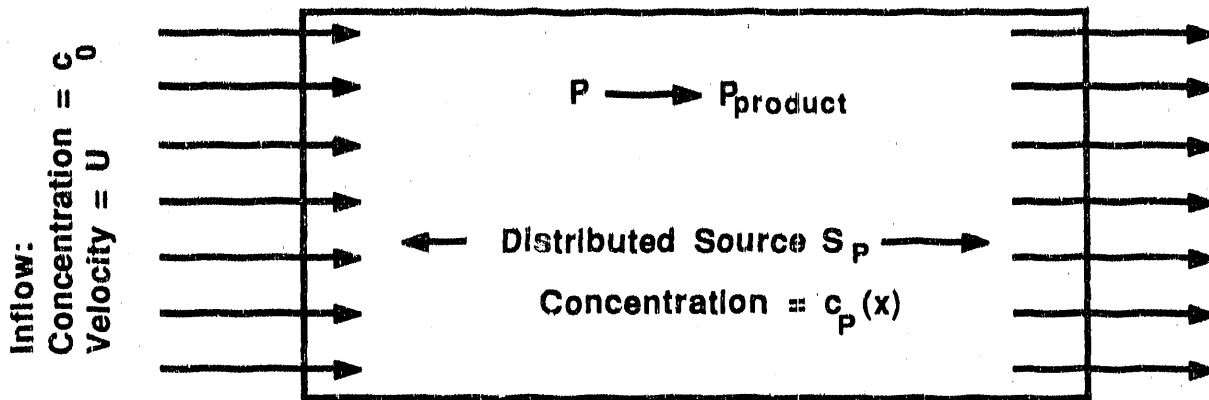


FIGURE 4. Schematic of an Idealized, One-Dimensional Linear System

where  $U$  is the  $x$ -component of the velocity vector  $\mathbf{v}$ . With the boundary-condition stipulation that  $c_p$  is equal to some concentration  $c_0$  at the system's inflow region, this linear differential equation has the solution

$$c_p(x) = \frac{S_p}{k} [1 - \exp(-k/Ux)] + c_0 \exp(-k/Ux). \quad (3.22)$$

Comparison of this expression with Equation (3.1) suggests that this simple system adheres to our expression for macroscopic linearity only if the inflow concentration is zero, that is, if all of the pollutant is introduced to the system through the source term  $S_p$ . In cases where  $c_0$  is not zero, one can define an *effective* source term as the sum of internal and boundary-condition inputs, allowing the system to conform to our description of linearity so long as  $c_0$  and  $S_p$  are varied in direct proportion to one another.<sup>(a)</sup>

This result, which can be extended to more complex and higher-dimensional systems, demonstrates the simple but important point that fundamentally linear systems can be interpreted in a nonlinear sense, if boundary-condition changes are not coordinated with changes in internal source strength. This seemingly trivial point is particularly important for regional-model investigations of linearity/nonlinearity. In such studies the pollutant's inflow boundary conditions must either be zero or must be incremented in direct proportion to changes of the internal sources to prevent inappropriate interpretation of linear features of system behavior. Failure to recognize

(a) Easter and Luecken (1988), for example, perform a linearity/nonlinearity analysis on a system having no internal sources whatsoever, with the total pollution burden entering through the boundaries.

this point by the modeler or policy analyst will invariably lead to misinterpretation of the linearity/nonlinearity analysis.

### Example 2: Zero-Dimensional Nonlinear Systems: Tracer Applications to Linearity/Nonlinearity Assessments.

We present this example to illustrate a potential pitfall involved with performing physical or computational analyses of nonlinearity, through interpretation of a defined component of pollutant emissions that interact within a larger total emission field. This situation can be interpreted either as an experiment involving a tracer that is injected into an existing emission field, or the specific analysis of a minor existing emission component that somehow can be distinguished from its surroundings. The simple example that we consider here is a hypothetical steady-state atmosphere contained in the well-mixed volume  $V$ , shown in Figure 5. Three pollutants are emitted continuously to this atmosphere at the rates  $S_P$ ,  $S_O$ , and  $S_T$ , and are removed by chemical reaction and flow through the boundaries. The mean dwell time of air passing through volume  $V$  is constant and is denoted by the symbol  $t^*$ . Since the volume is well mixed, the concentrations of these pollutants are uniform in space as well as being constant in time. The time-derivative of Equation (3.12) is zero and the divergence term can be expressed in terms of its boundary fluxes, leading to simple algebraic expressions of the relevant conservation equations. Chemical reactions of these pollutants have the mechanisms



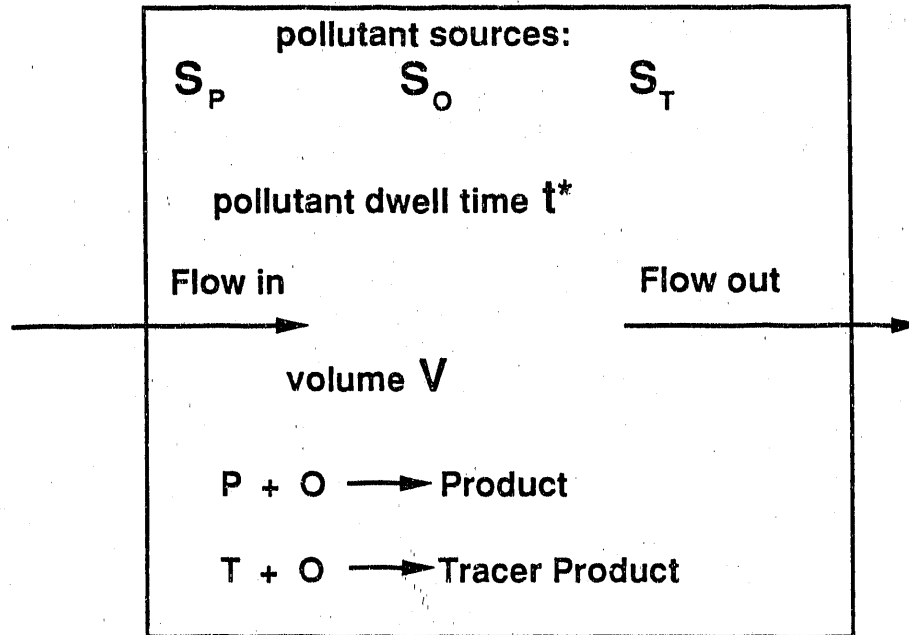
with rates described by the following equations

$$\partial C_P / \partial t |_{\text{reaction}} = -k C_P C_O, \quad (3.25)$$

$$\partial C_O / \partial t |_{\text{reaction}} = -k C_O (C_P + C_T), \quad (3.26)$$

$$\partial C_T / \partial t |_{\text{reaction}} = -k C_T C_O. \quad (3.27)$$

Although this is obviously a highly simplified situation, it strongly resembles a number of pollution phenomena of interest. This reaction sequence, for example, is quite similar to the aqueous-phase atmospheric reaction between  $S(IV)$  and  $H_2O_2$ .



**FIGURE 5.** Schematic of a Continuous Stirred-Atmosphere Reaction System

Here species P would represent SO<sub>2</sub> [or S(IV)], species O would depict H<sub>2</sub>O<sub>2</sub>, and species T some tagged version of SO<sub>2</sub> added as a tracer.

By application of the divergence theorem to Equation (3.12) (or simply by performing a material balance over the system depicted in Figure 4) one can set up the following steady-state material-balance equations for the three species:

$$S_P/V - c_P/t^* = k c_P c_O, \quad (3.28)$$

$$S_O/V - c_O/t^* = k (c_P + c_T) c_O, \quad (3.29)$$

$$S_T/V - c_T/t^* = k c_T c_O. \quad (3.30)$$

Furthermore, concentrations of the products resulting from reactions (3.23) and (3.24) can be expressed as

$$c_{P\text{product}} = \frac{t^* S_P}{V} - c_P, \quad (3.31)$$

$$c_{T\text{product}} = \frac{t^* S_T}{V} - c_T. \quad (3.32)$$

With some algebraic manipulation these equations can be rearranged to obtain explicit expressions for the concentrations  $c_P$ ,  $c_O$ ,  $c_T$ ,  $c_{P\text{product}}$ , and  $c_{T\text{product}}$ , and for

the linearity parameters  $L^*_{P_{product}}$  and  $L^*_{T_{product}}$ . Although easy to derive, these explicit forms are somewhat cumbersome. Rather than show the mathematical expressions here, we simply present some illustrative results obtained from computations for a single case example.

Shown in Figure 6, this computed output illustrates a case example whose parameters have been chosen to simulate P and O as dominant species and T as a minor constituent acting as a tracer for P. As can be observed for the S - concentration curves as well as the corresponding  $L^*$  curves, the concentration of species  $P_{product}$  is related to  $S_P$  in a moderately nonlinear manner, whereas the corresponding relationship for the tracer's product compound approximates linearity very closely. We

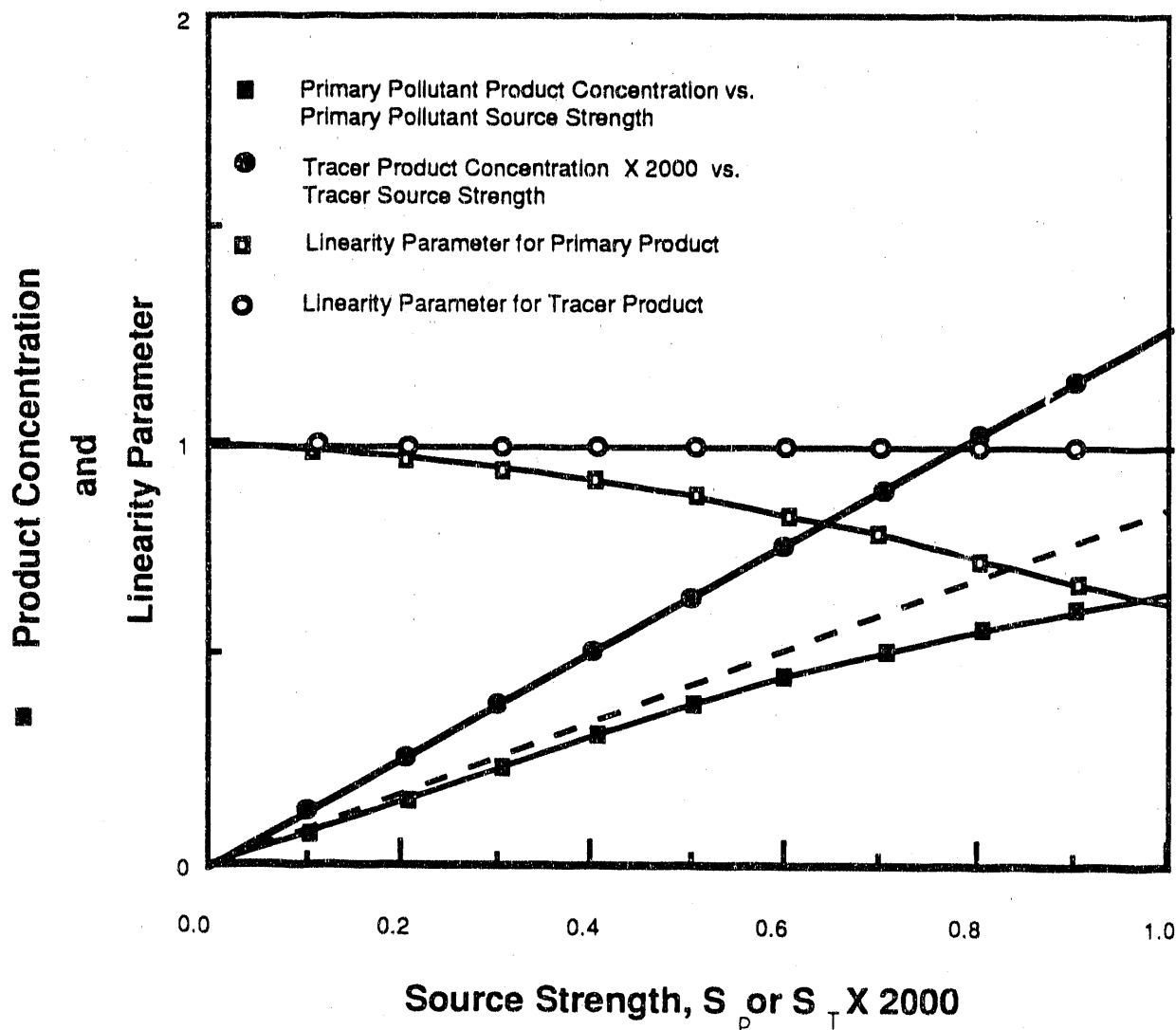


FIGURE 6. Linearity Plot for Example Reaction System

assert that this simple result has profound implications to physical and numerical experiments that propose to apply tagged species as measures of nonlinearity. If the microscopic origin of the nonlinearity derives from titration of a limiting species, then addition of tracer for Conceptual Experiments 1 or 2 can be expected to grossly underestimate the degree of global nonlinearity in most cases.<sup>(a)</sup> Furthermore, numerical tagging of a particular source or source array that is imbedded in a complex of other pollution sources can be expected in general to underestimate nonlinear behavior of the total system.

### 3.3 SUMMARY COMMENTS ON LINEARITY

Two general conclusions can be made to this discussion of linearity. First, it is obvious that the term "linearity" must be defined precisely, in order to avoid ambiguous conclusions in any associated analysis. Second, several competing factors may masquerade as false indications of nonlinearity or linearity in experimental and modeling investigations, and proper care to minimize or prevent such effects is imperative.

For the practical purposes of this report, we can characterize a linear macroscopic system as one whose source-receptor relationship complies with the definition of a linear operator as given in Equation (3.10) [cf., Equation (3.1)], and in addition conforms with conditions 1 through 5 in Section 3.1. A linear microscopic system is simply one whose mathematical statement can be characterized in terms of a linear operator.

This characterization satisfies the last three of the four objectives listed in the introduction to this Section. It is sufficiently well-posed to prevent ambiguity in interpretation, it is consistent over all scales of application, and it is reconcilable with standard mathematical terminology. Because the description given in this section is not particularly concise, we feel less satisfied with our ability to achieve the first objective in this list. Based on this analysis, however, we conclude that, owing to the involved and complex nature of the linearity/nonlinearity issue, a highly concise depiction is not possible without violating the remaining three requirements. Because it is naturally tempting to characterize linearity in simple terms for *ad hoc* purposes,

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(a) This result does not apply to all classes of nonlinear systems. For example, application of a tracer in Conceptual Experiment 2 to determine  $L^*$  for a system which derives its nonlinearity solely from a microscopic source such as Equation (3.8), will result in a direct measurement of global nonlinearity. Unfortunately, most systems of practical interest involve a complex of microscopic nonlinearity sources, and the observer is seldom totally aware of their exact nature.

there will continue to be a danger of misinterpretations in applied analyses. The material in this section has been presented with the hope of reducing this danger as much as possible.

#### 4.0 TEMPORAL ATTRIBUTES: TEMPORAL DISTRIBUTIONS AND RESIDENCE TIMES

Scientific analysis of temporal source-receptor features has been in progress for an extended period, and as a consequence terminology in this area is somewhat more well-established than is the case for nonlinearity analysis. Bolin and Rodhe (1973), for example, have presented a well-defined set of terms for this subject, which have been applied and extended by subsequent authors. The currently established terms and definitions have a number of shortcomings, however, and thus we introduce some additional concepts and terms, whose usefulness should become apparent to the reader upon consideration of the following text.

In introducing this section, we note that Bolin and Rodhe based their analysis on the idea of the atmosphere as a steady-state reservoir wherein pollutants are continuously emitted and removed, maintaining a constant resident mass of pollutant. We consider the Bolin-Rodhe idealization in our present analysis as well; but, first we develop a somewhat less restricted conceptual model involving the transient behavior of an instantaneous "puff" of pollutant. Besides having the advantage of greater generality, the transient-puff approach allows a somewhat easier visualization of key issues of the development. Subsequently, we compare this treatment directly with the Bolin-Rodhe approach to arrive at the final conclusions to this section.

#### 4.1 ATMOSPHERIC RESIDENCE TIMES AND TRANSIENT RESPONSE

##### 4.1.1 Isolated Mechanisms

We begin this development by considering a pollutant molecule (or aerosol particle) that is emitted to the atmosphere from some source at time 0. Ultimately that molecule will either:

- be removed by some sort of chemical (or possibly physical) transformation
- be removed by dry deposition
- be removed by wet deposition.

If a puff of several (say  $N_0$ ) molecules of the same type were released from this source at time 0, one would expect individual molecules to exit the atmosphere via the above pathways at different times, which depend on the individual experiences of separate molecules. If the function  $N(t)$  is defined as the number of molecules removed at times up to and including time  $t$  following the release, then an **instantaneous**



**temporal probability-density function**  $g(t)$  for pollutant removal can be defined such that the probability of an emitted molecule being removed in an element of time between  $t$  and  $t + dt$  is equal to  $g(t) dt$ :

$$g(t) = \frac{1}{N_0} \frac{dN}{dt}, \quad (4.1)$$

which can be rearranged to give

$$N(t) = N_0 \int_0^t g(t') dt'. \quad (4.2)$$

All of the molecules will have been removed at  $t = \infty$ , at which time  $N(t)$  equals the total number ( $N_0$ ) of molecules released in the instantaneous puff.

As was the case for spatial distributions, the temporal probability-density function  $g(t)$  can be treated using conventional statistical approaches. In particular, the mean residence time and variance of the ensemble of molecules released at time 0 can be expressed as

$$\tau = \int_0^{\infty} t g(t) dt \quad (4.3)$$

and

$$\sigma_t^2 = \int_0^{\infty} (t - \tau)^2 g(t) dt, \quad (4.4)$$

with higher moments of the distribution obtainable using direct extensions of Equations (4.3) and (4.4).  $\tau$ , which is usually referred to as the "atmospheric residence time," (cf. Junge 1963) has been applied extensively in the source-receptor literature, especially in European contributions to the field.

We now consider a hypothetical system almost identical to that just described, but which differs in the sense that it contains "switches," which can activate or deactivate specific removal mechanisms. With this hypothetical system one can perform repeated experiments with single mechanisms operative and thus measure

the effectiveness of each mechanism in isolation. We use the term  $g_{r,i}(t)$  to denote the "isolated" probability-density function describing the situation when all mechanisms save chemical conversion are inoperative. Similarly,  $g_{d,i}(t)$  denotes the density function when all mechanisms are "toggled off," except for dry deposition, and  $g_{w,i}(t)$  denotes the corresponding density function for wet deposition. This leads directly to

$$N_{x,i}(t) = N_0 \int_0^t g_{x,i}(t') dt' \quad (4.5)$$

$x = r, d, w$

with expressions for the corresponding statistical parameters  $\tau_{r,i}$ ,  $\tau_{d,i}$ , and  $\tau_{w,i}$  obtainable using direct extensions of Equation (4.3):

$$\tau_{x,i} = \int_0^{\infty} t g_{x,i}(t) dt \quad (4.6)$$

$x = r, d, w$

#### 4.1.2 Simultaneous Mechanisms

The terminology of Section 4.1 envisioned  $N(t)$  to be the number of molecules removed from the atmosphere by all active mechanisms, unless special conditions existed in our hypothetical system where specific mechanisms were toggled off.  $N_{x,i}(t)$ , on the other hand, denoted the molecules removed by specific mechanism  $x$  acting in isolation from competing mechanisms. Under the isolated-mechanism situations,

$$N(t) = N_{r,i}(t) \quad (\text{reaction only}) \quad (4.7)$$

$$N(t) = N_{d,i}(t) \quad (\text{dry removal only}) \quad (4.8)$$

$$N(t) = N_{w,i}(t) \quad (\text{wet removal only}). \quad (4.9)$$

Because, under conditions where simultaneous mechanisms are operative, the total number of molecules removed must equal the sum of contributions from the individual mechanisms, it is of some interest to define a corresponding set of terms that describes individual contributions under simultaneous circumstances. Specifically, we define

and

$$N_{x,s}(t) = N_{x,s,0} \int_0^t g_{x,s}(t') dt' \quad (4.10)$$

$$\tau_{x,s} = \int_0^{\infty} t g_{x,s}(t) dt \quad (4.11)$$

$x = r, d, w$

where the various terms take their obvious significance, the subscript  $s$  has been added to emphasize that these statistics are for simultaneously occurring pathways, and  $N_{x,s,0}$  denotes the total number of molecules removed by mechanism  $x$  at  $t = \infty$ . Simple material-balance considerations lead to the relationships

$$N(t) = N_{r,s}(t) + N_{d,s}(t) + N_{w,s}(t) \quad (4.12)$$

and

$$N_0 g(t) = N_{r,s,0} g_{r,s}(t) + N_{d,s,0} g_{d,s}(t) + N_{w,s,0} g_{w,s}(t) \quad (4.13)$$

Application of Equation (4.11) to the components of Equation (4.13) leads to the relationship

$$N_0 \tau = N_{r,s,0} \tau_{r,s} + N_{d,s,0} \tau_{d,s} + N_{w,s,0} \tau_{w,s} \quad (4.14)$$

Although  $\tau$  conforms to the definition of the "residence time" described in Section 4.1, the terms  $\tau_{x,s}$  are **not** the same as their isolated counterparts. While  $\tau_{x,s}$  is indeed the true residence time experienced by an ensemble of molecules being removed by pathway  $x$  in competition with other pathways,  $\tau_{x,j}$  is more of a conceptual standard and is only indirectly related to actual residence-time behavior in true, multi-pathway systems. This will be illustrated in more detail below, where a special case example is considered.

#### 4.1.3 Special Cases

Having distinguished between isolated and simultaneous characterizations, we next illustrate how to convert from one set of statistics to the other. Possession of just one set of statistics does not describe a system in sufficient detail to derive the second set unambiguously and additional constraints are required for this purpose. We illustrate this point by imposing one of the possible sets of constraints on a puff-release system, wherein statistics corresponding to the isolated characterization are known.

This constraint is simply one of system linearity; that is, removal rates corresponding to individual mechanisms are dependent on the remaining quantity of airborne material. For removal mechanism  $x$ , this constraint is equivalent to stating that, for the isolated mechanism case,

$$\frac{dN_{x,i}}{dt} = k_x(t) (N_0 - N_{x,i}) = N_0 g_{x,i}(t) \quad (4.15)$$

and for the simultaneous mechanism case

$$\frac{dN_{x,s}}{dt} = k_x(t) (N_0 - N) = N_{x,s,0} g_{x,s}(t) \quad (4.16)$$

where  $k_x(t)$  is a (possibly) time-dependent rate parameter and  $N_{x,s,0}$  is the total amount of emitted material that will ultimately be deposited by mechanism  $x$ . In the special situation where  $k_x$  is a time-independent constant, the corresponding isolated density function is exponential in form.

Since the total removal rate in a simultaneously operative system is equal to the sum of its components, one can write

$$\frac{dN}{dt} = [k_r(t) + k_d(t) + k_w(t)] (N_0 - N) = N_0 g(t) \quad (4.17)$$

where the subscripts  $r$ ,  $d$ , and  $w$  denote removal by reactive, dry, and wet processes, respectively. Integrating Equations (4.15) and (4.17) to obtain  $g_{x,i}$  and  $g$  as functions of time and inserting into Equation (4.3) gives

$$g_{x,i}(t) = k_x(t) \exp\left[-\int_0^t k_x(t') dt'\right], \quad (4.18)$$

$$g(t) = [k_r(t) + k_d(t) + k_w(t)] \exp\left[-\int_0^t [k_r(t') + k_d(t') + k_w(t')] dt'\right], \quad (4.19)$$

$$\tau_{x,i} = \int_0^{\infty} \exp\left[-\int_0^t k_x(t') dt'\right] dt, \quad (4.20)$$

and

$$\tau = \int_0^{\infty} \exp\left[-\int_0^t [k_w(t') + k_d(t') + k_r(t')] dt'\right] dt. \quad (4.21)$$

Although under the special circumstances where the rate coefficients are time-independent constants integration of (4.20) and (4.21) leads to the relationship

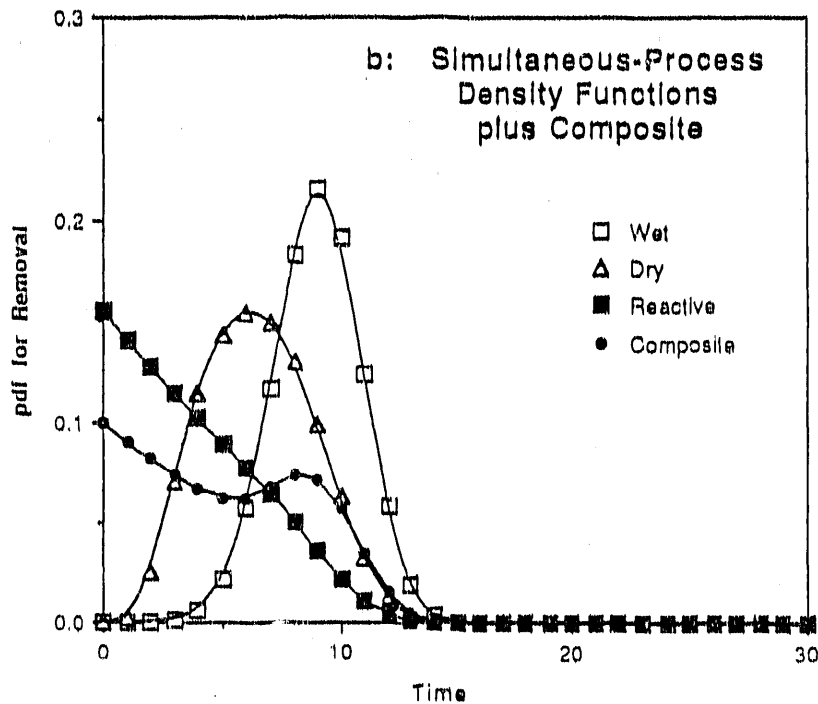
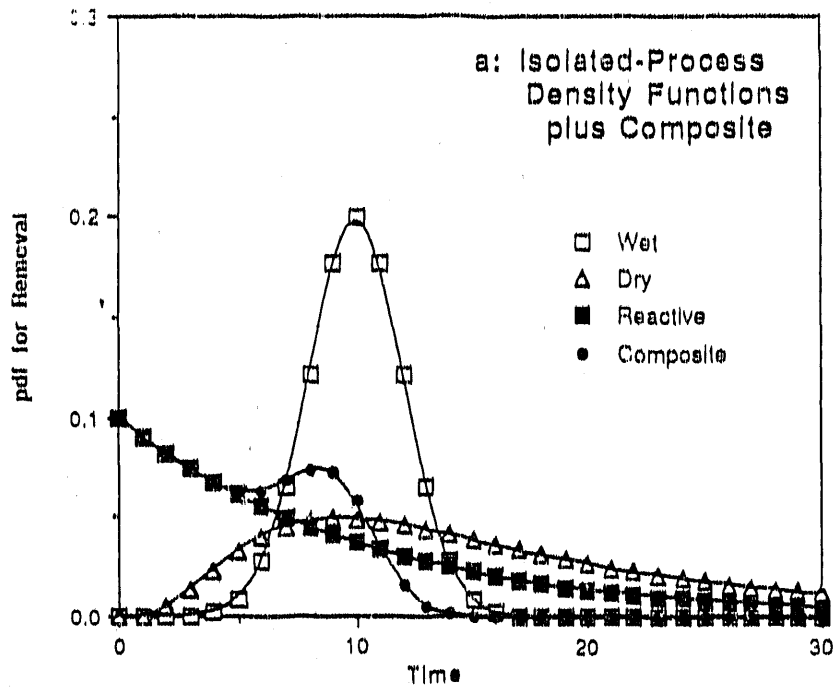
$$\frac{1}{\tau} = \frac{1}{\tau_{r,j}} + \frac{1}{\tau_{d,j}} + \frac{1}{\tau_{w,j}} \quad (4.22)$$

this equation does not hold in general for variable  $k_x$ . This finding is of some significance in view of the widespread application of Equation (4.22) in the atmospheric-sciences literature and will be examined in more detail below when steady-state systems are considered.

Equations (4.15) and (4.16) can be applied directly to derive isolated statistics from their simultaneous counterparts, and vice versa. An example is shown in Figure 7. From this one can observe that the residence times of pollutants associated with simultaneously operative systems are, in general, shorter than their isolated counterparts. This is not difficult to rationalize on an intuitive basis, since several mechanisms competing to remove material should reduce its lifetime compared to a situation wherein only one of these mechanisms is operative.

#### 4.1.4 Extension to Continuous Systems

Equations (4.1) through (4.22), which correspond to a single, instantaneous puff-release of pollutant at time 0, can be extended to longer-period releases by considering a sequential release of puffs over some time-period  $\theta$ . Thus a corresponding set of time-averaged statistical parameters (e.g.,  $\tau_\theta$ ,  $\tau_{\theta,r,s}$ ,  $\tau_{\theta,d,l}$ ,  $g_{\theta,w,s}$ , . . .) can be defined in a manner similar to that employed previously for spatial statistics. To illustrate this process, we consider a reservoir wherein a sequential series of puffs occurs, which are spaced evenly in time. Let  $g_{x,j}(t)$  and  $N_{x,j,0}$ , respectively, represent a density function and the number of molecules ultimately deposited, corresponding to the molecules in a puff emitted at time  $t_j$ , for some single removal pathway  $x$  that occurs in the reservoir. Because meteorological conditions change with time, each of the puffs will differ from their predecessors, exhibiting forms similar to the examples shown in Figure 8a. Their shapes can be averaged, however, by time-shifting so that the origins of all puffs coincide, weighting according to  $N_{x,j,0}$  and summing. If some particular puff, denoted by index  $j$ , is emitted at time  $t_j$  and displays the probability-density function  $g_{x,j}(t)$ , then its form, translated to the origin at  $t = 0$  is given by  $g_{x,j}(t + t_j)$ . Accordingly, a time-average of all density functions in the series, as translated to the origin can be expressed as



**FIGURE 7.** Hypothetical Probability-Density Functions for Reactive, Dry-Deposition, and Wet-Deposition Removal Pathways in a Linearly Interactive System: a) Density Functions Characterizing "Isolated" Pathways; b) "Simultaneous"-Pathway Density Functions Derived from Their Isolated Counterparts. The composite density function for simultaneously operative mechanisms is plotted on each of the figures. Isolated density functions for reaction, dry removal, and wet removal have been idealized as exponential, log-normal, and normal distributions, respectively.

$$\hat{g}_{\theta,x}(t) = \frac{\sum_{j=1}^J N_{x,j,0} g_{x,j}(t + t_j)}{\sum_{j=1}^J N_{x,j,0}} \quad (4.23)$$

where J is the index of the last puff emitted prior to time  $\theta$ . If  $g_{\theta,x,j}(t)$  is defined as the unshifted density function that corresponds to  $\hat{g}_{\theta,x}(t)$ , then all  $g_{\theta,x,j}$  will have the same shape but will be displaced in time, as shown in Figure 8b. From this

$$\tau_{\theta,x} = \int_0^{\infty} t \hat{g}_{\theta,x}(t) dt \quad (4.24)$$

is the average residence time experienced by the total ensemble of molecules, emitted during the time  $\theta$ , to be removed by pathway x.

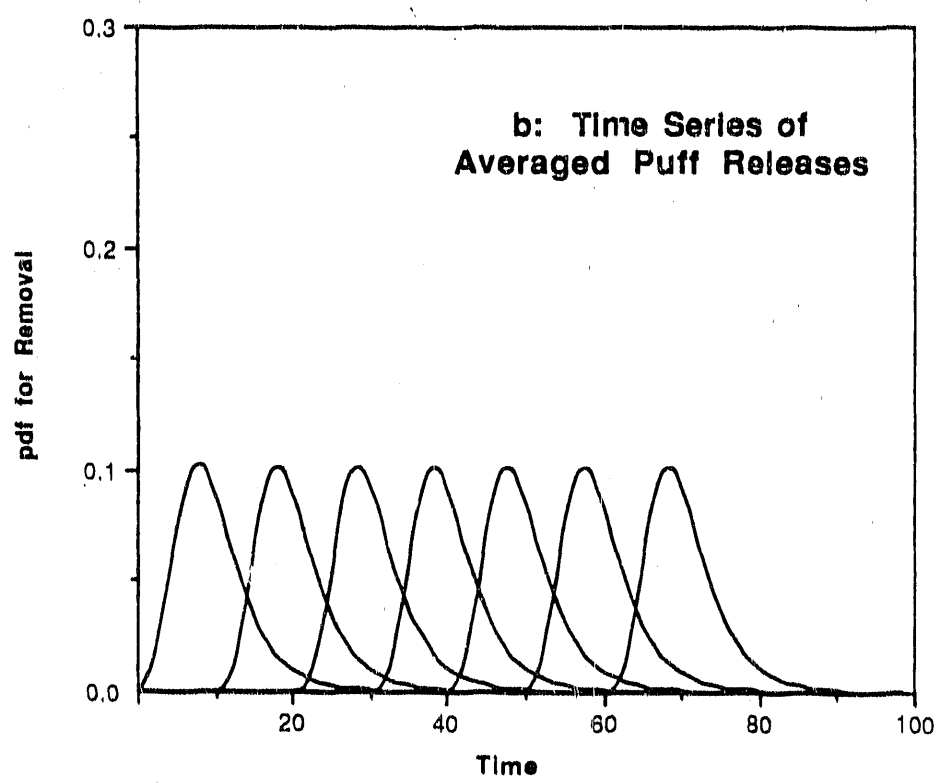
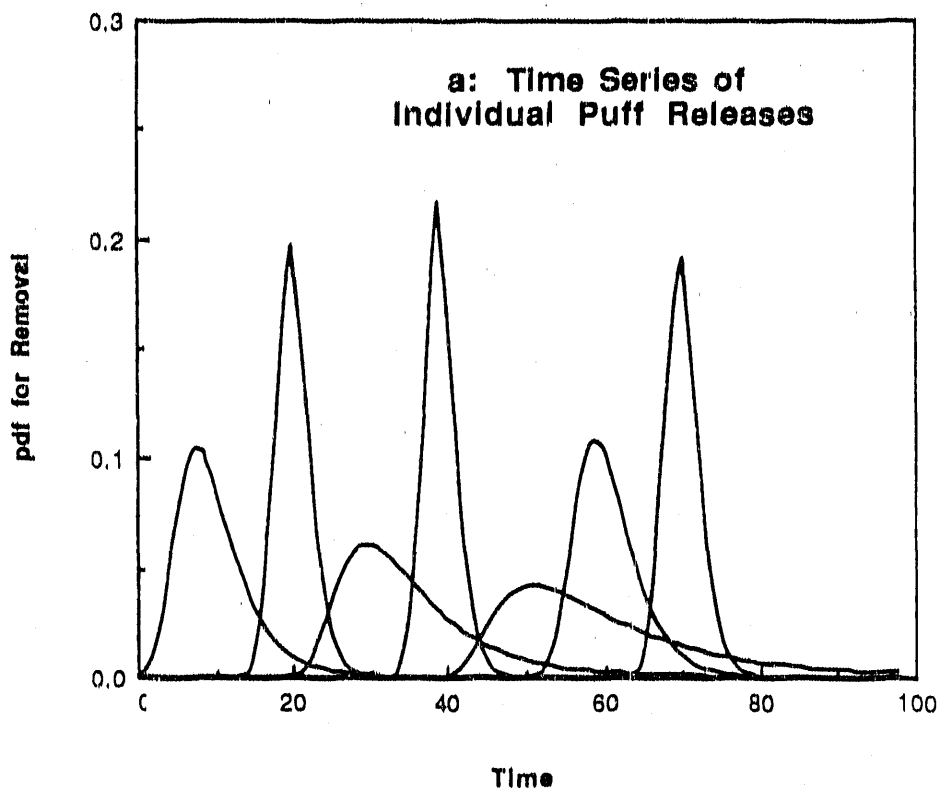
## 4.2 ATMOSPHERIC RESIDENCE TIMES AND STEADY-STATE SYSTEMS

In Section 4.1 we followed the transient behavior of an instantaneously emitted puff of pollutant, derived a number of statistical relationships describing this process, and finally examined the associated statistics for a release of several puffs in series. We now briefly examine the more traditional approach to this general problem, which is based on the concept of a steady-state reservoir. As noted earlier this general approach has been described most concisely by Bolin and Rodhe (1973). Accordingly we begin by summarizing their derivation and then extend it somewhat beyond their original treatment. Following this we present a comparative linkage between the two types of analysis and examine some practical aspects of conventional usage in the field.

### 4.2.1 Overview of Bolin-Rodhe Derivation

In the steady-state atmospheric reservoir visualized by Bolin and Rodhe, some (undefined) source continuously emits pollution, which is removed at rate  $F_0$  to result in the steady-state quantity  $M_0$  of material in the system. If one defines  $F(t)$  as the removal rate of molecules that have been resident for periods of time less than  $t$ , then the density function associated with  $F(t)$  is

$$\phi(t) = \frac{1}{F_0} \frac{dF(t)}{dt} \quad (4.25)$$



**FIGURE 8.** Time Series of Probability-Density Functions for a Series of Instantaneous Puffs: a) Un-averaged Density Functions; b) Averaged Density Functions



Similarly, if  $M(t)$  represents the number of molecules existing in the reservoir with lifetimes less than  $t$ , then the associated density function is

$$\varphi(t) = \frac{1}{M_0} \frac{dM(t)}{dt} \quad (4.26)$$

Now  $F_0 - F(t^*)$  is the exit rate of molecules older than  $t^*$ . At steady state this exit rate must equal the rate of production of molecules older than  $t^*$  in the system; that is,

$$\left. \frac{dM(t)}{dt} \right|_{t=t^*} = M_0 \varphi(t) \Big|_{t=t^*} = F_0 - F(t) \Big|_{t=t^*} \quad (4.27)$$

which, upon differentiation, gives

$$\phi(t) = - \frac{M_0}{F_0} \frac{d\varphi}{dt} \quad (4.28)$$

Bolin and Rodhe define three different time constants that have been applied to characterize steady-state systems of this type:

- the *turnover time*,

$$\tau_0 \equiv \frac{M_0}{F_0} \quad (4.29)$$

- the *average age*,

$$\tau_a \equiv \int_0^{\infty} t \varphi(t) dt \quad (4.30)$$

- and the *residence time*,

$$\tau_r \equiv \int_0^{\infty} t \phi(t) dt \quad (4.31)$$

Substituting Equation (4.28) into (4.31) and integrating formally gives

$$\tau_r = \frac{M_0}{F_0} \quad (4.32)$$

demonstrating that, for composite removal in a steady-state system, the residence time and the turnover time are equal.

Bolin and Rodhe also refer to  $\tau_t$  as a *transit time*, but suggest that the term "residence time" is preferable, because species transformed by chemical reaction do not exit by transit through the boundaries of the system. While the definition of  $\tau_t$  given in Equation (4.31) is consistent with that given for the residence time in transient-puff systems (cf. Equation (4.3)), we note that the turnover-time concept has no counterpart in systems not involving steady-state conditions.

#### 4.2.2 Extension of Bolin-Rodhe Derivation to Describe Individual Removal Pathways

Although Bolin and Rodhe did not consider individual mechanisms in their original paper, their results can be extended directly to describe component removal pathways. In so-doing we note that standard past practice has been to define individual-mechanism turnover times (cf. Rodhe 1978) as

$$\tau_{x,s,0} \equiv \frac{M_0}{F_{x,s,0}}, \quad (4.33)$$

$x = r, d, w$

where  $F_{x,s,0}$  denotes the contribution to the overall removal rate by pathway  $x$ , but  $M_0$  still pertains to the total amount of material in the reservoir. The distinction between isolated and simultaneous pathway behavior does not appear to have been dealt with explicitly in the past literature, and we have included the subscript  $s$  to emphasize our intention here to represent a system where all possible pathways occur simultaneously. Comparison of Equations (4.29) and (4.33) leads to the relationship

$$\frac{1}{\tau_0} = \frac{1}{\tau_{r,s,0}} + \frac{1}{\tau_{d,s,0}} + \frac{1}{\tau_{w,s,0}}. \quad (4.34)$$

If one were to maintain the emission rate in the reservoir, and toggle off all but removal pathway  $x$ ,  $M_0$  would increase and approach a new steady state  $M_{x,i,0}$ . One could proceed to use  $M_{x,i,0}$  to calculate an "isolated-mechanism" turnover time; it is obvious, however, that this turnover time will, in general, be larger than its simultaneous counterpart,  $\tau_{x,s,0}$ .

Turning our attention to component residence times, we note that application of the procedure described in Section 4.2.1 to individual removal pathways in simultaneously operative systems leads to the result

where

$$\tau_{x,s,t} = \frac{M_{x,s,0}}{F_{x,s,0}} \quad (4.35)$$

$x = r, d, w$

$M_{x,s,0}$  is the amount of material currently in the reservoir that will be removed ultimately by mechanism  $x$ . By comparison of Equations (4.33) and (4.35) it is obvious that the residence time for an individual mechanism differs from the corresponding turnover time; this contrasts to the composite system, where turnover time and residence time can be used interchangeably.

#### 4.2.3 Comparison of Transient-Puff and Steady-State Analyses

At this point we demonstrate closure between the transient-puff and steady-state reservoir analyses by reconsidering a time series of sequential puff releases somewhat similar to that described in Section 4.1.4. Here, however, we impose the additional constraint that each puff must contain an equal number of molecules  $N_0$ . We also stipulate that the progression of puffs has continued for an extended time so that a steady state has been reached where, on the average, the pollutant's input rate is balanced by its removal processes.

Following the general approach of Section 4.1.4 and the Bolin-Rodhe terminology, we describe the combined-mechanism pollutant removal rates as

and

$$F_0 = N_0 \sum_{j=1}^{j_{ss}} g_j(t_{ss}) \quad (4.36)$$

$$F(t) = N_0 \sum_{j=j_t}^{j_{ss}} g_j(t_{ss}) \quad (4.37)$$

where  $t_{ss}$  denotes some large value of time where steady-state conditions are attained,  $j_{ss}$  is the index of the corresponding puff, and  $j_t$  is the index of a puff occurring at any time  $t$ .

Based on the discussion in Section 4.1.4 we assume that, in the mean,

$$\sum g_j(t) = \sum g_{\theta,j}(t) \quad (4.38)$$

then

$$\begin{aligned}
F(t) &= N_0 \sum_{j=1}^{j_{ss}} g_{e,j}(t_{ss}) & (4.39) \\
&= N_0 \sum_{j=1}^{j_{ss}} \hat{g}_e(t_{ss} - t_j) \\
&\approx \frac{N_0}{\Delta t} \int_0^{t_{ss}-t_{j_1}} \hat{g}_e(t) dt \\
&= F_0 \int_0^{t_{ss}-t_{j_1}} \hat{g}_e(t) dt,
\end{aligned}$$

where  $\Delta t$  is the time interval between puffs. Direct comparison of Equation (4.39) with Equation (4.25) demonstrates the equivalency, for steady-state conditions, between our  $\hat{g}_e(t)$  (which was formulated on the basis of transient puffs) and the  $\phi(t)$  of Bolin and Rodhe (which is based on the concept of a steady-state reservoir). With reference to Equations (4.25) and (4.31), the Bolin-Rodhe residence time  $\tau_t$  is seen to be equal to that formulated on the basis of time-averaged puffs. This essentially provides the bridge between transient and steady-state analyses necessary to justify application of the relationships between the aggregate and component residence times, described above, to both types of situations.

#### 4.2.4 Summary Comments on Temporal Distributions and Residence Times

The discussion in the preceding subsections is essentially an extension of selected earlier work on pollutant lifetimes, particularly that by Bolin and Rodhe. This has led to several findings, many of which seem not to have been recognized in the previous literature; the more significant of these are itemized as follows:

- The steady-state analysis of pollutant residence times published by Bolin and Rodhe can be extended to describe transient systems as well. We have chosen to demonstrate this by working in the reverse direction, starting with a development describing transient systems, and then applying this to the special situation of a steady-state reservoir. Most statistical parameters, such as density functions for pollutant lifetimes and their associated residence times, have a common basis for both transient and steady-state systems. Parameters such as the turnover time, however, depend on a steady-state conceptual model and have no meaning for transient systems.
- When a system contains multiple removal pathways, temporal behavior of one pathway is usually affected by the behavior of others. Temporal statistics corresponding to an isolated removal process are not, in general, equal to those for this process when it takes place in competition with other removal pathways. Because of this one must use caution in applying statistics, such as residence times and turnover times, from one situation to the next.

- Bolin and Rodhe have demonstrated that the residence time and turnover time are equal when used to describe composite removal in multiple-pathway systems. A similar equivalency does not hold, however, for the description of individual pathways within the composite.
- Composite and individual turnover times, by definition, satisfy the relationship

$$\frac{1}{\tau_0} = \frac{1}{\tau_{r,s,0}} + \frac{1}{\tau_{d,s,0}} + \frac{1}{\tau_{w,s,0}} \quad (4.34)$$

A similar relationship for residence times is obeyed only under highly specialized conditions.

## 5.0 CONCLUSIONS

Concepts and terminology associated with the description of atmospheric source-receptor phenomena contain a number of important and sometimes rather subtle elements. This report has examined a number of these elements, which are summarized in the following conclusions:

- Averaging time is important in specifying all measures of source-receptor phenomena. Any characterization of spatial characteristics, temporal features, or linearity should be accompanied by an explicit statement of the associated averaging time or observation period.
- Source-receptor linearity has been interpreted in a variety of ways in past evaluations, and a well-posed, standardized description is needed. We have presented such a description and suggest that it be used as a standard by future investigators in this field.
- Owing to a variety of complications, source-receptor linearity is difficult to document on the basis of field measurements. Modeling analyses, with their acknowledged shortcomings, are much more amenable to such evaluations. Even model analyses, however, can be subject to conceptual pitfalls. Model (or field) tests of linearity involving the application of tracer species, for example, have been demonstrated capable of leading to erroneous results unless interpreted with caution.
- A transient analysis has been applied to the description of temporal variability. The relationship between statistics for transient systems and those of their steady-state counterparts has been examined to demonstrate that most relationships linking composite-mechanism statistics with their individual components apply in both transient and steady-state situations. Some of these linking relationships apply only for certain classes of density functions, however, and caution is mandatory to ensure valid usage.
- The statistical characterization of temporal source-receptor behavior can be carried out in a variety of ways. Some ambiguity is apparent in the past literature dealing with the temporal behavior of systems containing multiple removal pathways, and in this report we have attempted to resolve this problem by presenting two types of statistical characterizations: one based on the behavior of the component pathways "in isolation" from their counterparts, and the other based on simultaneous interaction of these mechanisms. Application of both types of statistics to a source-receptor evaluation, rather than just one or the other, will usually provide substantially greater insight to the analysis.

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APPENDIX

NOMENCLATURE



## APPENDIX

### NOMENCLATURE

- A normalization constant,  $t/l^3$  or  $l/l^2$
- $\bar{A}$  proportionality constant,  $t/l$  or dimensionless
- c pollutant concentration,  $m/l^3$
- E exposure to pollutant,  $m/l^3$  or  $m/(l^2 t)$
- $E_0$  normalization coefficient, (area-integrated exposure)  $m/l$  or  $m/t$
- $F(t)$  removal rate of molecules resident in a steady-state reservoir having lifetimes less than  $t$ ,  $m/t$
- $F_0$  total removal rate of molecules from a steady-state reservoir,  $m/t$
- f spatial probability-density function,  $1/l^2$
- g temporal probability-density function,  $1/t$
- $\hat{g}_0$  average density function for puffs emitted during time-interval  $q$ , and shifted to the origin,  $1/t$
- k reaction-rate coefficient,  $1/t$  or  $l^3/(m t)$
- $\mathcal{L}$  linear operator
- $L^*$  linearity parameter, dimensionless
- $M(t)$  number of molecules in a steady-state reservoir having lifetimes less than  $t$ ,  $m$
- $M_0$  total number of molecules in a steady-state reservoir,  $m$
- $N(t)$  number of molecules removed from an instantaneous puff at time  $t$ ,  $m$
- $N_0$  total number of molecules in instantaneous puff,  $m$
- q arbitrary function in equation (3.11)
- r reaction rate,  $m/(l^3 t)$

$S$	aggregate emission rate, $m/t$
$\tilde{S}$	instantaneous aggregate emission rate, $m/t$
$s$	spatial density function for pollutant emissions, $1/l^3$
$\tilde{s}$	spatial density function for instantaneous pollutant emissions, $1/l^3$
$t$	time, $t$
$t_j$	release time of puff $j$ , $t$
$t'$	dummy integration variable, $t$
$t^*$	dwelt time in hypothetical flow reactor, $t$
$U$	x-component of wind-velocity vector, $l/t$
$V$	volume of hypothetical reactor, $l^3$
$v$	wind velocity vector, $l/t$
$x$	spatial coordinate, $l$
$y$	spatial coordinate, $l$
$\bar{x}$	x centroid of spatial distribution, $l$
$\bar{y}$	y centroid of spatial distribution, $l$
$\Xi$	cumulative pollutant exposure for influence region, $m/l^3$
$\theta$	averaging time, $t$
$\phi(t)$	probability-density function for molecules of age $t$ removed from steady-state reservoir, $1/t$
$\varphi(t)$	probability-density function for the number of age- $t$ molecules existing in a steady-state reservoir, $1/t$
$\Sigma$	point emission rate, $m/(l^3 t)$
$\sigma_x^2$	x variance of spatial distribution, $l^2$

- $\sigma_y^2$  y variance of spatial distribution,  $l^2$
- $\sigma_t^2$  temporal variance associated with molecules in instantaneous puff,  $t^2$
- $\tau$  residence time associated with molecules in instantaneous puff,  $t$
- $\tau_a$  average age of molecules in a steady-state reservoir,  $t$
- $\tau_t$  residence time of molecules in a steady-state reservoir,  $t$
- $\tau_0$  turnover time in a steady-state reservoir,  $t$
- $\nabla$  divergence operator,  $1/l^2$

#### Subscripts

- $l$  pollutant-species index; alternatively isolated pathway
- $j$  source index; alternatively, puff index
- $d$  dry removal
- $r$  reaction
- $SS$  steady state
- $s$  simultaneously operating pathways
- $t$   $t$  dimension; also denotes residence time in the Bolin-Rodhe term  $t_t$
- $\theta$  time-averaged quantity
- $w$  wet removal
- $x$  arbitrary pathway index, or  $x$  dimension
- $y$   $y$  dimension

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