On tracer theory in geophysical systems in the steady and non-steady state. Part I

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ABSTRACT

Elements of tracer theory in the steady and non-steady state are presented in unified form, in terms common to system analysis in electronic and chemical engineering. Use of tracers requires re-examination of concepts used so far. Previous treatment is shown to be based on tacit assumptions of steady flux of matter through the system, resulting in steady state treatment. Description of tracer response in steady state system requires distinction between mass response and composition response. A system mass is described in terms of bivariate distribution in transit time, τ, and age, T. The non-steady state is shown to be of more common occurrence in description of tracer systems than for mass response systems.

The non-steady state requires separation of the concepts of weighting function from system response, and of composition response, $h^C(\tau)$, from tracer response, $h^T(\tau)$. Differences in normalization and in linearity properties of these functions are indicated. Several formal and heuristic examples demonstrate the properties and applications of these functions. While the theory of non-steady state system is still in the development stage, several analytical and numerical methods are available to provide deeper insight into the significance and utilization of tracer data in geoscience.

1.1. Introduction

For several decades now, isotopic tracer data have been used to increase the information on geophysical and environmental systems. To this category belong the attempts to describe the atmospheric dynamics with the aid of fission products, trajectories and evolution of meteorites with the aid of cosmic ray induced activities, geological history with the aid of uranium and thorium series and the hydrogeological dynamics with the aid of natural stable and radioactive isotopes (D, ^{3}H, ^{14}C, ^{18}O, ^{32}Si, ^{39}A, etc.). Isotopic tracers are not unique in this application, and they are mentioned because of more common awareness of their contribution to tracer applications.

Considering hydrogeology as an outstanding example, as probably more theoretical work was invested in this domain, we have the following classification of the conceptual contribution of tracer data (Nir, 1972): (*a*) determination of specific hydrologic parameters (*b*) confirmation or rejection of concurrent hypotheses or models (*c*) extension or reconstruction of time series of data for use as input in system analysis (*d*) strengthening the link between physical hydrology and system analysis (*e*) supply of preliminary description of regional hydrological systems lacking basic hydrologic data.

The procedure consists normally of superposition of tracer data on existing mass flow data. The addition of tracer mass balance to general dynamics and mass balance offers, in steady state systems, additional insight into its physical structure. The contribution is generally in categories (*a*) and (*b*). For example, the result of a tracer experiment expressed as probability density of transit times may provide the flow velocity, the ground water storativity, mixing pattern of importance to pollution problems, etc., the specific answer depending on other known or assumed parameters (Harpaz et al, 1963).

Until recently the steady state or constant parameter assumption in analyses of environmental systems has been prevalent. However, a steady state system as such is improbable in the natural environment and when it exists it is of limited interest. We are interested in the nature of fluctuations from steady state as they reflect the inner workings and responses of

the system. We are also interested in evaluating the response of a constant parameter system to natural or man-made changes in these parameters for purposes of prediction or control.

The common approximations to correct for the non-steady state consist of the use of average parameters. The average parameter approximation may be inadequate for several reasons. Models depending in non-linear manner on their parameters will not yield the average behaviour of the system when based on average parameters. Correlations of physical significance, liable to occur between tracer concentrations and parameter fluctuations, may be neglected. Any insight into the extreme values that system variables may attain is lost.

The objectives of this presentation are to formulate the existing theory of tracer behaviour in non-steady state systems, to exemplify it on synthetic and real data, to indicate its application to physical synthesis, system analysis and control of environmental systems. A significant by-product happens to be, as usual, the indication of open areas of research which this subject provides in abundance.

The presentation will begin with recollection of the elements of tracer theory in the steady state as a starting point for later developments. This will be of necessity brief, and some readers who may wish a more complete introduction are referred to more extensive presentation of this part of the subject (Sheppard, 1962; Nir, 1973).

An attempt is made to unify the concept of transit time probability density as used by the scientist employing tracers with that of weighting function of the chemical engineer and the system response function of the electronic engineer, by drawing freely from concepts and methods developed within these disciplines and also the life sciences. Conversely, the presentation developed here is expected to be of use beyond the realm of geosciences.

1.2. *List of symbols and definitions*

$C_i(t)$	tracer input concentration
$C_0(t)$	tracer output concentration
$F(\tau)$	probability distribution of flux
$h(\tau)$	(*a*) flux probability density, (*b*) weighting function, (*c*) system response
$h^c(\tau)$	$h(\tau)$ referring to composition response
$h^m(\tau)$	$h(\tau)$ referring to mass response
M	total mass in the system
$M(\tau)$	probability distribution of mass with respect to transit time, τ
$M(T)$	probability distribution of mass with respect to age, T
m_1^h	first moment of τ with respect to $h(\tau)$, $\bar{\tau}_h$
m_2^h	second moment of τ with respect to $h(\tau)$
$q_i(t)$	input flowrate
$q_0(t)$	output flowrate
t	chronological time
T	age; time elapsed since entry until observation in system
$\bar{T}_\psi$	average age in a system
V	system volume
$\delta(t)$	Dirac delta function
μ_k	kth central moment of τ with respect to $h(\tau)$, σ_k^h
σ_2^h	variance of flux transit time
τ	residence or transit time from entry to exit
$\bar{\tau}_h$	mean flux transit time, or m_1^h
$\bar{\tau}_\phi$	Mean mass transit time, or m_1^ϕ
$\phi(\tau)$	probability density of mass in the system with respect to transit time, τ
$\psi(T)$	probability density of mass in the system with respect to age, T

2. Elements of tracer theory in the steady state

2.1. *The $h(\tau)$ function and its properties*

2.1.1. *Introduction.* In general we observe that a quantity of tracer, entering a system at a given time, will not leave the system simultaneously, but different fractions of it will leave the system at different times. The case of simultaneous exit, referred to in the literature as piston or plug flow, is an exceptional case. It is often used as an approximation to a relatively small spread in transit times, as it offers a considerable simplification of the mathematical and physical description of the system. However, its use has to be justified in each case.

The transit time scales encountered in hydrologic systems are typically hours to days

for surface runoff, months to years for lakes, years to hundreds of years for groundwaters, and the spread can reach similar values.

2.1.2. *Several interpretations of the spread of transit times, $h(\tau)$.* There are several ways of looking at the spread of transit times in a physical system. One way is to consider it as a probability density of transit times of the molecules of the ingoing flux, $h(\tau)$.

We assume that the function $h(\tau)$ is constant from one experiment to the next so that valid predictions can be made regarding the future. In practice this is achieved when the flows and system parameters do not change significantly during the time of observation.

The use of $h(\tau)$ will help us also to quantify the definition of an ideal tracer. We will interpret this statement about tracers, requiring similar physical and chemical characteristics as the matter being traced, to mean that both have identical $h(\tau)$.

Another point of view is that of system analysis which regards the time distribution of the outgoing tracer as the system response of the lumped system, or a response to an instantaneous (δ-function) input.

A complementary point of view is the concept of the weighting function, i.e., the function describing the relative contribution of different inflows at times $(t-\tau)$ to the present outflow at time t. This action of the weighting function is given by the convolution integral:

$$q_0(t) = \int_0^\infty q_i(t-\tau)\, h(\tau)\, d\tau \qquad (1a)$$

However, this formulation has a different interpretation depending on the objectives of our observations. When we are interested only in quantity of response, $h(\tau)$ has a different meaning and value from that when $h(\tau)$ has to weigh both quantity and composition, the latter being relevant in the case of a tracer. Referring to Fig. 1, we observe that the response to an input $q_i(t) = V_i\delta(t)$ was $V_0\delta(\tau)$, $V_0 = V_i$, this meaning that there is an immediate flow or mass transfer response and $h(\tau) = \delta(\tau)$ (Fig. 1*a*). However if we require also identification in the molecular sense, as is the case with tracers, then the response will depend on the history of inflow and the type of dispersion in the system as shown in the following examples (Fig. 1*b* and *c*).

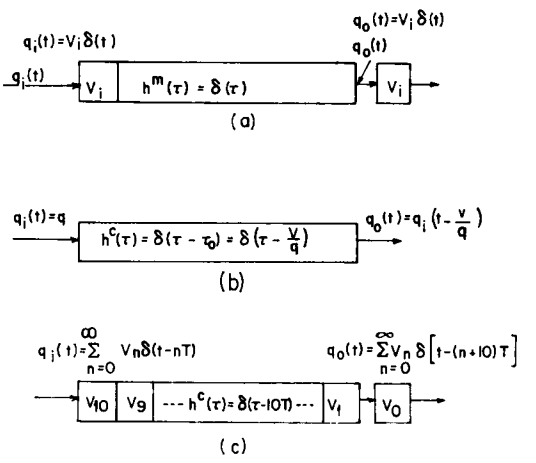

Fig. 1

If $q_i(t)$ is a constant flow rate into the system (i.e. $q_i(t) = q$), and no mixing takes place (piston flow), a molecule entering at time 0 will appear at the output after traversing the volume V, i.e. after a time $\tau_0 = V/q$ (Fig. 1*b*). The molecular or composition response will therefore be delayed by τ_0 and $h(\tau) = \delta(\tau - \tau_0)$.

Other mixing patterns would result in different forms of $h(\tau)$: complete mixing, 2 mixed compartments, etc. In order to distinguish mass response from composition response we will use $h^m(\tau)$ for the former and $h^c(\tau)$ for the latter, whenever ambiguity may arise, as in Fig 1. In general $h^m(\tau) \neq h^c(\tau)$.

Fig. 1*c* illustrates a different $h^c(\tau)$. The input in this case is pulsed, a constant volume, say one tenth of the total volume V, $V_n = V/10$ being injected into the system at equal time intervals, T. We can describe the input by the function $q_i(t) = \sum_{n=0}^{\infty} V_n\,\delta(t-nT)$. The first input component, V_0, will appear at the output when the 10th input, V_{10}, enters the system, and the composition response is $h^c(\tau) = \delta(\tau - 10T)$ while the composition output is, $q_0(t) = \sum_{n=0}^{\infty} V_n\,\delta[t-(n+10)\,T]$.

In both cases, the continuous and discrete, the composition response does not depend explicitly on the chronological time, t, as it does not appear in the definition of $h(\tau)$. However, when we consider the structure of the system, it is obvious that we have achieved this independence on t by a tacit assumption that

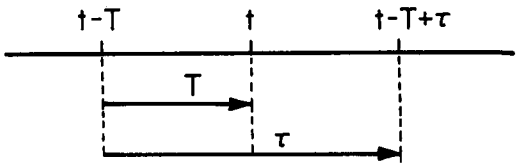

Fig. 2

all flow parameters do not depend on t: $q(t) = q$ in the continuous case, and V_n and T are also constants in the discrete case.

2.1.3. *The tracer integral equation.* We restate now (1a) specifying composition response

$$q_0(t) = \int_0^\infty q_i(t-\tau)\, h^c(\tau)\, d\tau \qquad (1\,b)$$

We can write now a corresponding equation for tracers. We assume again an ideal tracer, i.e. $h(\tau)$ is identical for bulk and tracer. Tracer loss and decay will be presently neglected.

Conservation of matter requires that each flow component $q_i(t-\tau)$ be multiplied by the corresponding tracer concentration $C_i(t-\tau)$

$$q_0(t)\, C_0(t) = \int_0^\infty q_i(t-\tau)\, C_i(t-\tau)\, h^c(\tau)\, d\tau \qquad (1\,c)$$

The steady state assumption implies $q_0(t) = q_i(t-\tau) = q$, which allows a simplified form of (1c)

$$C_0(t) = \int_0^\infty C_i(t-\tau)\, h^c(\tau)\, d\tau \qquad (1\,d)$$

$h^c(\tau)$ does not depend in this case on the time t but only on a variable of integration τ, which is the time difference between the present and the past composition.

While the formulation of (1d) regarding concentrations is identical with (1b), which deals with flow components, we must keep in mind that (1b) does not imply (1d) or vice versa, unless all the conditions discussed above, and primarily the steady flow condition, are fulfilled.

Equation (1d) in its discrete form

$$C_0(t) = \sum_{\tau=0}^{\infty} C_{t-\tau}\, h_\tau \quad t, \tau = 0, 1, 2, \ldots \qquad (1\,e)$$

was applied by Eriksson (1963) and Gat (1970) to river and lake systems. It is solved with respect to h_τ by standard numerical or analytical deconvolution techniques.

By introducing an input concentration in the shape of a δ-function we obtain from (1d) and the properties of δ-function

$$C_0(t) = \int_0^\infty \delta(t-\tau)\, h^c(\tau)\, d\tau = h^c(t) \qquad (2)$$

which shows that the system response is identical to the weighting function in steady state systems. These two concepts differ, however, under non-steady conditions, as discussed below.

2.2. *Time relations in the steady state*

2.2.1. *The concepts of time.* We refer to Fig. 2 in order to clarify the different concepts of time needed for subsequent discussion.

We use three different measures of time: the chronological time, t, also designated the instant, as given by the date and hour of observation; T, the time elapsed since the molecule entered the system up to the instant of observation t, commonly referred to as age in the system; and τ, the time a molecule spends in the system, from entry until it leaves at a boundary, usually termed the transit or residence time. Evidently, for a given molecule, $T \leqslant \tau$, the equality taking place at the instant of exit. All other quantities may be derived using these concepts and definitions introduced so far: t, T, τ and $h(\tau)$.

We can reexamine these concepts by reference to Fig. 2. The value of t runs consecutively from an arbitrary 0 (or $-\infty$) to $+\infty$. The value of T is reset to 0 for each molecule entering the system, in this case at the instant $t - T$, and it increases with $\Delta T = \Delta t$, $0 < T < \tau$. The value of τ we should regard as a constant preassigned to the molecule at entry, even if in some cases we cannot know its value.

2.2.2. *The $F(\tau)$ distribution.* The first derived quantity will be the distribution of the outgoing flux F, with respect to τ, the time spent in the reservoir. From the definition of $h(\tau)$ as probability density, we obtain this distribution as

$$F(\tau) = q \int_0^\tau h(\tau')\, d\tau' \qquad (3\,a)$$

$$\frac{dF(\tau)}{d\tau} = q h(\tau) \qquad (3\,b)$$

As $h(\tau)$ is a normalized density, $\int_0^\infty h(\tau)d\tau = 1$, and $F(\infty) = q$.

In the steady state, $F(\tau)$ of input and output flux are equal as a matter of definition. They are, however, not equal in the non-steady state, and care must be taken then to specify which distribution we observe.

The distribution $F(\tau)$ is shown in Fig. 3.

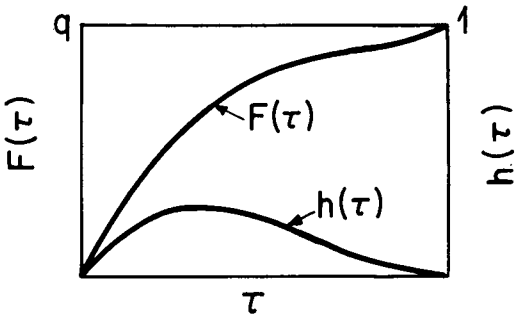

Fig. 3

2.2.3. *The population analogy.* In order to clarify these concepts it seems useful to consider similar concepts used in discussion of biological populations including the human population.

The transit time is equivalent to the life span, while the age in the system corresponds to the common usage of the word. Steady state system will correspond to a population in an equilibrium, with constant and equal birth and death rate, F, and constant distribution of life times, $h(\tau)$. $F(\tau)$ will correspond to the cumulative distribution by age of the dying group. M will be the total population while $M(\tau)$ and $M(T)$ will be the cumulative distributions with respect to life time, τ, and age, T. $\bar{\tau}$ will be equivalent to the life expectancy or the average age at death, while $\bar{T}$ will be the average age of the total population.

The distribution with respect to T has a physical meaning in the sense that it can be actually found out by individual classification. Distribution by τ can be made only in the statistical sense with respect to human or other biological population; however in certain geophysical systems we can recognize definite streamlines with assigned transit times and negligible mixing between them.

2.2.4. *The $\phi(\tau)$ density and the $M(\tau)$ distribution.* In analogy to $h(\tau)$ and $F(\tau)$, which relate to the flux, we will examine the density $\phi(\tau)$ and distribution $M(\tau)$, which relate to the total mass in the system.

We will first find the density of $\phi(\tau)$. From 4 we observe that the fraction of mass having transit time τ_2 to $\tau_2 + d\tau$ is given by $\tau_2 dF(\tau)/M$.

$$\phi(\tau)\,d\tau = \frac{dM(\tau)}{M} = \frac{\tau dF}{M} = \frac{\tau}{M}\frac{dF(\tau)}{d\tau}d\tau = \frac{\tau q h(\tau)\,d\tau}{M} \tag{4a}$$

Formally we have to integrate the incoming part of the flux with transit time between τ and $\tau + d\tau$, $dF(\tau) = qh(\tau)d\tau$, over the whole span of residence in the system, i.e., the age range 0 to τ

$$dM(\tau) = \int_0^\tau dF(\tau)\,dT = \tau dF(\tau) = \tau q h(\tau)\,d\tau \tag{4b}$$

which is equivalent to (4a). The physical significance of this formulation is that those parts of the flux having longer residence times occupy parts of the system in direct proportion to these times. This is demonstrated in Fig. 4.

The distribution of mass with respect to τ is obtained by integration of (4b)

$$M(\tau) = q\int_0^\tau \tau' h(\tau')\,d\tau' \tag{5}$$

$M(\tau)$ is the mass of all molecules having transit times less than τ (Fig. 4). The total mass, M, is given by

$$M = \lim_{\tau\to\infty} M(\tau) = q\int_0^\infty \tau h(\tau)\,d\tau = q\bar{\tau}_h \tag{6a}$$

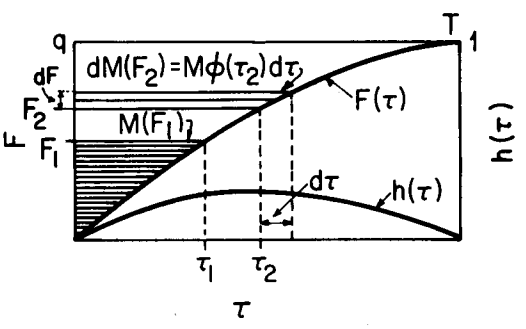

Fig. 4

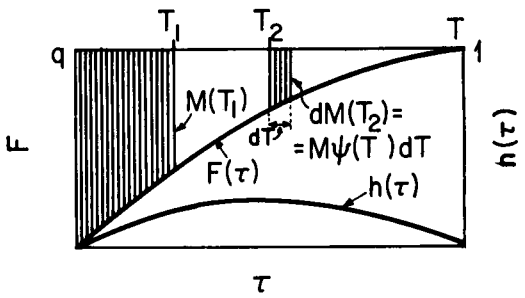

Fig. 5

where $\bar{\tau}_h$ is the mean flux transit time. The relation

$$\bar{\tau}_h = \frac{M}{q} \tag{6b}$$

holds therefore, without any specific assumptions about the mixing pattern or time distribution, for systems in a steady state.

2.2.5. *The $\Psi(T)$ density and the $M(T)$ distribution.* Let us observe an ingoing flux mass $q = F(\infty)$ while it traverses the system. After an elapsed time T in the system all molecules of this flux having transit times shorter than T have left the system. This amount is $F(T)$, according to (3a). The amount of material with ages between T and $T + \Delta T$ is therefore $[F(\infty) - F(T)]dT$. We define a new density $\Psi(T)$

$$\Psi(T) = \frac{F(\infty) - F(T)}{M} \tag{7}$$

$$\begin{aligned} M\Psi(T)\,dT &= [F(\infty) - F(T)]\,dT \\ &= q\left(1 - \int_0^T h(\tau)\,d\tau\right) dT \\ &= q\int_0^T \int_T^\infty h(\tau)\,d\tau\,dT \end{aligned} \tag{8}$$

Fig. 5 shows the function $M\Psi(T)$. It is an inversion of the $F(\tau)$, as seen from (7).

The distribution of mass with respect to age is obtained by integration of (8).

$$M(T) = \int_0^T M\Psi(T')\,dT' = \int_0^T q\,dT' \int_{T'}^\infty h(\tau)\,d\tau \tag{9}$$

$M(T)$ is also shown in Fig. 5. We expect on physical grounds that $\lim_{T\to\infty} M(T) = \lim_{\tau\to\infty} M(\tau) = M$, i.e., the two distributions given by (5) and (9) refer to the same total mass of the system. Appendix 1 discusses this equivalence.

2.2.6. *$M(\tau, T)$ as a bivariate distribution.* It is evident from the defining eqs. (5) and (9), and the corresponding Figs. 4 and 5, that $M(\tau)$ and $M(T)$ may have different values even when their arguments are equal, i.e. $\tau = T$. This apparent ambiguity is resolved if we consider M as a function of the orthogonal coordinates F and T, the dependence on τ being through $F(\tau)$ only, i.e., $M(\tau, T) = M(F(\tau), T)$. $M(\tau)$ will be defined then as a cumulative marginal distribution $M(\tau, \infty)$ and similarly $M(T)$ will stand for $M(\infty, T)$ (Mood & Graybill, 1963), (Appendix 3). $M(F(\tau), T)$ is shown in Fig. 6 for $\tau = \tau_1$ and $T = T_1$.

2.2.7. *Average transit time of flux and mass. Average age.* The mean or average flux transit time was already found to be from (6a)

$$\bar{\tau}_h = \int_0^\infty \tau h(\tau)\,d\tau = \frac{M}{q}$$

Using the terminology of section 2.3, $\bar{\tau}_h = m_1^h$. We can calculate the average mass transit time using the mass transit time density, $\phi(\tau)$, given by (4a).

$$\bar{\tau}_\phi = \int_0^\infty \tau\phi(\tau)\,d\tau = \int_0^\infty \tau^2 \frac{qh(\tau)\,d\tau}{M} \tag{10}$$

The numerator of (10) contains the second moment of $F(\tau)$ distribution,

$$m_2^h = \int_0^\infty \tau^2 h(\tau)\,d\tau.$$

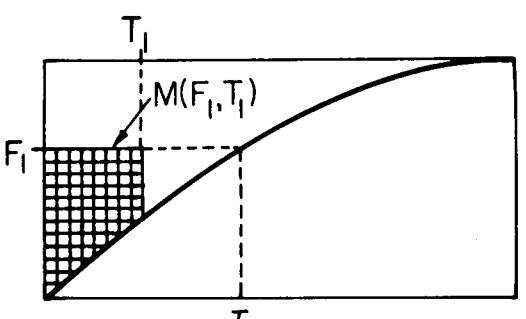

Fig. 6

Using again the moment terminology we obtain

$$m_1^{\phi} = \frac{m_2^h}{m_1^h} \tag{11}$$

The average age is found in a similar way, using the age density $\psi(T)$. Using (8) we have

$$\bar{T}_{\psi} = \frac{q}{M}\int_0^{\infty} T dT \int_T^{\infty} h(\tau)\, d\tau \tag{12}$$

In Appendix 2 we show that

$$\bar{T}_{\psi} = \frac{1}{2}\bar{\tau}_{\phi} = \frac{1}{2}\frac{m_2^h}{m_1^h} \tag{13}$$

An additional parameter of interest is the variance of the transit time of the flux, σ_h^2. This can be found directly if we know m_1^h and m_2^h, as

$$\mu_2^h = \sigma_h^2 - = m_2^h - (m_1^h)^2 \tag{14}$$

2.3. *Moment relations and their applications*

The usefulness of the moments of the density $h(\tau)$ is evident when combined with the rules of moment transformation in convolution (Diskin, 1967; Nir, 1973). Rewriting (1b) for simplicity as

$$y(t) = \int_0^{\infty} x(t-\tau)\, h(\tau)\, d\tau$$

we can apply the rules of additivity of moments

$$m_1^y = m_1^x + m_1^h \tag{15a}$$

$$\mu_2^y = \mu_2^x + \mu_2^h \tag{15b}$$

$$\mu_3^y = \mu_3^x + \mu_3^h \tag{15c}$$

Higher moments, while not simply additive, are deduced from these relations (Diskin, 1967).

The application of the moments of the output concentration is made in estimates of concentrations, with the aid of stochastic inequalities known as Tchebycheff theorem and its corrollary (Eadie et al., 1971). The Tchebycheff theorem implies that the probability that a random variable will differ from its mean, m_1, by more than k times the standard deviation σ, is less than $1/k^2$.

$$P[|x - m_1| \geq k\sigma] \leq 1/k^2 \tag{16}$$

With more information about the distribution, e.g. unimodality or knowledge of μ_4, more precise statements can be made.

Another example of application of moments is the case in which the input to a system may be described by a power series or a polynomial. Then we need to know only the moments of the system response function for exact prediction of the output, the highest moment being equal to the degree of the polynomial (Zadeh, 1963).

There is a different way to look at moment transformations, which provides additional insight into the effects of a system on an input function. Consider the average $\bar{C}$ of stationary time series, $C(t)$, given by

$$\bar{C} = \lim_{T\to\infty} \frac{1}{T}\int_0^T C(t)\, dt$$

Applying such an averaging to both sides of (1d) we obtain

$$\bar{C}_0 = \bar{C}_i \int_0^{\infty} h^C(\tau)\, d\tau$$

In conservative systems the average will be preserved as $\int_0^{\infty} h^C(\tau) d\tau = 1$. This will not hold for tracers undergoing radiactive decay, for example. For the variances of the concentrations σ_i^2 and σ_0^2 we obtain (Appendix 4)

$$\sigma_0^2 = \sigma_i^2 \int_0^{\infty} h(\tau)^2\, d\tau$$

Under the physical conditions that $h(\tau) > 0$, and $\int_0^{\infty} h(\tau)\, d\tau = 1$, we have

$\int_0^{\infty} h(\tau)^2 d\tau \leq 1$ which implies $\sigma_0^2 \leq \sigma_i^2$

The concentration variance is therefore reduced generally due to transformation by a constant parameter, linear system. This is a complementary observation to the increase in time variance as given by (15b)—increase in rise time is accompanied by a decrease in bandwidth.

2.4. *Examples*

It is instructive to calculate the average flux transit time $\bar{\tau}_h$ and the average age, $\bar{T}_{\psi}$, for some commonly encountered system response functions.

For the displacement movement or piston

flow $h^C(\tau) = \delta(\tau - \tau_0)$, where τ_0 is the delay between input and output. We obtain from (6a),

$$\bar{\tau}_h = \int_0^\infty \tau\delta(\tau - \tau_0)\, d\tau = \tau_0$$

as expected. There being no dispersion, there is only one value of transit time, which is also the average one.

The age is obtained from (13)

$$\bar{T}_\psi = \frac{m_2^h}{2m_1^h} = \frac{\int_0^\infty \tau^2\delta(\tau - \tau_0)\, d\tau}{2\tau_0} = \frac{\tau_0}{2} \qquad (17)$$

This could be predicted on inspection of the system—a population with uniform age distribution from 0 to τ_0 has an average age at half maximum value. Therefore, it should not be surprising to find these results in human populations with low infant mortality and fairly narrow life expectancy distribution (Bolin & Rhode, 1973).

For a completely mixed system we obtain in a similar manner

$$h(\tau) = ke^{-k\tau} \quad \text{and} \quad \bar{\tau}_h = \int_0^\infty \tau k e^{-k\tau} d\tau = \frac{1}{k} \qquad (18\,a)$$

$$\bar{T}_\psi = \frac{1}{2}\frac{\int_0^\infty \tau^2 k e^{-k\tau} d\tau}{1/k} = \frac{1}{k} \qquad (18\,b)$$

In this singular case we obtain the relation $\bar{\tau}_h = \bar{\tau}_\psi$, as the flux is sampling the average age of the well-mixed system.

It may be readily shown that a two component piston flow system may exhibit a wide range of relations $\bar{\tau}_h \lesssim \bar{T}_\psi$ according to the ratio of fluxes of these components.

2.5. *Dating in dynamic systms*

Dating in the domain of tracer applications is associated with the use of radioactive tracers, with their unique property of decay constant, which is not influenced by environmental conditions. Recently, the racemization property of amino acids seems to offer a similar possibility. The advantage of the dating with the aid of decay constant as compared to direct count of some time-dependent property like tree rings, varves, ice core isotope (^{18}O) cycles, etc., lies primarily in the economy of effort, as a single sample may be readily dated. The complication may arise in the assumptions about the structure and the parameters of the model which is subject to dating.

We will consider here dynamic systems with constant or variable flux of matter through them. We should recall, however, that the dating concept evolved first in static systems, such as dead biological matter or rocks, using the well-known methods of ^{14}C or ^{40}K–^{40}A, respectively. The result of an experiment results then in a date (an instant, t_0, on a chronological time scale, t) which is interpreted as the date of the closure of the system from the dynamic effects of the environment. Repeated experiments on the same system will provide the same date, t_0, within experimental precision.

In a dynamic system the "dating" does not, as a rule, provide a single date. The result may be the average transit time of the flux or another parameter of the transit time distribution, the actual interpretation depending on a priori knowledge or assumptions about the model of the system. The most common assumption is again the piston flow.

The weighting function will be modified by the decay of the tracer, from $h(\tau)$ to $h(\tau)e^{-\lambda\tau}$. The resulting equation for piston flow is

$$C_0(t) = \int_0^\infty C_i(t-\tau)\,\delta(\tau - \tau_0)\, e^{-\lambda\tau} d\tau = C_i(t-\tau_0)\, e^{-\lambda\tau_0} \qquad (19)$$

For unique determination of τ_0, we need information about $C_i(t)$. The simplest model has constant $C_i(t) = \bar{C}_i$. Therefore, $C_0(t) = \bar{C}_i e^{-\lambda\tau_0}$. This is a common assumption for environmental isotopes in the prethermonuclear period (^3H, ^{39}A, ^{85}Kr) or ^{14}C in the preindustrial era.

Another assumption about $C_i(t)$, which is common in environmental models is that it is constant for each tracer concentration, $\bar{C}_i^k$, with a modulating time-dependent coefficient, $A(t)$, common for all tracers, $C_0^k(t) = A(t)\bar{C}_i^k$. Such a model was applied to atmospheric ^{89}Sr and ^{90}Sr, which were diluted by non-radioactive air masses; tracers in oceanic sediments, where the variable coefficient may be due to varying sedimentation rate, varying tracer production or both e.g. $^{10}Be/^{26}Al$ (Lal, 1963) or $^{230}Th/^{232}Th$.

In these cases ratios of two tracers with decay constants, λ_1 and λ_2 provide a unique solution for τ_0

$$\frac{C_0^1(t)}{C_0^2(t)} = \frac{A(t-\tau_0)}{A(t-\tau_0)} \frac{\bar{C}_i^1}{\bar{C}_i^2} \frac{e^{-\lambda_1 \tau_0}}{e^{-\lambda_2 \tau_0}} = \frac{\bar{C}_i^1}{\bar{C}_i^2} e^{-(\lambda_1-\lambda_2)\tau_0} \tag{20}$$

In the case of a well-mixed system we obtain

$$C_0(t) = \int_0^\infty C_i(t-\tau)\, k e^{-k\tau} e^{-\lambda\tau} dt \tag{21a}$$

or for constant $\bar{C}_i$

$$C_0(t) = \int_0^\infty \bar{C}_i\, k e^{-(k+\lambda)\tau}\, d\tau = \frac{k\bar{C}_i}{k+\lambda} \tag{21b}$$

which determines k, the unknown parameter characterizing the distribution.

We may generalize these examples to state that a single tracer experiment will determine one unknown parameter of a known (assumed) distribution. The type of distribution (its shape) cannot be determined by such an experiment. Injustice was often done to the tracer method by assuming simple one parameter models without geophysical evidence.

A commonly encountered two-parameter model is the one dimensional convective-dispersive system (Nir, 1964), for which $h(\tau)$ is

$$h(\tau) = \frac{v}{(4\pi D\tau)\,1/2} \exp - \left[\frac{(x_0 - v\tau)^2}{4D\tau}\right] \tag{22}$$

with unknown v and D. It can be solved exactly with the aid of two decaying tracers, which will provide two independent equations. In many practical situations the geophysical limits on one unknown delimit the value of the other, even if one tracer only is available.

We can generalize this situation by requiring n isotopic radioactive tracers, to determine n parameter models. We still require, however, a priori assumption of the analytical structure of this model. A further generalization is possible which avoids this limitation:

Recalling the definition of the Laplace Transform as

$$H(\lambda) = \int_0^\infty h(\tau)\, e^{-\lambda\tau} dt \tag{23a}$$

we can regard the dating experiment as a singular value of the Laplace Transform of $h(\tau)$, for the kth isotope

$$\frac{C_0^k(t)}{\bar{C}_i^k} = \int_0^\infty h(\tau)\, e^{-\lambda_k \tau} d\tau = H(\lambda_k) \tag{23b}$$

Given a large number of radioactive tracers with wide range of λ, the shape of $H(\lambda)$ may be reconstructed, and $h(\tau)$ is obtained by inverse transformation, $h(\tau) = L^{-1}\{H(\lambda)\}$.

This approach was presented by Geiss et al. (1962) to reconstruct the irradiation history of meteorites, and by Beran & Assaf (1970) to determine turbulent dispersion patterns in the atmosphere and the oceans. In these cases, there is a large number of isotopes to provide the wide range of λ values. The essential difficulty in the turbulent media is in proving that the various tracers have a common turbulence pattern. The discussion was limited here to lumped systems in steady state, for simplicity of presentation.

We have observed previously (see 2.1.2) that reconstruction of the function $h(\tau)$, or identification, in tems of system analysis, does not require radioactive tracers. It can be achieved with a single time variable tracer, whose input and output from the system is known in analytical or numerical presentation, e.g. eq. (1e). For finite input duration we could readily deduce the average delay induced by a system, $\bar{\tau}_h$, using the rule of additivity of moments (15a). For infinite time series inputs similar information is provided by the cross-correlation between input and output concentrations (Bendat & Piersol, 1971). In using constant input radioactive tracers we compensate by multiplicity of decay constants for the time variability of the input of a single non-radioactive tracer.

2.6. *Summary of steady state theory*

(*a*) Tracer theory is presented in unified form in terms common to system analysis in electronic and chemical engineering.

(*b*) Extension of tracer theory requires distinction between mass response and composition response.

(*c*) Distinction is made between chronological time, t, transit time, τ, and age, T, with analogies to biological population.

(*d*) A system is described as a function of two independent variables, τ and T.

(*e*) The radioactive dating concept is extended to general transit time distributions.

Appendix 1. Equivalence of total mass formulations

From (5) and (9) we postulate

$$\int_0^\infty \tau h(\tau)\,d\tau = \int_0^\infty dT \int_T^\infty h(\tau)\,d\tau \qquad \text{(A 1.1)}$$

Integrating right hand side by parts

$$\int_0^\infty dT \int_T^\infty h(\tau)\,d\tau = T\int_T^\infty h(\tau)\,d\tau\Big|_0^\infty + \int_0^\infty Th(T)\,dT \qquad \text{(A 1.2)}$$

The first right hand side term vanishes at 0 for all $h(\tau)$. It also vanishes at infinity for physically realizable $h(\tau)$, which vanish identically for large values of $\tau > \tau_{\text{maximum}}$. The remaining term of (A 1.2) is identical to (A 1.1).

Appendix 2. Proof of the relation $\bar{T}_\psi = \frac{1}{2}\tau_\phi$

From (1.2) we obtain, integrating by parts

$$T_\psi = \frac{q}{M}\int_0^\infty T\,dT \int_T^\infty h(\tau)\,d\tau = \frac{q}{M}\left[\frac{T^2}{2}\int_T^\infty h(\tau)\,d\tau\right]_0^\infty + \frac{q}{M}\int_0^\infty \frac{T^2}{2}h(T)\,dT \qquad \text{(A 2.1)}$$

The first right hand side term vanishes at 0 and inifinity, as discussed in Appendix 1. The second right hand term is by (10) equal $\frac{1}{2}\bar{\tau}_\phi$.

Appendix 3. The bivariate density

We define the probability density of a molecule belonging to the system of total mass M, to have the transit time between τ and $\tau + d\tau$ and age between T and $T + dT$ as the mass ratio

$$\frac{dM}{M} = \frac{dF(\tau)\,dT}{M} = \frac{dM}{M}(F(\tau), T) \qquad \text{(A 3.1)}$$

Integration of $dM(F, T)$ over all values of T will provide the marginal distribution density (Mood & Graybill, 1963)

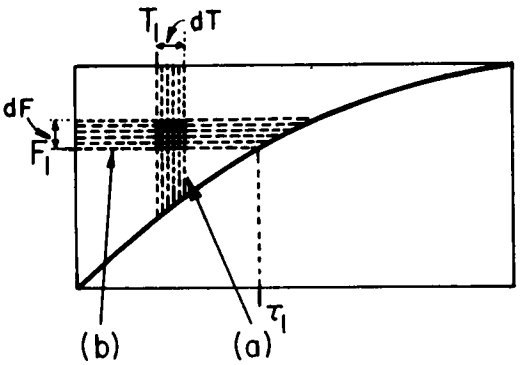

Fig. 7. (*a*) Integration over all τ yields $M\Psi(T)dT$. (*b*) Integration over all T yields $M\phi(\tau)d\tau$.

$$\frac{dM(F(\tau))}{M} = \int_0^\infty \frac{dM(F(\tau), T)}{M}\,dT \qquad \text{(A 3.2)}$$

$$= d\tau \int_0^\tau \frac{qh(\tau)\,d\tau}{M}\,dT = \tau\frac{qh(\tau)\,d\tau}{M} = \phi(\tau)\,d\tau \qquad \text{(A 3.3)}$$

In the above derivation we used the definition of $\phi(\tau)$ from (4a). Similarly the marginal density of $dM(T)/M$ is

$$\frac{dM(T)}{M} = \int_0^\infty \frac{dM(F(\tau), T)}{M}\,d\tau = \frac{qdT}{M}\int_T^\infty h(\tau)\,d\tau = \phi(T)\,dT \qquad \text{(A 3.4)}$$

where we used the definition of $\phi(T)$ from (8)

$$dM(F(\tau), T) = dF(\tau)\,dT = h(\tau)\,d\tau\,dT$$

Appendix 4. Proof of the relation $\sigma_0 \leqslant \sigma_i$

We have seen in section 2.3 that the averages of the input and output of a stationary process are equal, provided we consider a constant parameter conservative system.

We can deal therefore with deviations from these averages for both time series, as they are the sole contributors to the respective variances.

Starting from (1d), namely

$$C_0(t) = \int_0^\infty C_i(t-\tau)\,h^C(\tau)\,d\tau$$

we form the autocovariance

$$A_{00}(\tau) = \overline{C_0(t)\, C_0(t-\tau)} \qquad \text{(A 4.1)}$$

$$\sigma_0^2 = A_{00}(0)$$

$$= \int_0^\infty \int_0^\infty \overline{C_i(t-\tau_1)\, C_i(t-\tau_2)}\, h^C(\tau_1)\, h^C(\tau_2)\, d\tau_1\, d\tau_2$$

$$= \int_0^\infty \int_0^\infty A_{ii}(\tau_2-\tau_1)\, h^C(\tau_1)\, h^C(\tau_2)\, d\tau_1\, d\tau_2 \qquad \text{(A 4.2)}$$

(Bendat & Piersol, 1971).

The crosscovariance is defined similarly

$$A_{i0}(\tau) = \overline{C_i(t)\, C_0(t+\tau)}$$

$$= \int_0^\infty \overline{C_i(t)\, C_i(t+\tau-\tau_1)}\, h(\tau_1)\, d\tau_1$$

$$= \int_0^\infty A_{ii}(\tau-\tau_1)\, h(\tau_1)\, d\tau_1 \qquad \text{(A 4.3)}$$

$A_{i0}(\tau) > 0$ as both integrands are positive.

We can rewrite (A4.2) by integrating with respect to τ_1 and substitution of $A_{i0}(\tau)$ from (A 4.3)

$$\sigma_0^2 = \int_0^\infty A_{i0}(\tau_2)\, h^C(\tau_2)\, d\tau_2 \qquad \text{(A 4.4)}$$

We use the inequality

$$A_{i0}(\tau) \leqslant \sqrt{A_{ii}(0)\, A_{00}(0)} = \sigma_i\, \sigma_0 \qquad \text{(A 4.5)}$$

$$\sigma_0^2 \leqslant \sigma_i\, \sigma_0 \int_0^\infty h^C(\tau_2)\, d\tau_2 \qquad \text{(A 4.6)}$$

Normalization of $h^C(\tau)$ ensures that $\sigma_0 \leqslant \sigma_i$. For $C_i(t)$ having the characteristic of random noise input, $A_{ii}(\tau) = \sigma_i^2 \delta(\tau)$, and (A 4.2) simplifies to

$$\sigma_0^2 = \sigma_i^2 \int_0^\infty h(\tau)^2\, d\tau \qquad \text{(A 4.7)}$$

$\int_0^\infty h(\tau)^2 d\tau \leqslant 1$ under the existing conditions of positivity and normalization.

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О ТЕОРИИ ТРАССЕРОВ В ГЕОФИЗИЧЕСКИХ СИСТЕМАХ В СТАЦИОНАРНЫХ И НЕСТАЦИОНАРНЫХ СОСТОЯНИЯХ. ЧАСТЬ I

Элементы теории трассеров в стационарных и нестационарных состояниях представлены в единой форме в терминах, общих системному анализу в электронной и химической технике. Использование трассеров требует пересмотра концепций, использовавшихся до сих пор. Показано, что предыдущие рассмотрения основываются намолчаливых предположениях о стационарности потоков вещества через систему, что приводит к рассмотрению стационарных состояний. Описание реакции трассеров в стационарном состоянии требует различения между реакциями массы и состава. Масса системы описывается в терминах распределения по двум переменным — времени перехода τ и возраста T. Показано, что нестационарное состояние при описаниях систем трассеров встречается более часто, чем при описаниях систем, реагирующих на массу. Нестационарное состояние требует разделения концепций весовой функции и реакции системы, и реакции состава $h^c(\tau)$ и реакции трассеров $h^T(\tau)$. Указываются различия этих функций в свойствах нормализации и линейности. Несколько формальных и эвристических примеров показывают свойства и применения этих функций. Хотя теория нестационарных состояний системы находится все еще в стадии развития, имеются различные аналитические и численные методы для более глубокого проникновения в значимость и использование трассерных данных в науках о Земле.