

MARC: Monitoring and Assessment Research Centre
GEMS: Global Environmental Monitoring System



MARC REPORT NUMBER 12

**AN INTRODUCTION TO
THE EXPOSURE
COMMITMENT CONCEPT
WITH REFERENCE TO
ENVIRONMENTAL MERCURY**

Technical Report

Prepared by:
MONITORING AND ASSESSMENT RESEARCH CENTRE
Chelsea College, University of London

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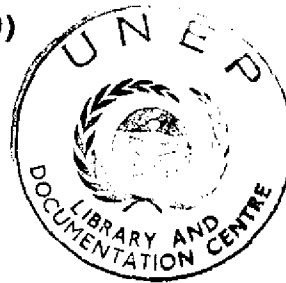
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**An introduction to the exposure
commitment concept
with reference to
environmental mercury**

by P. J. Barry*

A Technical Report (1979)



Prepared by:
Monitoring and Assessment Research Centre
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ABSTRACT

When a toxic substance is released to the environment, it may not immediately reach and affect a population of sensitive receptors. This is particularly true if the substance must pass through a sequence of environmental compartments each of which causes a delay in the transfer process. Nevertheless, the act of introducing that substance into the environment constitutes on behalf of the receptors a commitment to a future exposure. The totality of that future exposure is called the exposure commitment. In this report, relevant concepts and the use of this approach to environmental assessment are discussed.

A fundamental concept of exposure commitment analyses is the transfer coefficient, indicating fractional transfer of the pollutant between successive reservoirs in an environmental system. The relationships between transfer coefficients and the parameters of conventional dynamic models are given. The general principles of evaluating transfer coefficients are illustrated by referring to a specific practical example, that of mercury released to the atmosphere or to soil. The advantages and limitations of time-dependent and time-independent assessments are briefly indicated.

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1.0 Introduction

When a pollutant is introduced into the environment it may impinge directly or indirectly upon the life and well-being of man in such a way as to produce physical, social and psychological effects, some of which are judged to be either advantageous or disadvantageous, significant or insignificant, according to the standards of the time. Before man embarks on activities that will alter the state of environmental systems, it is prudent and sometimes mandatory to estimate the magnitude of the consequential changes in the state of the system and to assess the possible effects.

Important characteristics of changes in the state of an environmental system are the time and space intervals over which these changes are assessed. In general, the finer the resolution of time and space required, the greater the need for detailed information. High resolving power is desirable in some situations, e.g. close to discrete sources of atmospheric pollution where space and time gradients of concentrations of toxic substances are relatively large and some critical limit, statutory air quality standard, or toxic threshold concentration may be exceeded.

On the other hand, a wide range of situations do not need to be resolved so finely; longer averaging intervals can be used without loss of relevant information. Situations of this type may include, for example, low-level continuous air pollution affecting relatively large regions at greater distances from the source.

For some situations, it may be possible to neglect altogether short time fluctuations in the state of a system and, without serious loss of useful information, estimate instead the sum or integral over the time during which the state of the system changes. For example, if $m(t)$ is the magnitude of a variable in a system at a given place at time t and \bar{m} is its mean value in the undisturbed system, the magnitude of the disturbance at time t , $p(t)$, is

$$p(t) = m(t) - \bar{m} \quad (1)$$

The overall disturbance, $P(\infty)$, can be assessed as the integral over time of $p(t)$, i.e.

$$P(\infty) = \int_{-\infty}^{\infty} p(t) dt \quad (2)$$

where the use of $-\infty$ to ∞ in the integration limits avoids the necessity of specifying the time during which the system is perturbed.

If $P(\infty)$ is finite (i.e. the original state of the system is restored) it is a convenient indicator of the total effect. It is termed a commitment in the sense that a finite disturbance will ultimately result in the occurrence of the total effect. It is usually easier to estimate the integral quantity $P(\infty)$ than the time dependent function $p(t)$. As $P(\infty)$ is one number it may also be of more value to decision-makers than a long time series such as $p(t)$.

If the source of the disturbance is applied continuously, the system will adjust to a new steady state. It will be seen later that the value of the new steady-state concentration per continuing unit release rate is equal numerically to the commitment per unit release.

An interesting example of a successful use of this approach in assessing environmental contamination problems is provided by the United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) (1962, 1964, 1966, 1969, 1972 and 1977). The Committee applied it to estimate the effects of the testing of nuclear weapons in the atmosphere. The effects of exposing human beings to ionizing radiation were assumed to be directly proportional to the mean per capita quantity of energy deposited in unit mass of various organs or tissues, i.e. to the mean per capita dose. This is equivalent in the general case mentioned above to the commitment $P(\infty)$, which was referred to by UNSCEAR as the dose commitment. The instantaneous rate of energy deposited in an organ or tissue is the dose rate which, as a measure of the disturbance in the system, is equivalent to $p(t)$.

Changes induced by the introduction of potentially toxic chemicals into the environment can also be assessed by the commitment approach. In UNSCEAR's application of the commitment concept the term 'dose' has a very limited and special meaning. In most cases of non-radioactive pollutants it is the concentration of a pollutant in a reservoir or the integral of the concentration over time, i.e. exposure, which is commonly related to an effect. Since this reservoir may or may not be the site of the effect, the term 'exposure' is used instead of 'dose'. The exposure during the time interval t_1 to t_2 is defined as:

$$E_i(t_1, t_2) = \int_{t_1}^{t_2} C_i(t) dt \quad (3)$$

where $C_i(t)$ is the concentration of a pollutant in a reservoir i at time t .

The 'exposure commitment' is defined as the integral of the concentration over infinite time. Thus:

$$E_i = \int_{-\infty}^{\infty} C_i(t) dt \quad (4)$$

is the 'exposure commitment' to reservoir i. The exposure commitment will be expressed in units of concentration times time, e.g. $\mu\text{g m}^{-3}\text{y}$ which is normally written $\mu\text{g y m}^{-3}$.

It has also been the practice in writing equations to introduce the notation (I) to denote the mathematical operation of integrating over infinite time. Thus the exposure commitment E_i can also be expressed as

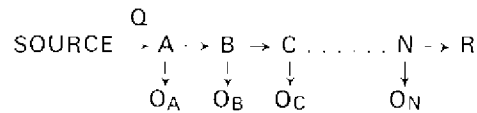
$$E_i = IC_i = \int_{-\infty}^{\infty} C_i(t) dt \quad (5)$$

The aim of the present paper has been to explore the potential of the exposure commitment approach and to develop the necessary methodology. In section 2 the procedure for estimating exposure commitments is discussed. The relative simplicity of the commitment approach and its relationship to more conventional transfer models are illustrated. In section 3 the transport of mercury through the environment is assessed using both the exposure commitment method and a time dependent transport model.

2.0 Transport models for estimating exposure commitments

2.1 Basic relationships

Consider a transfer sequence in which a substance is introduced into reservoir A, passing sequentially through reservoirs B, C, D, etc., until it eventually reaches a sensitive receptor, R. It is required to estimate the exposure commitment to R following the release of a given amount of the substance. The transfer sequence is represented in the following flow diagram



where Q is the amount of the substance released to A. Within and between reservoirs many processes other than those of immediate concern, i.e. transfer along the main pathway (A → B → C . . . N → R), may operate on the substance. Such processes represent losses from the main pathway and are collectively depicted in the flow diagram as

O_A from compartment A, O_B from compartment B, etc. In some cases, e.g. radioactive or chemical transformations, such losses are absolute and are equivalent to transfers to true sinks. In other cases, these transfer processes may lead ultimately by other pathways to the same receptor. It would then be necessary to set up appropriate flow diagrams and perform the necessary calculations for each pathway.

To describe the transfer of a substance from one reservoir to another UNSCEAR introduced the transfer coefficient P_{ij} which was defined as

$$P_{ij} = \frac{IC_j}{IC_i} \quad (6)$$

where IC_j and IC_i are the integrals over infinite time of the concentrations of the substance in the receptor and donor reservoirs respectively. The transfer coefficient is thus the ratio of exposure commitments in the two reservoirs.

The transfer coefficient is determined by the properties of the two reservoirs and the nature of the substance transferred. For a specific transfer the transfer coefficient is a constant, independent of the amount of the substance present. This latter assumption cannot be valid generally. Most substances, when present in sufficient quantity, will adversely affect certain biotic processes that contribute directly or indirectly to a transfer. There may even be a lower limit to the amount present in a reservoir below which the assumption will also be invalid. Thus, certain elements or compounds must be present in sufficient quantity for some enzymes to function properly and for transfers to proceed normally. Nevertheless it could reasonably be expected that for many substances the range between minimum and maximum limits is such that, for practical purposes, the assumption is valid.

Considering the sequential transfer of the pollutant amount Q along the pathway

Source \xrightarrow{Q} A \rightarrow B \rightarrow C $\dots\dots$ N, we can write from the definition of the transfer coefficient in equation (6)

$$\begin{aligned} P_{SN} &= \frac{IC_N}{Q} = \frac{IC_A}{Q} \cdot \frac{IC_B}{IC_A} \cdot \frac{IC_C}{IC_B} \dots\dots\dots \frac{IC_N}{IC_M} \\ &= P_{SA} \times P_{AB} \times P_{BC} \dots\dots\dots \times P_{MN} \end{aligned} \quad (7)$$

In this case the integral of the amount of pollutant from the source S is simply Q. From the above equation the time integral of the concentration of the pollutant in reservoir N via this pathway, due to a given pollutant input Q, is therefore

$$IC_N = Q \cdot P_{SN} \quad (8)$$

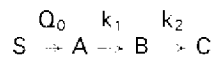
If the reservoir receives the same substance from two or more sources or pathways, the exposure commitment to the reservoir is the sum of the exposure commitments from each source and each pathway.

So far the exposure commitment has been directly related to the amount of the substance released to the environment, and indeed this relationship provides a most useful potential application of the commitment approach to pollution management as a rational means of controlling sources. However, many situations will arise where neither the number and strengths of sources are known nor are there direct means available to plan or control them. For such situations the integral over time of the concentration in a reservoir must be estimated from the results of monitoring that substance in a convenient precursor reservoir. For example, in the case of radioactive contamination from nuclear weapons testing, the quantities of individual radionuclides released in each test explosion could not be stated. To estimate dose commitments due to this source, UNSCEAR had to rely for input to the transfer model on the amounts of radionuclides deposited on the earth's surface. This was obtained from results of two independent global sampling networks designed for the purpose.

2.2 Relationships between exposure commitment and time-dependent pollutant transfer models

It is instructive now to derive relationships for the transfer coefficient P_{ij} using arguments and assumptions commonly used to construct conventional time-dependent models of pollutant transfer. This is being done here to show the relationships between the two methods.

For this purpose it is assumed that all transfers follow first order kinetics, i.e. the rate of transfer is proportional to the amount of a substance in the donor reservoir. It is also assumed that the reservoirs have a constant size or mass. Consider the simple transfer sequence



where Q_0 is the amount of the substance introduced as a pulse from the

source S and k_1 and k_2 are the first order transfer rate constants. * The initial concentration in A is, assuming instant mixing, $C_A(0) = Q_0/M_A$ where M_A is the mass of compartment A. Since the rate of transfer is proportional to the amount of the substance in the donor compartment, the concentration in A at any subsequent time t is

$$C_A(t) = \frac{Q_0}{M_A} \exp(-k_1 t) \quad (9)$$

and the integral over infinite time of the concentration is

$$IC_A = \int_{-\infty}^{\infty} C_A(t) dt = \frac{Q_0}{k_1 M_A} \quad (10)$$

If the substance is conserved in passing from A to B, the integral over infinite time of the concentration in B is

$$IC_B = \frac{Q_0}{k_2 M_B} \quad (11)$$

where M_B is the mass of compartment B.

The transfer coefficient P_{AB} for the transfer from A to B is, by definition,

$$P_{AB} = \frac{IC_B}{IC_A} \quad (12)$$

Hence from (10) and (11)

$$P_{AB} = \frac{k_1 M_A}{k_2 M_B} \quad (13)$$

and similarly,

$$P_{SA} = \frac{IC_A}{Q_0} = \frac{1}{k_1 M_A} \quad (14)$$

*For a more complete analysis of this system see Appendix I.

Another set of relations can be derived by considering the case of a continuous source of strength q (amount per unit time) such that the steady-state situation would eventually be reached. The rate of change of concentration in A is

$$\frac{dC_A}{dt} = \frac{q}{M_A} - k_1 C_A$$

At steady state ($dC_A/dt=0$), therefore

$$\frac{q}{M_A} = k_1 C_A^* \quad \text{that is,} \quad \frac{1}{k_1 M_A} = \frac{C_A^*}{q} \quad (15)$$

where C_A^* is the steady-state concentration in A. Thus from equations (14) and (15) can be seen that

$$P_{SA} = \frac{1}{k_1 M_A} = \frac{C_A^*}{q}$$

Similarly, the rate of change of the concentration in B is

$$\frac{dC_B}{dt} = \frac{k_1 C_A \cdot M_A}{M_B} - k_2 C_B$$

at steady state

$$\frac{dC_B}{dt} = 0$$

$$\therefore \frac{C_B^*}{C_A^*} = \frac{k_1}{k_2} \cdot \frac{M_A}{M_B}$$

Thus from equation (13) can be seen that

$$P_{AB} = \frac{k_1 M_A}{k_2 M_B} = \frac{C_B^*}{C_A^*} \quad (16)$$

Three relationships have been derived for the transfer coefficients, each of which may be used either to determine the value of P_{ij} or to estimate the exposure commitment to a reservoir from a stated source. These relationships are

$$\begin{aligned}
 P_{ij} &= \frac{IC_j}{IC_i} && \text{(definition)} \\
 &= \frac{C_j^*}{C_i^*} && \text{(under steady-state situation)} \\
 &= \frac{k_i \cdot M_i}{k_j \cdot M_j} && \text{(by kinetic analysis)}
 \end{aligned}$$

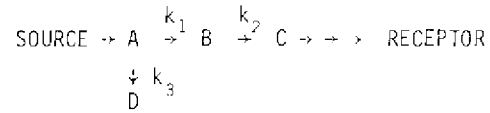
Similarly transfer coefficients between a source and the receiving reservoir are

$$\begin{aligned}
 P_{SA} &= \frac{IC_A}{Q_S} && \text{(definition)} \\
 &= \frac{C_A^*}{q} && \text{(under steady-state situation)} \\
 &= \frac{1}{k_1 M_A} && \text{(by kinetic analysis)}
 \end{aligned}$$

The foregoing describes a simple situation; it is now necessary to consider more complex and realistic situations to see what changes, if any, must be made to the basic relationships so far developed. Two aspects of the problem are considered: first, transfer patterns other than the simple straight chain; second, what happens when the substance is not uniformly mixed in a reservoir.

2.3 Complex transfer pathways

In passing from one reservoir to another, a substance is often not conserved. Some material may be diverted to reservoirs outside the main pathway of interest. Some material may be transformed chemically or through radioactive disintegration within the compartment. Irrespective of the detailed mechanism, the overall process can be represented by the one flow diagram, thus



Here the pathway of interest is through C to an ultimate receptor. Material is diverted from this pathway to D. D may be one or more sinks.*

The transfer coefficient from the source to A is by definition

$$P_{SA} = \frac{I_C}{Q_0}$$

but in terms of the transfer rate constants, this is now given by

$$P_{SA} = \frac{1}{(k_1 + k_3)M_A}$$

and, similarly,

$$P_{AB} = \frac{k_1}{k_2} \cdot \frac{M_A}{M_B}$$

The overall transfer from the source to B is

$$P_{SB} = P_{SA} \times P_{AB} = \frac{k_1}{k_2 M_B (k_1 + k_3)}$$

*For a more complete analysis of this system see Appendix II.

i.e. as for the straight chain ($1/k_2M_B$) reduced in proportion to the chain branching ratio $k_1/(k_1 + k_3)$.

Equations applicable to some other transfer patterns are summarized in Table 1*. The list is not exhaustive but the sequences given will cover many situations likely to arise in practice. Sequences 4a, 4b and 5 will be considered in greater detail when in a later section they are applied to a transfer model for mercury.

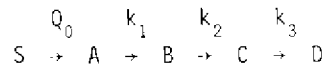
2.4 Non-uniform concentrations in compartments

It has been assumed so far that a substance upon entering a reservoir is instantly and uniformly distributed within it. However, internal mixing proceeds simultaneously with transfers into and out of the reservoir. Chemical or physical transformations may also affect the amounts of the substance present. The rates of these simultaneous processes may be similar so that a reservoir acted upon by discrete sources and sinks may not achieve an even approximately uniform concentration. In this case, the concentration distribution within a reservoir, and consequently the transfer coefficients, may be appreciably altered depending on the place of injection. In such a situation a more elaborate transport model would have to be used.

If, on the other hand, transfers within a reservoir are rapid compared with those into or out of it, the compartment as a whole can be assumed to be well mixed, even though the distribution of material within it is highly non-uniform. It may be sufficient for determining transfer relationships that the distribution of the substance in the reservoir remains relatively constant with time.

Sometimes problems arise because important transfer parameters vary with time. When such variability consists of periodic or random fluctuations about a constant time average, the problem may be resolved by using averaging times that are long compared with the time period of the fluctuations. For example, diurnal or seasonal variations can be eliminated by taking daily or annual averages respectively.

It is instructive now to consider some of these points more formally within the framework of this particular transport model. Consider again the simple linear transfer sequence through which it is assumed, for the sake of simplicity, that the substance is conserved as it moves. Thus



*For a more complete analysis of all these systems see Appendices i-VI.

Such a chain could, for example, represent the one-dimensional transfer of a substance initially injected into the stratosphere (compartment A) which passes sequentially through the upper and lower troposphere, compartments B and C respectively. Compartment D could be soil or vegetation.

It can be shown that with first order kinetics between reservoirs, the concentration of the substance in reservoir C at time t after an amount Q_0 has been injected as a pulse into A, at time $t=0$, is

$$C_C(t) = \frac{Q_0}{M_C} \cdot \frac{k_1 k_2}{k_2 - k_1} \left[\frac{1}{k_1 - k_3} (e^{-k_3 t} - e^{-k_1 t}) - \frac{1}{k_2 - k_3} (e^{-k_3 t} - e^{-k_2 t}) \right] \quad (17)^*$$

In order to determine the time course of the concentration in C and hence also the rate of transfer to D, it is necessary to assign values to the three rate constants k_1 , k_2 and k_3 . On the other hand, to calculate an exposure commitment it is the time integral of the concentration which is needed and this is simply

$$IC_C = \frac{Q_0}{k_3 M_C}$$

This can be readily verified by integrating the above expression for $C_C(t)^*$. The transfer coefficient P_{SC} is therefore simply inversely proportional to the single rate constant k_3 .

Thus, for the conserved substance passing through the linear compartment sequence, such as might be the case for movement through atmospheric regions, the integral concentration of the substance in the final reservoir does not depend on the rate constants for movement through preceding reservoirs. The exposure commitment to reservoir C is the same for a given source input, irrespective of whether the source was introduced into reservoir A, B, or C. However, the time variation of concentration following the injection may be very different in each case.

If the substance is not conserved in the atmosphere, the problems posed by time-dependent spatial distributions are less tractable. For

*See Appendix I section II for full derivation of this relationship.

example, the amount of a particular radioactive substance reaching ground level may be very much reduced if the transport time through successive layers is long compared to the radioactive mean life. A non-radioactive substance may undergo chemical transformations at rates which vary from one layer to another, e.g. because of photochemical reactions. There is no easy solution along the lines discussed above to the problems arising from these and other processes. Fortunately, if steady state has been reached (for example, in the natural cycle of a substance), the transfer coefficient can still be determined as the ratio of the equilibrium concentrations of the substance in the receiving and in the donor reservoirs.

2.5 Further considerations

It may at times be useful to obtain population weighted estimates of exposure commitments for regions of widely varying exposure. For example, consider the global atmosphere divided into n subcompartments, e.g. by latitudinal bands, and a source Q_0 injected into one of the subcompartments. This leads to time integrals of concentration in ground-level air, $ICA_1, ICA_2, \dots, ICA_n$ in subcompartments 1, 2, 3, ... n .

Let N_i be the population living in the i^{th} subcompartment, then the weighted mean per capita time integral of the ground-level air concentration is

$$\frac{\sum_{i=1}^n N_i ICA_i}{\sum_{i=1}^n N_i}$$

and the transfer coefficient weighted by population density (N_i) from this source Q_0 is

$$P_{SA} = \frac{\sum_{i=1}^n N_i ICA_i}{Q_0 \sum_{i=1}^n N_i} \quad (18)$$

The corresponding expression for the steady-state condition is

$$P_{SA} = \frac{\sum_{i=1}^n N_i C_{A_i}^*}{q \sum_{i=1}^n N_i} \quad (19)$$

It has been shown in this section that for a continuous source the transfer coefficient P_{ij} is equal to the ratio of the steady-state concentrations in the j^{th} and i^{th} reservoirs respectively. That the ratio of the steady-state concentrations in two adjacent reservoirs resulting from a continuous source is equal to the ratio of the time integrals of the concentrations in the same reservoirs due to a finite source has valuable practical implications for the evaluation of transfer coefficients and the analysis of pollution situations. The exposure commitments for certain complex situations can be determined in this way, whereas it would be extremely difficult to model the specific transfer processes.

For potential pollutants such as the heavy metals and compounds of sulphur and phosphorus which have natural cycles, it may be assumed that steady state has been reached with respect to natural sources. This means that transfer coefficients can be simply determined from the ratio of the concentrations observed in natural situations. This procedure has the advantage that any contribution to the transfer by very slow processes is automatically allowed for in the value of P_{ij} obtained. This is so, even if the existence of such processes is unsuspected. For the same reasons it is possible when calculating exposure commitments to ignore completely intermediate steps in the transfer pathway that are not well understood or for which the transfer rate constants are unknown.

This method of evaluating transfer coefficients is not necessarily limited to pollutants with a natural occurrence. Situations frequently exist where a source or group of sources have been operating for several years and it may be reasonable to assume that steady state has been approximated locally. Transfer coefficients determined from the observed concentration ratios may then be usefully applied elsewhere.

It has been shown that the transfer coefficients for a wide range of situations can be expressed in terms of combinations of products of transfer rate constants and reservoir sizes. While both these quantities are difficult to evaluate separately, their products define factors which

are more readily measured. Some of these points are dealt with in more detail in the next section where the exposure commitment approach is applied to environmental mercury.

3.0 A transfer model for mercury in air and soil

It is instructive now to apply some of the relationships discussed in the previous section to an actual chemical pollutant, namely, mercury. No attempt will be made to estimate exposure commitments to man due to natural and man-made sources of environmental mercury – a task which is beyond the scope of the present document; in fact, only a part of the mercury cycle is explored. The purpose is to amplify some of the earlier discussion by taking a particular case, showing by means of a worked example how transfer coefficients may be evaluated.

The particular part of the mercury cycle with which this report is concerned is shown in Figure 1. In the natural cycle of mercury, bedrock is presumed to be the source from which mercury enters the soil by weathering and the atmosphere by volcanism. These processes are indicated by the broken lines, and although they will be referred to later

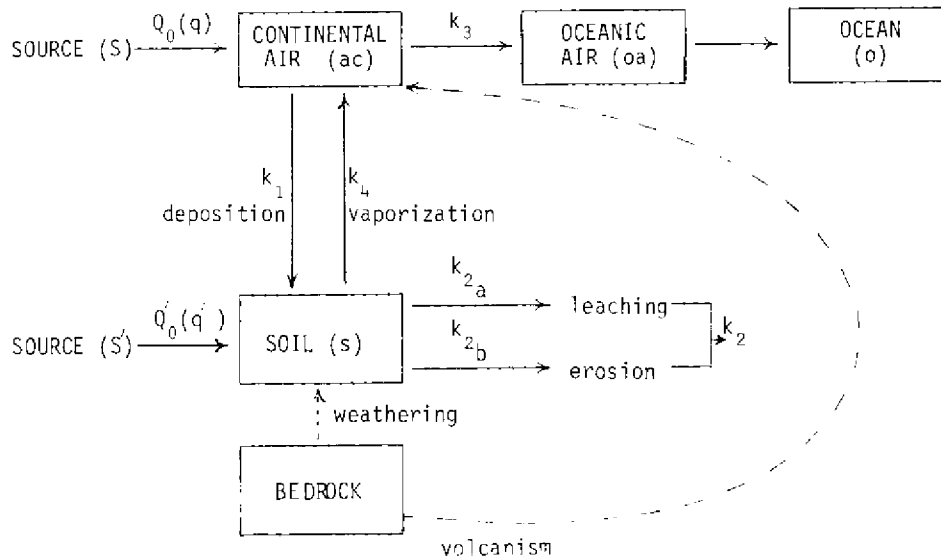


Figure 1 Part of the Mercury Cycle

in an attempt to validate the transfer model, they are of no direct concern. For the purpose of this report, of greater interest is to develop relationships for man-made sources of mercury in which direct releases to the atmosphere or to soil are assumed. These sources are S and S' respectively. The relationships for the transfer coefficients derived from the first order kinetic model were given in sequences 4a and 4b of Table 1 in terms of rate constants k_i and reservoir sizes M_i . Nevertheless, for convenience they are summarized below:*

1. For a pulsed release of a pollutant from source (S) of strength (Q_0) directly to the continental atmosphere (ac) or for a continuous release of strength (q)

$$\begin{array}{l} \text{from source (S)} \\ \text{to continental} \\ \text{air (ac)} \end{array} P_{S,ac} = \frac{C_{ac}^*}{q} = \frac{IC_{ac}}{Q_0} = \frac{k_2 + k_4}{\phi M_{ac}} = \frac{k_2 + k_4}{\phi \sigma_c h} \quad (20)$$

$$\begin{array}{l} \text{from continental} \\ \text{air (ac) to} \\ \text{soil (s)} \end{array} P_{ac,s} = \frac{C_s^*}{C_{ac}^*} = \frac{IC_s}{IC_{ac}} = \frac{k_1}{k_2 + k_4} \cdot \frac{M_{ac}}{M_s} = \frac{k_1 h}{(k_2 + k_4) \rho_s Z} \quad (21)$$

$$\begin{array}{l} \text{from source (S)} \\ \text{to soil (s)} \end{array} P_{S,s} = \frac{C_s^*}{q} = \frac{IC_s}{Q_0} = \frac{k_1}{\phi M_s} = \frac{k_1}{\phi \rho_s \sigma_c Z} \quad (22)$$

2. For a pulsed release of a pollutant from source (S') of strength (Q'_0) directly to soil (s) or a continuous release of strength (q')

$$\begin{array}{l} \text{from source (S')} \\ \text{to soil (s)} \end{array} P_{S',s} = \frac{C_s^*}{q'} = \frac{IC_s}{Q'_0} = \frac{k_1 + k_3}{\phi M_s} = \frac{k_1 + k_3}{\phi \rho_s \sigma_c Z} \quad (23)$$

$$\begin{array}{l} \text{from soil (s)} \\ \text{to continental} \\ \text{air (ac)} \end{array} P_{s,ac} = \frac{C_{ac}^*}{C_s^*} = \frac{IC_{ac}}{IC_s} = \frac{k_4}{k_1 + k_3} \cdot \frac{M_s}{M_{ac}} = \frac{k_4}{k_1 + k_3} \cdot \frac{\rho_s Z}{h} \quad (24)$$

$$\begin{array}{l} \text{from source (S')} \\ \text{to continental} \\ \text{air (ac)} \end{array} P_{S',ac} = \frac{C_{ac}^*}{q'} = \frac{IC_{ac}}{Q'_0} = \frac{k_4}{\phi M_{ac}} = \frac{k_4}{\phi \sigma_c h} \quad (25)$$

*For derivation of equations (20) - (25) in the general case see Appendix IV.

Table 1

SUMMARY OF ANALYSIS OF SIMPLE POLLUTANT PATHWAY MODELS USING TRANSPORT KINETICS: THE RELATIONSHIPS BETWEEN TRANSFER COEFFICIENTS, RATE CONSTANTS AND RESERVOIR MASSES.

Symbol	Transfer coefficient from source (S) of strength Q ₀ to reservoir A of mass M _A	Transfer coefficient from reservoir A of mass M _A to reservoir B of mass M _B	Transfer coefficient from source (S) of strength Q ₀ to reservoir B of mass M _B
P_{SA}	$P_{SA} = \frac{P_{SA}^*}{k_1 + k_3}$	P_{AB}	$P_{SB} = \frac{P_{SA}^* P_{AB}}{k_1 + k_3}$
IC_A/Q_0	IC_A/Q_0	IC_B/IC_A	IC_B/Q_0
C_A^*/q	C_A^*/q	C_B^*/C_A^*	C_B^*/q
Steady State Result			
Pathway Sequence	Expression for P_{SA}	Expression for P_{AB}	Expression for P_{SB}
1 (1-1) S → Q ₀ → A → k ₁ → B → k ₂ → C	$\frac{1}{k_1 M_A}$	$\frac{k_1 M_A}{k_2 M_B}$	$\frac{1}{k_2 M_B}$
2 (2) S → Q ₀ → A → k ₁ → B → k ₂ → C k ₃ ↓ D	$\frac{1}{(k_1 + k_3) M_A}$	$\frac{k_1 M_A}{k_2 M_B}$	$\frac{k_1}{k_2 (k_1 + k_3) M_B}$
3 (3) S → Q ₀ → A → k ₁ → B → k ₂ → C k ₃ ↓ D → E	$\frac{1}{(k_1 + k_3) M_A}$	$\frac{(k_1 + k_3) M_A}{k_2 M_B}$	$\frac{1}{k_2 M_B}$

where $\phi = (k_1 + k_3)(k_2 + k_4) - k_1k_4$
 $\rho_s =$ soil density (1.25 g cm^{-3})
 $\sigma_c =$ area of continents ($1.5 \times 10^{18} \text{ cm}^2$)
 $Z =$ depth of soil reservoir
 $h =$ height of atmospheric reservoir
 Note: $\rho_s \sigma_c Z = M_s$, the mass of the soil reservoir
 $\sigma_c h = M_{ac}$, the volume of the continental atmospheric reservoir
 $C_s =$ concentration of mercury in the soil reservoir (g g^{-1})
 $C_{ac} =$ concentration of mercury in the continental air reservoir (g cm^{-3}).

It is assumed throughout this discussion that mercury is in the elemental vapour state in the atmosphere. This is unlikely to be entirely true, but not enough is known about the distribution of the various chemical and physical forms present nor of the transformations they undergo within and between reservoirs to assume otherwise. In principle, however, equations of the type given above could be set up for each form together with equations which describe the rates of change from one form to another.

Since neither the transfer rate constants k_i , nor the depths of the reservoirs Z and h are known, it is necessary to develop relationships by means of which the transfer coefficients P_{ij} may be evaluated from measurable environmental parameters.

3.1 Deposition of mercury from continental air to soil Determination of k_1 .

Chamberlain (1960) has described the deposition of gases, vapours and particles from the atmosphere by the velocity of deposition V_d defined by

$$V_d = \frac{F(h')}{C_{ac}(h')} \quad (26)$$

where $F(h')$ is the downward flux of the depositing material per unit area at the height h' above the surface and $C_{ac}(h')$ is the concentration of the material in air at reference height h' .

The flux through the lower atmosphere is very nearly constant with height and equal to its value at the surface ($h' = 0$) so that $F(h') \cong F(0)$.

However, the mercury concentration in air decreases with height so that the value of V_d is a function of h' . Nevertheless, well away from discrete sources, the rate of change of concentration with height is relatively small. It is not necessary, therefore, to be very precise about the exact height of measurement, and $C_{ac}(h')$ can be replaced by C_{ac} which is to be understood to refer to the concentration measured within a metre or so of the surface and is generally referred to as the 'air concentration at ground level'.

Using the definition of the deposition velocity, the rate of deposition from the atmosphere to the land surface is:—

$$V_d C_{ac} \sigma_c$$

Using the rate constant k_1 , the rate of deposition is

$$k_1 C_{ac} \sigma_c h$$

Since these are equal

$$k_1 C_{ac} \sigma_c h = V_d C_{ac} \sigma_c$$

$$\therefore k_1 = \frac{V_d}{h} \quad (27)$$

3.2 Transfer of mercury from continental air to oceanic air

Determination of k_3

In the absence of a more adequate model for the transport of mercury from continental to oceanic air, it is sufficient for the present purpose to use a very simple model in which it is assumed that

- (a) the amounts of mercury in continental and oceanic air are equal, reflecting the direct, unidirectional physical transport between these compartments. The concentrations are thus related to the inverse ratio of the areas of the two surfaces, thus

$$\frac{C_{ac}}{C_{ao}} = \frac{\sigma_o}{\sigma_c} \quad (28)$$

where the subscripts o and c denote oceanic and continental compartments respectively.

- (b) the steady-state transport of mercury from continental to oceanic air is equal to the rate of deposition from oceanic air to the ocean surface. Thus at equilibrium the rate of deposition to the ocean surface equals the input rate from continental to oceanic air.

i.e.
$$V_d C_{ao} \sigma_o = k_3 C_{ac} \sigma_c h$$

$$k_3 = \frac{V_d C_{ao} \sigma_o}{C_{ac} \sigma_c h}$$

$$\therefore \text{from (28)} \quad k_3 = \frac{V_d}{h}$$

and from (27)
$$k_1 = k_3 = \frac{V_d}{h} \quad (29)$$

3.3 Vaporization of mercury from the soil

Determination of k_4

The upward flux of mercury from the soil, F^{\uparrow} , can, by analogy to equation (26), be related to the concentration of mercury in the donor reservoir, which in this case is the soil. A new term V_v is defined which will be referred to henceforth as the vaporization velocity and will be understood to include both evaporation from soil and transpiration from vegetation.

$$V_v = \frac{F^{\uparrow}}{C_s \rho_s} \quad (30)$$

The use of ρ_s , the density of soil, with C_s gives the concentration of mercury in soil on a volumetric basis.

Using the definition of V_v , the rate of mercury vaporization from the

soil is therefore $V_v C_s \rho_s \sigma_c$ and, using the rate constant, it equals k_4 times the total amount of mercury in the soil, i.e. $k_4 C_s \rho_s \sigma_c Z$. Since these expressions for the rate of vaporization from soil are equal

$$k_4 = \frac{V_v}{Z} \quad (31)$$

where Z = depth of soil.

3.4 Leaching and erosion of mercury from soil

3.4.1 Leaching of mercury from soil

Determination of k_{a2}

As rain runs across the surface or percolates through the soil, mercury is redistributed between the soil and water phases. A distribution coefficient, D , can be defined by

$$D = \frac{\text{Concentration of mercury in drainage water (g g}^{-1}\text{)}}{\text{Concentration of mercury in soil (g g}^{-1}\text{)}} = \frac{C_r^*}{C_s^*} \quad (32)$$

At steady state, D is constant for a given type of soil and a given chemical composition of local rain-water.

If r is the run-off rate of water per unit area from soil ($\text{cm}^3 \text{ cm}^{-2} \text{ s}^{-1}$), then the amount of mercury in the water, i.e. leaching per unit area per unit time, is $rC_r^* \rho_w$. The density of water is ρ_w and $C_r^* \rho_w$ expresses the mercury concentration on a volumetric basis. It is useful to define, by analogy to V_d , a velocity of leaching V_L , which is the ratio of the rate of mercury leaving the soil due to leaching per unit area to the concentration of mercury in soil.

$$V_L = \frac{rC_r^* \rho_w}{C_s^* \rho_s} = \frac{rD\rho_w}{\rho_s} \quad (33)$$

The transfer of mercury from soil due to leaching can also be expressed in terms of a rate constant, k_{2a} times the total amount of mercury in

soil $k_{2a} C_s^* \rho_s \sigma_c Z$. Equating the total amount of mercury leaving the continental area from both expressions

$$r C_r^* \rho_w \sigma_c = k_{2a} C_s^* \rho_s \sigma_c Z$$

$$k_{2a} = \frac{r C_r^* \rho_w}{C_s^* \rho_s Z}$$

$$k_{2a} = \frac{V_L}{Z} \quad (34)$$

3.4.2 Erosion of mercury from soil

Determination of k_{2b}

Erosion is the bulk transport of soil particles, still carrying their mercury content, suspended in water draining from the continents. Erosion refers to the movement of mercury in particulate form while leaching refers to the movement of dissolved mercury.

If F_E is the erosion rate of soil per unit area ($\text{g cm}^{-2}\text{s}^{-1}$), then the amount of mercury carried away per unit time per unit area is $F_E C_s^*$. The velocity of erosion, V_E , is defined as the ratio of the rate of mercury leaving soil due to erosion per unit area to the concentration of mercury in soil

$$\text{i.e. } V_E = \frac{F_E C_s^*}{C_s^* \rho_s} \quad (35)$$

The total amount of mercury leaving soil due to erosion is $V_E C_s^* \rho_s \sigma_c$ and this equals the amount determined by multiplying the rate constant k_{2b} by the total amount of mercury in soil, thus

$$V_E C_s^* \rho_s \sigma_c = k_{2b} C_s^* \rho_s \sigma_c Z$$

$$\therefore k_{2b} = \frac{V_E}{Z}$$

The total loss of mercury from the soil by both leaching and erosion can be expressed using the sum of the velocity factors, $V_E + V_L$, which can be called V_Ψ . The corresponding rate constant then has the value

$$k_2 = \frac{V_\Psi}{Z}$$

3.5 Expressions for transfer coefficients

It has been found that the transfer rate constants k_i are related to the velocity factors by the following equations:—

$$k_1 = k_3 = \frac{V_d}{h} ; \quad k_4 = \frac{V_v}{Z} \quad \text{and} \quad k_2 = \frac{V_\Psi}{Z}$$

Substituting these values into equations (20) to (25), the following expressions for the transfer coefficients are obtained:

1. For a release directly to the continental atmosphere

from source (S) to
continental air (ac)

$$P_{S,ac} = \frac{V_v + V_\Psi}{V_c V_d (V_v + 2V_\Psi)} \quad (36)$$

from continental air
(ac) to soil (s)

$$S_{ac,s}^P = \frac{V_d}{V_s (V_v + V_\Psi)} \quad (37)$$

from source (S) to
soil (s)

$$P_{S,s} = \frac{1}{V_s V_c (V_v + 2V_\Psi)} \quad (38)$$

2. For release directly to soil
from source (S') to
soil (s)

$$P_{S',s} = \frac{2}{V_s V_c (V_v + 2V_\Psi)} \quad (39)$$

from soil (s) to
continental air (ac)

$$P_{s,ac}^p = \frac{\rho_s V_v}{2V_d} \quad (40)$$

from source (S') to
continental air (ac)

$$P_{S',ac}^j = \frac{V_v}{\sigma_c V_d (V_v + 2V_w)} \quad (41)$$

The transfer coefficients are now expressed entirely in terms of parameters which are more directly measurable. More important to note, however, is that equations (36) to (41) could and normally would be derived directly without involving the kinetic model. The purpose of introducing the latter in the first instance was, as then noted, to show the relationship between the two approaches and to demonstrate how commitment models overcome the severe practical problems posed by the need in kinetic models to evaluate separately the transfer rate constants k_i and the reservoir size parameters Z and h .

Before proceeding, it may be useful to show how equations (36) to (41) could be derived directly without the necessity for introducing the additional assumptions associated with the kinetic model. This is demonstrated for one transfer coefficient only; the same procedures would be followed to derive the other five.

Consider the case of mercury being introduced directly to the atmosphere. The rate at which mercury enters the continental atmosphere is $q + V_v C_s^* \rho_s \sigma_c$, i.e. the sum of the rate of release from the source, q , and the rate of vaporization from the soil, $V_v C_s^* \rho_s \sigma_c$. The rate of loss of mercury from the atmosphere is equal to the sum of the rates of deposition to the oceanic and continental surfaces, i.e. $V_d C_{ac}^* \sigma_c + V_d C_{ao}^* \sigma_o$. Since $C_{ao}^* = C_{ac}^* \sigma_c / \sigma_o$, [equation (28)], the total rate of loss is $2V_d C_{ac}^* \sigma_c$.

Therefore at steady state:—

$$q + V_v C_s^* \rho_s \sigma_c = 2V_d C_{ac}^* \sigma_c \quad (42)$$

Continuing the pathway into the soil reservoir, it can be shown that

$$V_d C_{ac}^* \sigma_c = (V_v + V_L + V_E) C_s^* \rho_s \sigma_c \quad (43)$$

Solving between (42) and (43) and writing $V_L + V_E - V_{\psi}$ one obtains

$$P_{S,S} = \frac{C_S^*}{q} = \frac{1}{\rho_s \sigma_c (V_V + 2V_{\psi})}$$

i.e. identical to equation (38).

3.6 Evaluation of velocity factors

3.6.1 Velocity of deposition, V_d

The velocity of deposition of mercury has not been measured. It has, however, been determined experimentally for several other gases, vapours and aerosols. The velocity of deposition of iodine vapour has been particularly well studied in several countries and over a wide range of surfaces. The velocity of deposition is a function of the molecular diffusivity of the diffusing entity and it would therefore be expected that V_d for mercury vapour would be less than that for iodine vapour. The effect, however, is relatively small and can be ignored here. The experimental values of V_d for iodine vapour and for ambient aerosols with adsorbed iodine extend over a wide range with some dependence on weather conditions and the type and density of surface cover. Most observed values lie in the range 0.1 to 1.0 cm s^{-1} and a value of 0.3 cm s^{-1} would appear to be representative.

3.6.2 Velocity of vaporization, V_v

Kothny (1973) has measured the upward flux of mercury from soil over a 100 km long stretch inland from the Pacific coast of California in the U.S.A. He obtained a value of $4 \times 10^{-6} \text{ t km}^{-2} \text{ d}^{-1}$ § equivalent to $4.63 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$. From Table V of the same reference, the soil in that region had a mercury concentration of from 0.2 to 0.5 $\mu\text{g g}^{-1}$. Using a density of soil of 1.25 g cm^{-3} , the range of V_v values would be

$$\text{from } \frac{4.63 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}}{0.2 \times 10^{-6} \text{ g g}^{-1} \times 1.25 \text{ g cm}^{-3}} = 18.52 \times 10^{-3} \text{ cm s}^{-1}$$

§Metric tons per square kilometre per day.

$$\text{to } \frac{4.63 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}}{0.5 \times 10^{-6} \text{ g g}^{-1} \times 1.25 \text{ g cm}^{-3}} = 7.41 \times 10^{-9} \text{ cm s}^{-1}$$

The geometric mean value is $11.7 \times 10^{-9} \text{ cm s}^{-1}$. For the present purpose the rounded value $1 \times 10^{-8} \text{ cm s}^{-1}$ will be adopted for V_v .

3.6.3 Velocity of leaching, V_L

On several well-drained aerated soils, Kothny (1973) has obtained a value of 6×10^{-4} for the distribution coefficient D , where D is the ratio of the steady-state concentration of mercury in drainage water to that in soil. The annual mean run-off from the continents is almost equal to the annual mean river flow to the oceans, about $3 \times 10^{19} \text{ cm}^3 \text{ y}^{-1}$ or about $9.51 \times 10^{11} \text{ cm}^3 \text{ s}^{-1}$.

The run-off rate per unit area r , using the area of the continents $1.5 \times 10^{18} \text{ cm}^2$, is

$$r = \frac{9.51 \times 10^{11} \text{ cm}^3 \text{ s}^{-1}}{1.5 \times 10^{18} \text{ cm}^2}$$

$$= 6.3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2}$$

Thus from equation (33)

$$V_L = \frac{6.3 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \text{ cm}^{-2} \times 6 \times 10^{-4} \times 1 \text{ g cm}^{-3}}{1.25 \text{ g cm}^{-3}}$$

$$= 3 \times 10^{-10} \text{ cm s}^{-1}$$

3.6.4 Velocity of erosion, V_E

Since mercury and soil are lost simultaneously, erosion does not of itself cause a change in the concentration of mercury in the soil. However, the assumption that all the physical reservoirs have a constant mass means that the soil losses are exactly made up by new soil derived

from the weathering of bedrock. It is this replacement which, if at a different concentration from old soil, results after mixing in a change of concentration.

The flow of solids carried to the sea by the major rivers of the world is about $3 \times 10^{10} \text{ t y}^{-1}$ which is equivalent to about $1 \times 10^9 \text{ g s}^{-1}$. Kothny (1973) estimates that about half of the mercury reaching lakes and rivers is lost to a sink in the sediments. This means that the annual rate of erosion must be about $6 \times 10^{10} \text{ t y}^{-1}$, equivalent to $2 \times 10^9 \text{ g s}^{-1}$. The erosion rate per unit area, using the continental area $1.5 \times 10^{18} \text{ cm}^2$, is $F_E = 1.3 \times 10^{-9} \text{ g s}^{-1} \text{ cm}^{-2}$.

Thus from equation (35)

$$V_E = \frac{F_E}{\rho_s} = \frac{1.3 \times 10^{-9} \text{ g s}^{-1} \text{ cm}^{-2}}{1.25 \text{ g cm}^{-3}} = 1.1 \times 10^{-10} \text{ cm s}^{-1}$$

The value of $V_\Psi = V_E + V_L$ is, therefore, $1.4 \times 10^{-10} \text{ cm s}^{-1}$.

3.6.5 Summary of values calculated for velocity factors

The values of the velocity factors from this section are:—

$$V_d = 0.3 \text{ cm s}^{-1}; V_v = 1 \times 10^{-8} \text{ cm s}^{-1} \text{ and } V_\Psi = 1.4 \times 10^{-10} \text{ cm s}^{-1}$$

3.7 Computation of transfer coefficients

Inserting these values into equations (36) to (41) the following estimates of the transfer coefficients are obtained:

1. For a release directly to the continental atmosphere

from source (S) to continental air (ac)	$P_{S,ac} = 2.0 \times 10^{-18} \text{ g s cm}^{-3} \text{ per g released}$ $= 63 \text{ ng y m}^{-3} \text{ per Mt}^{\S} \text{ released}$
--	--

from continental air (ac) to soil (s)	$sP_{ac,s} = 2.1 \times 10^7 \text{ g s g}^{-1} \text{ per g s cm}^{-3}$ $= 0.021 \text{ } \mu\text{g y g}^{-1} \text{ per ng y m}^{-3}$
--	---

from source (S) to soil (s)	$P_{S,s} = 4.2 \times 10^{-11} \text{ g s g}^{-1} \text{ per g released}$ $= 1.3 \text{ } \mu\text{g y g}^{-1} \text{ per Mt released}$
--------------------------------	--

[§]1 Mt = 1 Megatonne = 10^6 tonne.

2. For release directly to soil

$$\begin{aligned} \text{from source (S')} \text{ to soil (s)} \quad P_{S',s} &= 8.3 \times 10^{-11} \text{ g s g}^{-1} \text{ per g released} \\ &= 2.6 \mu\text{g y g}^{-1} \text{ per Mt released} \end{aligned}$$

$$\begin{aligned} \text{from soil (s) to continental air (ac)} \quad S'P_{s,ac} &= 2.1 \times 10^{-9} \text{ g s cm}^{-3} \text{ per g s g}^{-1} \\ &= 21 \text{ ng y m}^{-3} \text{ per } \mu\text{g y g}^{-1} \end{aligned}$$

$$\begin{aligned} \text{from source (S')} \text{ to continental air (ac)} \quad P_{S',ac} &= 1.7 \times 10^{-18} \text{ g s cm}^{-3} \text{ per g released} \\ &= 55 \text{ ng y m}^{-3} \text{ per Mt released} \end{aligned}$$

These values for the transfer coefficients have been estimated directly from experimental determinations of the velocity factors. They can be used to give an indication of the exposure commitment to air and to soil associated with a given release of mercury to either air or soil, i.e. the exposure commitment equals the transfer coefficient times the total amount of pollutant releases, e.g. from source S to the continental atmosphere (ac)

$$E_{ac}(\text{ng y m}^{-3}) = P_{S',ac} \left(\frac{\text{ng y m}^{-3}}{\text{Mt}} \right) \times Q_0(\text{Mt})$$

In principle, the transfer coefficients could also be estimated from the ratios of the concentrations of natural mercury in each reservoir. Such a procedure is complicated in the case of mercury because natural sources release mercury simultaneously into the atmosphere through volcanism and into the soil through weathering of bedrock. Furthermore, the concentrations of mercury in the atmosphere and soil are variable and uncertain. It is useful, therefore, to derive expressions for the transfer coefficients for the combined release of mercury to air and soil. These can then be applied to estimates of source strengths to obtain estimates of C_{ac}^* and C_s^* which can then be compared with reported values.

It can be shown that for an emission of a pollutant from a source S of strength Q_0 into the atmosphere at the same time as the emission of a similar pollutant from a source S' of strength Q'_0 into the soil that if

$Q_o = RQ'_o$ or $q = Rq'$, the equations for the transfer coefficients corresponding to equations (36) to (41) are[§]:-

$$P_{S_T, S} = \frac{C_s^*}{q_T} = \frac{IC_s}{Q_T} = \frac{2 + R}{(1+R)(V_v + 2V_\psi)\rho_s\sigma_c} \quad (44)$$

$$P_{S_T, ac} = \frac{C_{ac}^*}{q_T} = \frac{IC_{ac}}{Q_T} = \frac{R(V_v + V_\psi) + V_v}{(1+R)(V_v + 2V_\psi)V_d\sigma_c} \quad (45)$$

$$T_{S, ac}^P = \frac{C_{ac}^*}{C_s^*} = \frac{IC_{ac}}{IC_s} = \frac{\rho_s [R(V_v + V_\psi) + V_v]}{V_d(2+R)} \quad (46)$$

The total source strength Q_T is equal to $Q_o + Q'_o$, and the total rate of release q_T equals $q + q'$. After substituting the values of the velocity factors obtained earlier, the values of these transfer coefficients are

$$P_{S_T, S} = \frac{4.2 \times 10^{-11} (2+R)}{1 + R} \quad \text{g s g}^{-1} \text{ per g released} \quad (47)$$

$$P_{S_T, ac} = \frac{1.7 \times 10^{-18} (1+1.14R)}{1 + R} \quad \text{g s cm}^{-3} \text{ per g released} \quad (48)$$

$$T_{S, ac}^P = \frac{4.2 \times 10^{-8} (1+1.14R)}{2 + R} \quad \text{g s cm}^{-3} \text{ per g s g}^{-1} \quad (49)$$

Measurements of the concentration of total mercury in uncontaminated air fall in the range 2 to $9 \times 10^{-15} \text{ g cm}^{-3}$ (2 to 9 ng m^{-3}).

The geometric mean of the observed limits on the value of C_{ac}^* is 4.2 ng m^{-3} and this may be taken as reasonably representative (i.e.

[§] See appendix V for derivation of these results.

within a factor of two) of the mean global concentration of mercury from natural sources in continental air.

We can obtain a rough idea of q' , the source strength into the soil, if following the earlier assumption that the size of the soil reservoir is constant, the rate of weathering equals the rate of soil erosion. The latter was given earlier as $2 \times 10^9 \text{ g s}^{-1}$ ($6 \times 10^{10} \text{ t y}^{-1}$). Taking the mean concentration of mercury in the earth's crust to be 500 ng g^{-1} (Mason 1952) means that $q' = 2 \times 10^9 \times 500 \times 10^{-9} \text{ g s}^{-1}$ or about 1000 g s^{-1} .

From equation (48) and remembering that $q = Rq'$ so that $q_T = q'(1+R)$ one obtains

$$\begin{aligned} C_{ac}^* &= P_{S_T,ac} \cdot q_T = P_{S_T,ac} (1+R)q' \\ &= 1.7 \times 10^{-18} \left(\frac{1+1.14R}{1+R} \right) \text{g s cm}^{-3} \text{g}^{-1} (1+R) 1000 \text{ g s}^{-1} \end{aligned}$$

Substituting $C_{ac}^* = 4.2 \times 10^{-15} \text{ g cm}^{-3}$ and solving, R is found to have a value of 1.3. Hence q is equal to 1300 g s^{-1} and $q_T = 2300 \text{ g s}^{-1}$ ($72 \times 10^3 \text{ t y}^{-1}$), a value in the middle of the range of 25 to $150 \times 10^3 \text{ t y}^{-1}$ of mercury estimated by Weiss, Koide and Goldberg (1971) to be the natural release rate accounting for levels of mercury in Greenland ice deposited before 1900. With the other parameter values used above and with equation (47), the value of C_{s}^* is found to be 140 ng g^{-1} . Most observers agree that the concentration of mercury in uncontaminated non-mineralized soil is less than 200 ng g^{-1} . It can be concluded, therefore, that the estimates of the values of the transfer coefficients P_{ij} are at least of the right order of magnitude.

4.0 Summary and Conclusions

It has been seen that the exposure commitment provides a convenient measure of the disturbance in an environmental system. In the usual sense, the disturbance is a change in the concentration of a pollutant substance in the environment due to its release from a pollution source. The exposure commitment to an environmental subregion is the infinite time integral of the concentration of the pollutant in the subregion or reservoir.

For the passage of the pollutant along a chain of environmental

reservoirs, the transfer coefficient defines the fractional transfer of the pollutant between successive reservoirs. The transfer coefficient can be expressed as the ratio of exposure commitments in receptor and donor reservoirs for a specific input of the pollutant into the system or as the ratio of steady-state concentrations for a constant, continuing input from the pollution source. The exposure commitment to a receptor reservoir is determined by sequential multiplication of transfer coefficients and the input amount into the system. The exposure commitment approach gives a time-independent description of the pollutant behaviour in the environment.

The alternative analysis of the movement of a pollutant through an environmental system is to formulate a time-dependent dynamic model. First order kinetics for pollutant transfers are usually assumed. The changes in concentrations of the pollutants in the various reservoirs are expressed as differential equations, the solutions of which require estimates of the transfer rate constants and the size or mass of the reservoirs.

Transfer coefficients can also be expressed in terms of the parameters of the dynamic models, i.e. using rate constants and reservoir sizes. This has been done for a number of pathway configurations which might be encountered in environmental systems. It was noted, however, that there are practical difficulties in determining the proper values of these parameters. It is sometimes possible to transform the expressions for transfer coefficients in terms of rate constants to relationships involving velocity factors. The velocity factors relate fluxes and concentrations between successive reservoirs, and these quantities are more directly measurable. This approach has been illustrated for the case of environmental mercury in air and soil.

Alternatively, the expressions for the transfer coefficients can be defined directly in terms of velocity factors, without recourse to rate constants. This, in fact, may be the more appropriate approach, since any assumptions about the kinetics of the transfers are avoided.

A properly formulated kinetic model is, of course, a more complete description of an environmental system. The rate constants and reservoir sizes are key parameters in a simulation calculation based on the model intended to show the temporal variations of concentrations in the interconnecting reservoirs. Sensitivity analyses are used to establish credibility in dynamic models when the values of certain parameters are imperfectly known. It cannot always be discovered, however,

whether or not the model is correctly formulated. It may include transfers which do not, in fact, occur, or exclude others which do.

The commitment approach, on the other hand, avoids formulation difficulties. It deals with observed relationships between environmental reservoirs. It is not necessary to resolve or individually assess complex interacting pathways or to understand the transport mechanisms. The implications of the transfer are inherent in the observed relationships. The relationships may even overlap intervening reservoirs if information is lacking. For example, the concentrations of a pollutant in air and vegetation may be noted, giving the transfer coefficient between air and plant without separate evaluations of the transfer coefficients from air to soil and from soil to plant. The commitment approach can therefore be applied on a much more limited data base or on a more limited understanding of environmental processes.

The use of the commitment approach to environmental assessment also has implications for the design of monitoring systems. Once the transfer coefficients for a pollutant in an environmental system are determined, it is not necessary to acquire detailed data on each separate reservoir. If the amount of pollutant released from the source is known, the exposure commitment to intermediate reservoirs or to sensitive receptors can be estimated. Once these relationships are understood, (i.e. to what extent there will be continued transfer or buildup of pollutant amounts in the environment with commitment to exposure in the immediate or long-term future), we should be in a better position to decide the policies which shall govern the release of pollutants from man-made sources into the environment.

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APPENDICES

Introduction

The appendices provide a more comprehensive treatment of the model systems which are discussed briefly in the main text and include the full derivations of mathematical relationships. The examples given illustrate the procedures for a range of compartment and pathway configuration and provide guidance for the development of relationships for other models when first order kinetic transfers are considered to be the appropriate point of departure for the estimation of steady-state concentrations, transfer coefficients, exposure and intake commitments, and the like.

It is hoped that the appendices will be of particular assistance to readers unfamiliar with the mathematics of either kinetic or commitment modelling procedures.

- APPENDIX I : Kinetic analysis of model sequence 1
- APPENDIX II : Kinetic analysis of model sequence 2
- APPENDIX III : Model sequence 3 : steady state analysis
- APPENDIX IV-A : Kinetic analysis of model sequence 4a
- APPENDIX IV-B : Model sequence 4a : steady state analysis
- APPENDIX IV-C : Kinetic analysis of model sequence 4b
- APPENDIX V : Model sequence 5 : steady state analysis – simultaneous releases to two reservoirs
- APPENDIX VI : Model sequence 6 : steady state analysis

Each appendix is presented using a comparable layout, based on the following twelve headings[§]:

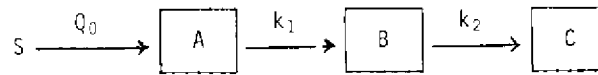
1. System diagram (as in Table 1)
2. General assumptions
3. Initial conditions
4. Graphical description of solutions
5. Mass or flux conservation relations
6. Relations between parameters and variables
7. Application of general relations to the system of interest
8. Solution of equations for concentrations as functions of time or for steady-state concentrations as applicable
9. Integration of concentrations over time
10. Computation of transfer coefficients: P_{SA} , P_{AB} , P_{SB} . (It is these results that form the basis of Table 1.)
11. Additional analyses (where relevant)
12. Direct solutions for integrated concentrations

[§]Some of the appendices do not include all twelve of the headings.

Appendix I

Kinetic analysis of model sequence 1

1. System diagram



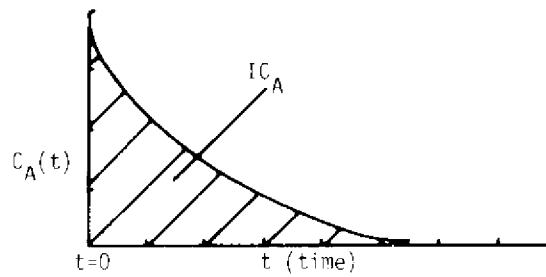
2. General assumptions

- the reservoirs (A, B and C) have a constant size or mass – M_A , M_B , M_C .
- all transfers follow first order kinetics, i.e. the rate of transfer is proportional to the amount of substance in a donor reservoir. The rate constants k_i (where $i = 1, 2, 3, \dots$) are as indicated in the system diagram.
- a pulse of pollutant of amount Q_0 is introduced from a source S into reservoir A at time $t = 0$ by choice of origin.

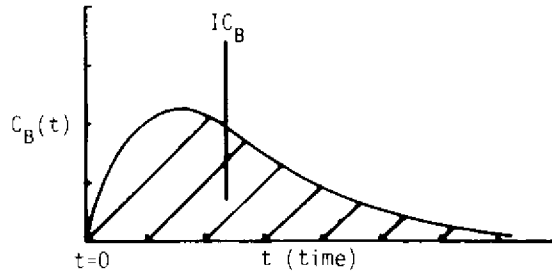
3. Initial conditions, ($t = 0$)

- assuming rapid mixing, the initial concentration of pollutant in reservoir A, $C_A(0)$, will be $\frac{Q_0}{M_A}$.
- initially there will be no pollutant in reservoirs B and C, i.e. $C_B(0) = 0$ and $C_C(0) = 0$

4. Graphical description of solution



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- $C_A(t)$ is the concentration of pollutant in reservoir A at time (t).
- $I C_A$ is the integral over time of $C_A(t)$ (equivalent to hatched area).

5. Mass conservation relations

Let $Q_X(t)$ be the amount of pollutant in reservoir X at time t; for any reservoir the rate of change in the amount of pollutant is equal to the difference between input and output fluxes, i.e. in the general case $\frac{dQ_X}{dt} = (\text{input flux} - \text{output flux})$.

6. Relationship between mass of the reservoir (M_X), concentration (C_X) and amount (Q_X) of pollutant in the reservoir:

$$Q_X = C_X \cdot M_X$$

7. Application of general relationships to the system of interest

In this case, there is only one output from reservoir A to reservoir B. In the case of reservoir B, there is an input flux from reservoir A and an output flux to reservoir C.

i.e. $\frac{dQ_A}{dt} = -k_1 Q_A$

Appendix I

and
$$\frac{dQ_B}{dt} = k_1 Q_A - k_2 Q_B$$

or
$$\frac{dM_A C_A}{dt} = -k_1 M_A C_A$$

and
$$\frac{dM_B C_B}{dt} = k_1 M_A C_A - k_2 M_B C_B$$

∴
$$\frac{dC_A}{dt} = -k_1 C_A \quad [1]$$

and
$$\frac{dC_B}{dt} = k_1 \frac{M_A}{M_B} C_A - k_2 C_B \quad [2]$$

8. Solution of equations [1] and [2] for $C_A(t)$ and $C_B(t)$
Equation [1] can be rewritten as

$$\frac{1}{C_A} \cdot \frac{dC_A}{dt} = -k_1$$

which is a standard form of differential equation with solution

$$C_A(t) = C_A(0)e^{-k_1 t}$$

but
$$C_A(0) = \frac{Q_0}{M_A}$$

∴
$$C_A(t) = \frac{Q_0}{M_A} e^{-k_1 t} \quad [3]$$

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Substituting this expression into [2], we obtain

$$\frac{dC_B}{dt} = k_1 \frac{M_A}{M_B} - \frac{Q_0}{M_A} e^{-k_1 t} - k_2 C_B$$

i.e.
$$\frac{dC_B}{dt} + k_2 C_B = k_1 \frac{Q_0}{M_B} e^{-k_1 t}$$

This is also a standard form of differential equation which can be solved by multiplying through by $e^{k_2 t}$ to give the differential of a product on the left-hand side

i.e.
$$e^{k_2 t} \frac{dC_B}{dt} + k_2 e^{k_2 t} C_B = k_1 \frac{Q_0}{M_B} e^{(k_2 - k_1)t}$$

or
$$\frac{d}{dt} (C_B e^{k_2 t}) = k_1 \frac{Q_0}{M_B} e^{(k_2 - k_1)t}$$

∴ integrating with respect to t

$$C_B e^{k_2 t} = \frac{k_1 Q_0}{M_B (k_2 - k_1)} e^{(k_2 - k_1)t} + K$$

but at t = 0, $C_B(0) = 0$

∴
$$K = \frac{-k_1 Q_0}{M_B (k_2 - k_1)}$$

Appendix I

$$\therefore C_B e^{k_2 t} = \frac{k_1 Q_0}{M_B (k_1 - k_2)} \left[1 - e^{(k_2 - k_1)t} \right]$$

$$\text{or } C_B(t) = \frac{k_1 Q_0}{M_B (k_1 - k_2)} \left[e^{-k_2 t} - e^{-k_1 t} \right] \quad [4]$$

9. Integration of $C_A(t)$ in equation [3] and $C_B(t)$ in equation [4] to compute IC_A and IC_B

$$IC_A = \int_{-\infty}^{\infty} C_A(t) dt = \int_0^{\infty} C_A(t) dt$$

since $C_A(t)$ is by choice of origin zero for times less than zero
 \therefore from equation [3]

$$\begin{aligned} IC_A &= \int_0^{\infty} \frac{Q_0}{M_A} e^{-k_1 t} dt \\ &= \frac{Q_0}{M_A} \left(-\frac{1}{k_1} \right) e^{-k_1 t} \Big|_0^{\infty} \\ &= \frac{Q_0}{M_A} \left(-\frac{1}{k_1} \right) (e^{-k_1 \infty} - e^{-k_1 \cdot 0}) \\ IC_A &= \frac{-Q_0}{M_A k_1} (0 - 1) = \frac{Q_0}{M_A k_1} \quad [5] \end{aligned}$$

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Similarly, from equation [4]

$$\begin{aligned} IC_B &= \frac{k_1 Q_0}{M_B(k_1 - k_2)} \int_0^{\infty} (e^{-k_2 t} - e^{-k_1 t}) dt \\ &= \frac{k_1 Q_0}{M_B(k_1 - k_2)} \left(\frac{1}{k_2} - \frac{1}{k_1} \right) \\ &= \frac{k_1 Q_0 (k_1 - k_2)}{M_B (k_1 - k_2) (k_2 k_1)} \end{aligned}$$

$$\therefore IC_B = \frac{Q_0}{M_B k_2} \quad [6]$$

10. Computation of transfer coefficients P_{SA} , P_{AB} and P_{SB} . Using the definition of P_{XY} .

$$P_{SA} = \frac{IC_A}{Q_0} = \frac{Q_0}{k_1 M_A Q_0} = \frac{1}{k_1 M_A} \quad [7]$$

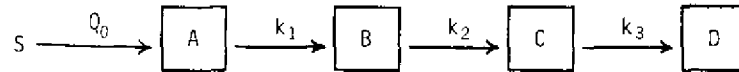
$$P_{AB} = \frac{IC_B}{IC_A} = \frac{Q_0 M_A k_1}{M_B k_2 Q_0} = \frac{k_1 M_A}{k_2 M_B} \quad [8]$$

$$P_{SB} = \frac{IC_B}{Q_0} = \frac{Q_0}{k_2 M_B Q_0} = \frac{1}{k_2 M_B} \quad [9]$$

Appendix I

11. Additional analyses

The original system diagram can be readily extended to the following :



Reservoir C can be treated in an analogous manner to reservoir B to yield the differential equation

$$\frac{dC_C}{dt} = k_2 C_B \frac{M_B}{M_C} - k_3 C_C$$

$$\frac{dC_C}{dt} + k_3 C_C = k_2 \frac{M_B}{M_C} C_B$$

or

$$\frac{d}{dt} \left(e^{k_3 t} C_C \right) = k_2 \frac{M_B}{M_C} e^{k_3 t} C_B$$

But from equation [4]

$$C_B(t) = \frac{k_1 Q_0}{M_B (k_1 - k_2)} \left(e^{-k_2 t} - e^{-k_1 t} \right)$$

which we can substitute above to yield

$$\frac{d}{dt} \left(e^{k_3 t} C_C \right) = k_2 \frac{M_B}{M_C} \frac{k_1 Q_0}{M_B (k_1 - k_2)} \left[e^{(k_3 - k_2)t} - e^{(k_3 - k_1)t} \right]$$

Appendix I

therefore

$$e^{k_3 t} C_C = \frac{k_2 k_1 Q_0}{(k_1 - k_2) M_C} \left[\frac{e^{(k_3 - k_2) t}}{(k_3 - k_2)} - \frac{e^{(k_3 - k_1) t}}{(k_3 - k_1)} \right] + K$$

But at $t = 0$ $C_C = 0$

$$\therefore K = \frac{-k_2 k_1 Q_0}{(k_1 - k_2) M_C} \left[\frac{1}{(k_3 - k_2)} - \frac{1}{(k_3 - k_1)} \right]$$

$$\therefore e^{k_3 t} C_C = \frac{k_2 k_1 Q_0}{(k_1 - k_2) M_C} \left[\frac{(1 - e^{(k_3 - k_1) t})}{(k_3 - k_1)} - \frac{(1 - e^{(k_3 - k_2) t})}{(k_3 - k_2)} \right]$$

$$\text{i.e. } C_C(t) = \frac{k_2 k_1 Q_0}{(k_1 - k_2) M_C} \left[\frac{(e^{-k_3 t} - e^{-k_1 t})}{(k_3 - k_1)} - \frac{(e^{-k_3 t} - e^{-k_2 t})}{(k_3 - k_2)} \right]$$

$$\text{or } C_C(t) = \frac{Q_0}{M_C} \cdot \frac{k_1 k_2}{(k_2 - k_1)} \left[\frac{(e^{-k_3 t} - e^{-k_1 t})}{(k_1 - k_3)} - \frac{(e^{-k_3 t} - e^{-k_2 t})}{(k_2 - k_3)} \right] \quad [10]$$

Appendix I

$$\begin{aligned}
 \therefore \text{IC}_C &= \int_0^{\infty} C_C(t) dt = \frac{Q_0}{M_C} \cdot \frac{k_1 k_2}{(k_2 - k_1)} \left[\frac{\frac{1}{k_3} - \frac{1}{k_1}}{(k_1 - k_3)} - \frac{\frac{1}{k_3} - \frac{1}{k_2}}{(k_2 - k_3)} \right] \\
 &= \frac{Q_0}{M_C} \cdot \frac{k_1 k_2}{(k_2 - k_1)} \left[\frac{(k_1 - k_3)}{k_1 k_3 (k_1 - k_3)} - \frac{(k_2 - k_3)}{k_2 k_3 (k_2 - k_3)} \right] \\
 &= \frac{Q_0}{M_C} \cdot \frac{k_1 k_2}{(k_2 - k_1)} \cdot \frac{(k_2 - k_1)}{k_1 k_2 k_3} \\
 \therefore \text{IC}_C &= \frac{Q_0}{M_C k_3} \quad [11]
 \end{aligned}$$

12. Direct solutions for integrated concentrations

We are given above in equations [1] and [2]

$$\frac{dC_A}{dt} = -k_1 C_A \quad [1]$$

and

$$\frac{dC_B}{dt} = k_1 \frac{M_A}{M_B} C_A - k_2 C_B \quad [2]$$

Integrating both sides of equation [1] between the limits $t=0$ and $t=\infty$ we obtain:

Appendix I

$$\int_0^{\infty} \frac{dC_A}{dt} dt = -k_1 \int_0^{\infty} C_A dt = -k_1 IC_A$$

or

$$C_A(t) \Big|_0^{\infty} = -k_1 IC_A$$

or

$$C_A(\infty) - C_A(0) = -k_1 IC_A$$

For a pulsed release to reservoir A, assuming rapid mixing, we know that:

$$C_A(0) = \frac{Q_0}{M_A}$$

and on inspection of the system as a whole, it is seen that $C_A(\infty) = 0$
Therefore:

$$k_1 IC_A = \frac{Q_0}{M_A} - 0$$

or

$$IC_A = \frac{Q_0}{k_1 M_A} \quad \text{as equation [5] above}$$

Similarly from equation [2] above:

$$C_B(\infty) - C_B(0) = k_1 \frac{M_A}{M_B} IC_A - k_2 IC_B$$

but we know that for a pulsed release to reservoir A, $C_B(\infty) = C_B(0) = 0$

Appendix I

Therefore :

$$k_2 IC_B = k_1 \frac{M_A}{M_B} IC_A$$

substituting for IC_A from equation [5]

$$IC_B = \frac{Q_0}{k_2 M_B} \quad \text{as equation [6] above}$$

This procedure can also be applied to the more general case when a source of strength $q(t)$ acts for a finite time such that

$$\int_0^{\infty} q(t) dt = Q$$

is finite. Q is the total intake of material from the source.

The appropriate equations when the source acts on reservoir A are :

$$\frac{dC_A}{dt} = \frac{q(t)}{M_A} - k_1 C_A \quad [1']$$

and

$$\frac{dC_B}{dt} = k_1 \frac{M_A}{M_B} C_A - k_2 C_B \quad [2']$$

Integrating both sides of equation [1'] between the limits $t=0$ and $t=\infty$ we obtain :

$$C_A(t) \Big|_0^{\infty} = \frac{1}{M_A} \int_0^{\infty} q(t) dt - k_1 \int_0^{\infty} C_A dt$$

Appendix I

or

$$C_A(\infty) - C_A(0) = \frac{Q}{M_A} - k_1 IC_A$$

Let us assume $C_A(0) = \frac{Q_0}{M_A}$ and arguing as before $C_A(\infty) = 0$

Therefore :

$$IC_A = \frac{1}{k_1 M_A} (Q_0 + Q) \quad [3']$$

In this case the exposure commitment for reservoir A, IC_A , depends on k_1 , M_A , Q_0 and Q . Q_0 is the initial amount in reservoir A. Q is the total intake to reservoir A from sources.

Similarly from equation [2'] we obtain :

$$C_B(\infty) - C_B(0) = k_1 \frac{M_A}{M_B} IC_A - k_2 IC_B$$

as before :

$$C_B(\infty) = C_B(0) = 0$$

Therefore :

$$k_2 IC_B = k_1 \frac{M_A}{M_B} IC_A$$

and substituting for IC_A we obtain :

$$IC_B = \frac{1}{k_2 M_B} (Q_0 + Q) \quad [4']$$

Appendix I

It is instructive to demonstrate the formal connexion between the above treatment and the treatment appropriate for steady-state situations. The steady-state equations can be derived from equations [1'] and [2'] by setting $\frac{dC_A}{dt}$ and $\frac{dC_B}{dt}$ to zero and replacing $q(t)$ and C_A and C_B with steady-state values q , C_A^* and C_B^* respectively. We then obtain the following equations:

$$0 = \frac{q}{M_A} - k_1 C_A^* \quad [1'']$$

$$0 = k_1 \frac{M_A}{M_B} C_A^* - k_2 C_B^* \quad [2'']$$

From [1'']:

$$C_A^* = \frac{1}{k_1 M_A} (q) \quad [3'']$$

From [2'']

$$C_B^* = \frac{k_1 M_A}{k_2 M_B} C_A^* = \frac{1}{k_2 M_B} (q) \quad [4'']$$

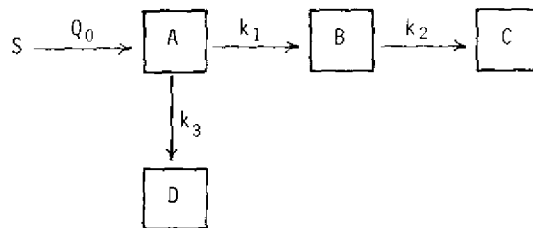
By comparing [3'] with [3''] and [4'] with [4''] it is seen that the relations obtained are structurally similar, with IC_A and IC_B replaced by C_A^* and C_B^* and $(Q_0 + Q)$ replaced by q .

In some of the examples in the following appendices, the steady-state procedure is followed as this corresponds more closely to situations of practical interest. However, it is emphasized that the same set of equations would have required solution had the direct procedure for integrated concentrations been followed.

Appendix II

Kinetic analysis of model sequence 2

1. System diagram



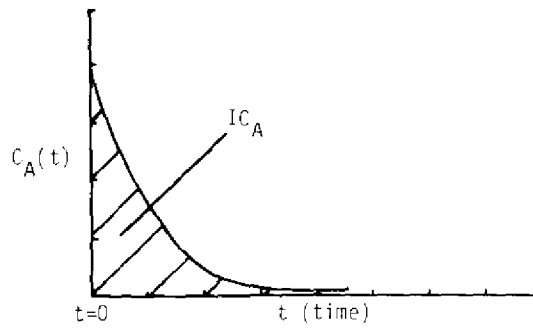
2. General assumptions – see Appendix I

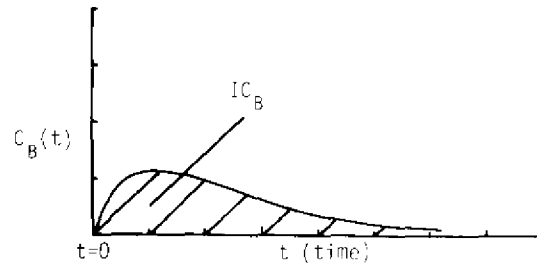
3. Initial conditions, (t = 0)

$$C_A(0) = \frac{Q_0}{M_A}$$

$$C_B(0) = 0; \quad C_C(0) = 0; \quad C_D(0) = 0$$

4. Graphical description





5. Mass conservation relations – as for Appendix I

6. Relations between parameters and variables – as for Appendix I

7. Application of general relations to the system of interest

In this case there are two output fluxes from reservoir A, one to reservoir B and one to reservoir D. In the case of reservoir B, there is an output flux to reservoir C and an input flux from reservoir A,

i.e.
$$\frac{dQ_A}{dt} = -k_1 Q_A - k_3 Q_A$$

and
$$\frac{dQ_B}{dt} = k_1 Q_A - k_2 Q_B$$

or
$$\frac{dM_A C_A}{dt} = -k_1 M_A C_A - k_3 M_A C_A$$

and
$$\frac{dM_B C_B}{dt} = k_1 M_A C_A - k_2 M_B C_B$$

Appendix II

i.e.
$$\frac{dC_A}{dt} = - (k_1 + k_3) C_A \quad [1]$$

and
$$\frac{dC_B}{dt} = k_1 \frac{M_A}{M_B} C_A - k_2 C_B \quad [2]$$

8. Solution of equations [1] and [2] for $C_A(t)$ and $C_B(t)$

Equation [1] can be rewritten as

$$\frac{1}{C_A} \cdot \frac{dC_A}{dt} = - (k_1 + k_3)$$

This is the same equation as in Appendix I with k_1 replaced by $(k_1 + k_3)$
 \therefore the solution is:

$$C_A(t) = \frac{Q_0}{M_A} e^{-(k_1 + k_3)t} \quad [3]$$

and again following Appendix I and from [2] and [3]

$$\frac{dC_B}{dt} + k_2 C_B = k_1 \frac{Q_0}{M_B} e^{-(k_1 + k_3)t}$$

multiplying through by $e^{k_2 t}$

$$e^{k_2 t} \frac{dC_B}{dt} + k_2 e^{k_2 t} C_B = k_1 \frac{Q_0}{M_B} e^{(k_2 - (k_1 + k_3))t}$$

$$\frac{d}{dt} e^{k_2 t} C_B = k_1 \frac{Q_0}{M_B} e^{(k_2 - (k_1 + k_3))t}$$

Appendix II

integrating with respect to t

$$\therefore e^{k_2 t} C_B = \frac{k_1 Q_0}{M_B (k_2 - (k_1 + k_3))} e^{(k_2 - (k_1 + k_3))t} + K$$

but at t = 0, C_B = 0

$$\therefore K = \frac{-k_1 Q_0}{M_B (k_2 - (k_1 + k_3))}$$

substituting for this value of K

$$\therefore e^{k_2 t} C_B = \frac{k_1 Q_0}{M_B (k_2 - (k_1 + k_3))} \cdot \left[e^{(k_2 - (k_1 + k_3))t} - 1 \right]$$

$$\therefore C_B(t) = \frac{k_1 Q_0}{M_B (k_1 + k_3 - k_2)} \left[e^{-k_2 t} - e^{-(k_1 + k_3)t} \right] \quad [4]$$

9. Integration of C_A(t) in equation [3] and C_B(t) in equation [4] to compute I_{CA} and I_{CB}

As in Appendix I, making suitable substitutions

$$I_{C_A} = \frac{Q_0}{M_A (k_1 + k_3)} \quad [5]$$

$$\begin{aligned} I_{C_B} &= \frac{k_1 Q_0}{M_B (k_1 + k_3 - k_2)} \left[\frac{1}{k_2} - \frac{1}{k_1 + k_3} \right] \\ &= \frac{k_1 Q_0}{M_B (k_1 + k_3 - k_2)} \cdot \frac{(k_1 + k_3 - k_2)}{k_2 (k_1 + k_3)} \end{aligned}$$

Appendix II

$$IC_B = \frac{k_1 Q_0}{M_B k_2 (k_1 + k_3)} \quad [6]$$

10. Computation of transfer coefficients PS_A , P_{AB} , PS_B

$$P_{SA} = \frac{IC_A}{Q_0} = \frac{1}{(k_1 + k_3) M_A} \quad [7]$$

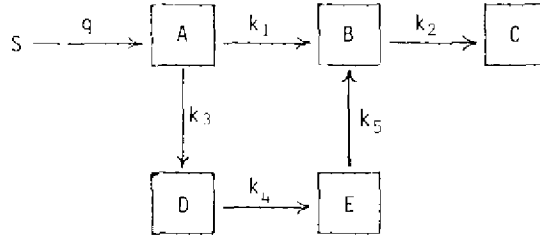
$$P_{AB} = \frac{IC_B}{IC_A} = \frac{k_1}{k_2} \frac{M_A}{M_B} \quad [8]$$

$$P_{SB} = \frac{IC_B}{Q_0} = \frac{k_1}{k_2 (k_1 + k_3) M_B} \quad [9]$$

Appendix III

Model sequence 3 – steady state analysis

1. System diagram



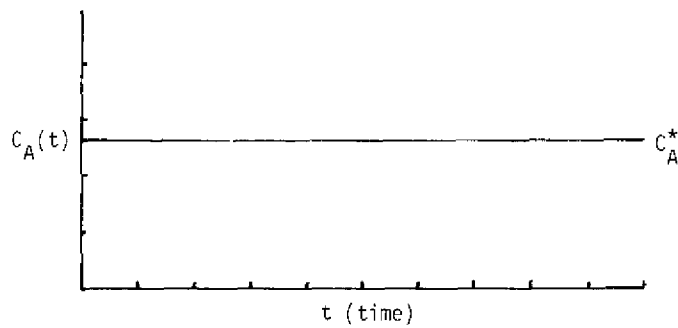
2. General assumptions – as for Appendix I

3. Initial conditions

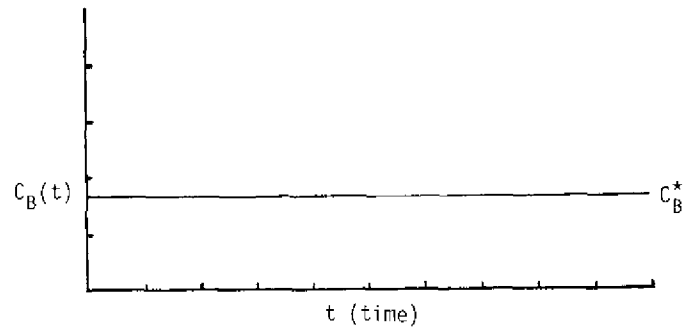
As we are concerned with a steady-state situation, the relevant conditions are:

$$\frac{dC_A}{dt} = 0; \quad \frac{dC_B}{dt} = 0; \quad \frac{dC_C}{dt} = 0; \quad \frac{dC_D}{dt} = 0; \quad \frac{dC_E}{dt} = 0$$

4. Graphical description of solutions



Appendix III



5. **Mass conservation relations** -- as Appendix I except for continual input, q , to reservoir A

6. **Relations between parameters and variables** -- as Appendix I

7. **Application of general relations to the system of interest**

By considering the input and output fluxes from the four reservoirs A, B, D and E we can write

$$\frac{dQ_A}{dt} = q - (k_1 + k_3)Q_A$$

$$\frac{dQ_B}{dt} = k_1 Q_A + k_5 Q_E - k_2 Q_B$$

$$\frac{dQ_D}{dt} = k_3 Q_A - k_4 Q_D$$

$$\frac{dQ_E}{dt} = k_4 Q_D - k_5 Q_E$$

Appendix III

But we can write $Q_X = M_X C_X$ for each case and divide through by M_X to yield the following equations :

$$\frac{dC_A}{dt} = \frac{q}{M_A} - (k_1 + k_3)C_A \quad [1]$$

$$\frac{dC_B}{dt} = k_1 C_A \frac{M_A}{M_B} + k_5 C_E \frac{M_E}{M_B} - k_2 C_B \quad [2]$$

$$\frac{dC_D}{dt} = k_3 C_A \frac{M_A}{M_D} - k_4 C_D \quad [3]$$

$$\frac{dC_E}{dt} = k_4 C_D \frac{M_D}{M_E} - k_5 C_E \quad [4]$$

but in the steady-state situation, $\frac{dC_X}{dt} = 0$, $X = A - E$

∴ we can write :

$$0 = \frac{q}{M_A} - (k_1 + k_3)C_A^* \quad [5]$$

$$0 = k_1 C_A^* \frac{M_A}{M_B} + k_5 C_E^* \frac{M_E}{M_B} - k_2 C_B^* \quad [6]$$

$$0 = k_3 C_A^* \frac{M_A}{M_D} - k_4 C_D^* \quad [7]$$

Appendix III

$$0 = k_4 C_D^* \frac{M_D}{M_E} - k_5 C_E^* \quad [8]$$

where C_X^* for $X = A - E$ is the steady-state value of C_X .

From equation [5] :

$$C_A^* = \frac{q}{(k_1 + k_3)M_A} \quad [9]$$

substituting equation [9] into equation [7] we obtain :

$$C_D^* = \frac{k_2}{k_4} \cdot \frac{M_A}{M_D} \cdot \frac{q}{(k_1 + k_3)M_A}$$

or

$$C_D^* = \frac{k_2}{k_4} \cdot \frac{q}{(k_1 + k_3)M_D} \quad [10]$$

Substituting equation [10] into equation [8] we obtain :

$$C_E^* = \frac{k_4}{k_5} \cdot \frac{M_D}{M_E} \cdot \frac{k_2}{k_4} \cdot \frac{1}{M_D} \cdot \frac{q}{(k_1 + k_3)}$$

or

$$C_E^* = \frac{k_2}{k_5} \cdot \frac{1}{(k_1 + k_3)} \cdot \frac{q}{M_E} \quad [11]$$

Appendix III

substituting equations [9] and [11] into equation [6] we obtain :

$$k_2 C_B^* = k_1 \frac{M_A}{M_B} \cdot \frac{q}{(k_1 + k_3)M_A} + k_5 \frac{M_E}{M_B} \cdot \frac{k_3}{k_5} \cdot \frac{1}{(k_1 + k_3)} \cdot \frac{q}{M_E}$$

or
$$C_B^* = \frac{k_1}{k_2} \cdot \frac{1}{(k_1 + k_3)} \cdot \frac{q}{M_B} + \frac{k_3}{k_2} \cdot \frac{1}{(k_1 + k_3)} \cdot \frac{q}{M_B}$$

or
$$C_B^* = \frac{q}{M_B (k_1 + k_3)} \left(\frac{k_1}{k_2} + \frac{k_3}{k_2} \right)$$

$$= \frac{q(k_1 + k_3)}{M_B (k_1 + k_3)k_2}$$

∴
$$C_B^* = \frac{q}{k_2 M_B} \quad [12]$$

10. Computation of transfer coefficients from the steady-state concentrations

$$P_{SA} = \frac{C_A^*}{q} = \frac{1}{(k_1 + k_3)M_A} \quad [13]$$

$$P_{AB} = \frac{C_B^*}{C_A^*} = \left(\frac{k_1 + k_3}{k_2} \right) \frac{M_A}{M_B} \quad [14]$$

Appendix III

$$P_{SB} = \frac{C_B^*}{q} = \frac{1}{k_2 M_B} \quad [15]$$

12. Direct solutions for integrated concentrations (pulsed emission)

Equation [1] above can be modified to suit a pulsed emission situation to the following form :

$$\frac{dC_A}{dt} = - (k_1 + k_3) C_A$$

Hence

$$C_A(t) \Big|_0^{\infty} = - (k_1 + k_3) I C_A$$

But $C_A(0) = \frac{Q_0}{M_A}$ and by inspection $C_A(\infty) = 0$

$$\therefore 0 - \frac{Q_0}{M_A} = - (k_1 + k_3) I C_A$$

$$\therefore \frac{I C_A}{Q_0} = \frac{1}{(k_1 + k_3)} \cdot \frac{1}{M_A} = P_{SA} \quad \text{as equation [13] above}$$

Similarly, from equation [3] :

$$C_D(t) \Big|_0^{\infty} = k_3 \frac{M_A}{M_D} I C_A - k_t I C_D$$

Appendix III

But $C_D(0) = C_D(\infty) = 0$ and substituting for IC_A from above we obtain :

$$IC_D = \frac{k_3}{M_D} \cdot \frac{Q_0}{(k_1 + k_3)k_4}$$

and from equation [4] :

$$C_E(t) \Big|_0^{\infty} = k_4 IC_D \frac{M_D}{M_E} - k_5 IC_E$$

and therefore, as previously :

$$C_E(0) = C_E(\infty) = 0$$

so that :

$$IC_E = k_4 \cdot \frac{k_3}{M_D} \cdot \frac{Q_0}{(k_1 + k_3)k_4} \cdot \frac{M_D}{M_E} \cdot \frac{1}{k_5}$$

or
$$IC_E = \frac{k_3}{k_5} \cdot \frac{1}{(k_1 + k_3)} \cdot \frac{Q_0}{M_E} \quad (\text{corresponding with equation [11]})$$

From equation [2] :

$$C_B(t) \Big|_0^{\infty} = k_1 \frac{M_A}{M_B} IC_A + k_5 \frac{M_E}{M_B} IC_E - k_2 IC_B$$

following a similar argument to the above :

$$IC_B k_2 = \frac{k_1}{M_B} \cdot \frac{Q_0}{(k_1 + k_3)} + \frac{k_3}{M_B} \cdot \frac{Q_0}{(k_1 + k_3)}$$

Appendix III

$$\text{or } IC_B = \frac{Q_0}{M_B} \cdot \frac{1}{(k_1 + k_3)} \cdot \frac{(k_1 + k_3)}{k_2}$$

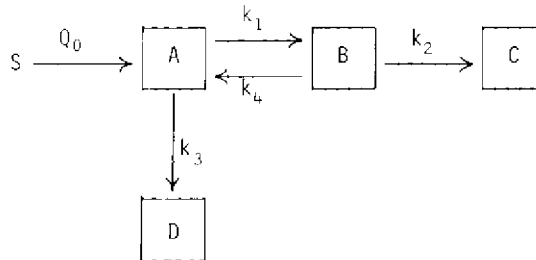
$$\text{or } \frac{IC_B}{Q_0} = \frac{1}{k_2 M_B} = P_{SB}$$

as equation [15]

Appendix IV-A

Kinetic analysis of model sequence 4a

1. System diagram

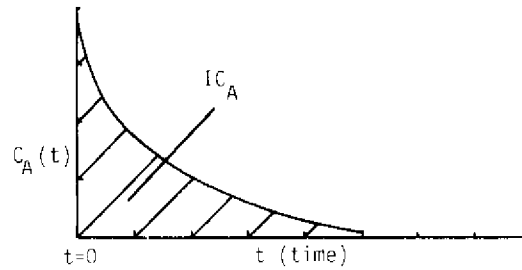


2. General assumptions – as for Appendix I

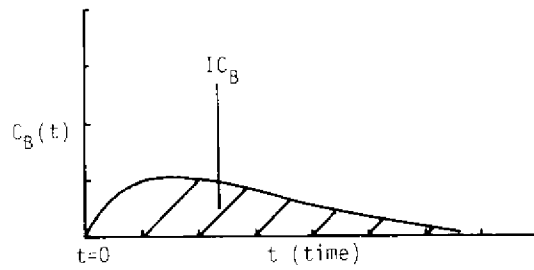
3. Initial conditions

$$c_A(0) = \frac{Q_0}{M_A}; \quad c_B(0) = 0; \quad c_C(0) = 0; \quad c_D(0) = 0$$

4. Graphical descriptions of solution



Appendix IV-A



5. Mass conservation relations – as for Appendix I

6. Relations between parameters and variables – as for Appendix I

7. Application of general relations to the system of interest

In this case there are two output fluxes from reservoir A, one to reservoir B and one to reservoir D. Reservoir A receives an input flux from reservoir B. In the case of reservoir B, there are output fluxes to reservoirs A and C and an input flux from reservoir A.

or
$$\frac{dQ_A}{dt} = -k_1 Q_A - k_3 Q_A + k_4 Q_B$$

and
$$\frac{dQ_B}{dt} = k_1 Q_A - k_2 Q_B - k_4 Q_B$$

or
$$\frac{dM_{A,C}}{dt} = -k_1 M_{A,C} - k_3 M_{A,C} + k_4 M_{B,C}$$

Appendix IV-A

and
$$\frac{dM_B C_B}{dt} = k_1 M_A C_A - k_2 M_B C_B - k_4 M_B C_B$$

i.e.
$$\frac{dC_A}{dt} = -(k_1 + k_3) C_A + k_4 \frac{M_B}{M_A} C_B \quad [1]$$

and
$$\frac{dC_B}{dt} = k_1 \frac{M_A}{M_B} C_A - (k_2 + k_4) C_B \quad [2]$$

8. and 9. Solution of equations [1] and [2] for ICA and ICB

For analytical convenience let :

$$\begin{aligned} a &= k_1 + k_3 \\ b &= k_4 \\ c &= k_1 \\ d &= k_2 + k_4 \\ C_A &= x \\ C_B &= y \end{aligned}$$

Using the notation $\dot{x} = \frac{dx}{dt}$ $\ddot{x} = \frac{d^2x}{dt^2}$ $\dot{y} = \frac{dy}{dt}$ $\ddot{y} = \frac{d^2y}{dt^2}$

etc. and substituting in [1] and [2], we obtain the equations :

$$\dot{x} = -ax + b \frac{M_B}{M_A} y \quad [1']$$

$$\dot{y} = c \frac{M_A}{M_B} x - dy \quad [2']$$

Appendix IV-A

differentiating [1'] and [2'] with respect to time, we obtain :

$$\ddot{x} = -a\dot{x} + b \frac{M_B}{M_A} \dot{y} \quad [3]$$

$$\ddot{y} = c \frac{M_A}{M_B} \dot{x} - d\dot{y} \quad [4]$$

by substituting for \dot{y} from [2'] into [3] and by substituting for \dot{x} from [1'] into [4] we obtain :

$$\ddot{x} = -a\dot{x} + b \frac{M_B}{M_A} \left(c \frac{M_A}{M_B} x - dy \right) \quad [5]$$

$$\ddot{y} = c \frac{M_A}{M_B} \left(-ax + b \frac{M_B}{M_A} y \right) - d\dot{y} \quad [6]$$

Similarly we can use [1'] and [2'] to replace y and x respectively in [5] and [6] to obtain :

$$\ddot{x} = -a\dot{x} + bcx - db \frac{M_B}{M_A} (\dot{x} + ax) \frac{M_A}{bM_B} \quad [7]$$

and
$$\ddot{y} = -ac \frac{M_A}{M_B} (\dot{y} + dy) \frac{M_B}{cM_A} + bcy - d\dot{y} \quad [8]$$

or
$$\ddot{x} = -a\dot{x} + bcx - d\dot{x} - adx \quad [9]$$

Appendix IV-A

$$\ddot{y} = -a\dot{y} - ady + bcy - d\dot{y} \quad [10]$$

i.e. $\ddot{x} + (a + d)\dot{x} + (ad - bc)x = 0 \quad [11]$

$$\ddot{y} + (a + d)\dot{y} + (ad - bc)y = 0 \quad [12]$$

These are homogeneous second order differential equations which can be solved by standard methods.

If we let: $m = a + d$
 $n = ad - bc$

the standard equations are:

$$\ddot{x} + m\dot{x} + nx = 0$$

and $\ddot{y} + m\dot{y} + ny = 0$

The general solutions will be of the form:

$$x(t) = A e^{r_1 t} + B e^{r_2 t} \quad [13]$$

$$y(t) = C e^{r_1 t} + D e^{r_2 t} \quad [14]$$

where A, B, C and D are constants determined by the initial conditions and r_1 and r_2 are the roots of the equation

$$r^2 + mr + n = 0 \quad [13']$$

i.e. $r_1 = \frac{-m + \sqrt{m^2 - 4n}}{2}$

$$r_2 = \frac{-m - \sqrt{m^2 - 4n}}{2}$$

Appendix IV-A

Note also that : $r_1 + r_2 = -m$

$$(r_1)(r_2) = n$$

The solutions for [11] and [12] above will differ on account of differences in the initial conditions for each variable.

Identifying x with C_A and y with C_B , let the initial conditions be :

$$x(0) = \alpha \qquad \dot{x}(0) = \beta$$

$$y(0) = 0 \qquad \dot{y}(0) = \gamma$$

\therefore from [13] and [14] we obtain :

$$\alpha = A + B$$

$$0 = C + D$$

differentiating [13] and [14] yields :

$$\dot{x}(t) = Ar_1 e^{r_1 t} + Br_2 e^{r_2 t} \qquad [15]$$

$$\dot{y}(t) = Cr_1 e^{r_1 t} + Dr_2 e^{r_2 t} \qquad [16]$$

and substituting the initial conditions

$$\beta = Ar_1 + Br_2$$

$$\gamma = Cr_1 + Dr_2$$

Appendix IV-A

by solving these equations we obtain the following values of A, B, C and D

$$A = \frac{\beta - \alpha r_2}{r_1 - r_2}$$

$$B = \frac{\alpha r_1 - \beta}{r_1 - r_2}$$

$$C = \frac{\gamma}{r_1 - r_2}$$

$$D = \frac{-\gamma}{r_1 - r_2}$$

Thus we can write the solutions [13] and [14] in the form :

$$x = \left(\frac{\beta - \alpha r_2}{r_1 - r_2} \right) e^{r_1 t} + \left(\frac{\alpha r_1 - \beta}{r_1 - r_2} \right) e^{r_2 t} \quad [17]$$

$$y = \left(\frac{\gamma}{r_1 - r_2} \right) e^{r_1 t} - \left(\frac{\gamma}{r_1 - r_2} \right) e^{r_2 t} \quad [18]$$

Without substituting at this time the values of r_1 and r_2 , we can integrate these expressions for $x(t)$ and $y(t)$ over time to obtain :

$$IX = \left(\frac{\beta - \alpha r_2}{r_1 - r_2} \right) \left(-\frac{1}{r_1} \right) + \left(\frac{\alpha r_1 - \beta}{r_1 - r_2} \right) \left(-\frac{1}{r_2} \right) \quad [19]$$

Appendix IV-A

$$IY = \left(\frac{\gamma}{r_1 - r_2} \right) \left(-\frac{1}{r_1} \right) - \left(\frac{\gamma}{r_1 - r_2} \right) \left(-\frac{1}{r_2} \right) \quad [20]$$

or

$$IX = \frac{-r_2(\beta - \alpha r_2) - r_1(\alpha r_1 - \beta)}{(r_1 - r_2)(r_1)(r_2)} \quad [21]$$

$$IY = \frac{-r_2\gamma + r_1\gamma}{(r_1 - r_2)(r_1)(r_2)} \quad [22]$$

or

$$IX = \frac{-\alpha(r_1^2 - r_2^2) + \beta(r_1 - r_2)}{(r_1 - r_2)(r_1)(r_2)} \quad [23]$$

$$IY = \frac{\gamma(r_1 - r_2)}{(r_1 - r_2)(r_1)(r_2)} \quad [24]$$

or

$$IX = \frac{-\alpha(r_1 + r_2) + \beta}{r_1 r_2} \quad [25]$$

$$IY = \frac{\gamma}{r_1 r_2} \quad [26]$$

Appendix IV-A

Equations [25] and [26] show that we can calculate IX and IY when we know $(r_1 + r_2)$ and $r_1 r_2$ rather than r_1 and r_2 independently. $(r_1 + r_2)$ and $r_1 r_2$ are readily obtained from [13'] as explained earlier.

i.e.
$$r_1 + r_2 = -m$$

$$r_1 r_2 = n$$

but
$$m = a + d$$

$$n = ad - bc$$

\therefore
$$r_1 + r_2 = -(a + d)$$

$$r_1 r_2 = ad - bc$$

Similarly, substituting for a, b, c and d

$$(r_1 + r_2) = -(k_1 + k_3 + k_2 + k_4) \quad [27]$$

$$r_1 r_2 = (k_1 + k_3)(k_2 + k_4) - k_4 k_1 = \phi, \text{ say} \quad [28]$$

since $x = C_A$ and $y = C_B$, IX = IC_A, IY = IC_B

Appendix IV-A

Also
$$x(0) = \dot{C}_A(0) = \alpha = \frac{Q_0}{M_A} \quad [29]$$

∴ from equation [1]

$$\dot{x}(0) = \ddot{C}_A(0) = \beta = -(k_1 + k_3) \frac{Q_0}{M_A} \quad [30]$$

and from equation [2]

$$\dot{y}(0) = \dot{C}_B(0) = \gamma = k_1 \frac{Q_0}{M_A} \quad [31]$$

From equations [25] and [26] substituting for α , β , γ , $(r_1 + r_2)$ and $(r_1 r_2)$ we obtain

$$IC_A = \frac{\frac{Q_0}{M_A} (k_1 + k_2 + k_3 + k_4) - (k_1 + k_3) \frac{Q_0}{M_A}}{(k_1 + k_3)(k_2 + k_4) - k_1 k_4}$$

or
$$IC_A = \frac{Q_0}{M_A} \left[\frac{(k_2 + k_4)}{(k_1 + k_3)(k_2 + k_4) - k_1 k_4} \right] \quad [32]$$

and
$$IC_B = \frac{k_1 Q_0}{M_B \left[(k_1 + k_3)(k_2 + k_4) - k_1 k_4 \right]} \quad [33]$$

10. Computation of transfer coefficients

$$P_{SA} = \frac{IC_A}{Q_0} = \frac{k_2 + k_4}{[(k_1 + k_3)(k_2 + k_4) - k_1 k_4]} M_A \quad [34]$$

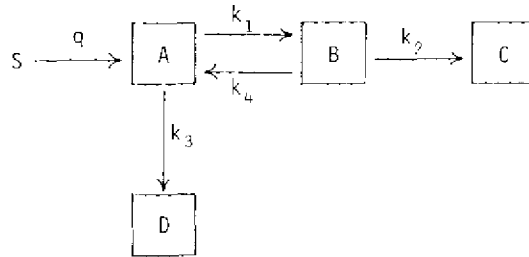
$$P_{AB} = \frac{IC_B}{IC_A} = \frac{k_1 M_A}{(k_2 + k_4) M_B} \quad [35]$$

$$P_{SB} = \frac{IC_B}{Q_0} = \frac{k_1}{[(k_1 + k_3)(k_2 + k_4) - k_1 k_4]} M_B \quad [36]$$

Appendix IV-B

Model sequence 4a: Steady state analysis

1. System diagram



2. General assumptions

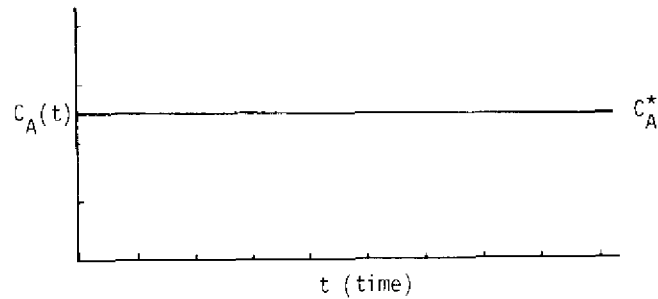
In contrast to the case in Appendix IV-A, there is a constant input rate, q , of pollutant from source, S, to reservoir A.

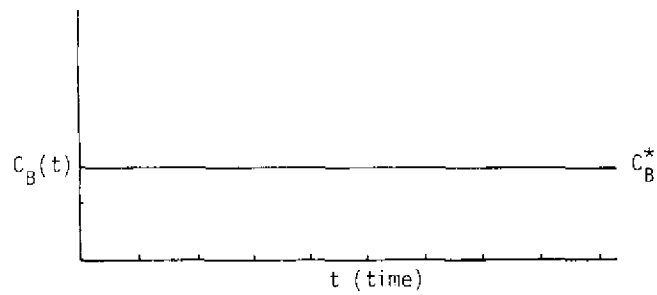
3. Initial conditions

Since we are dealing with a steady-state situation, the relevant conditions are that the concentrations, C_A and C_B , do not change in time,

i.e.
$$\frac{dC_A}{dt} = 0; \quad \frac{dC_B}{dt} = 0$$

4. Graphical description of solutions





5. **Mass conservation relations** – as for Appendix IV-A except for constant input, q , to reservoir A.

6. **Relations between parameters and variables** – as for Appendix IV-A

7. **Applications of general relations to the system of interest**

In this case, reservoir A receives a constant input, q , from S in addition to the inputs and outputs in Appendix IV-A.

This leads to the equations:

$$\frac{dC_A}{dt} = \frac{q}{M_A} - (k_1 + k_3)C_A + k_4 \frac{M_B}{M_A} C_B \quad [1]$$

$$\frac{dC_B}{dt} = k_1 \frac{M_A}{M_B} C_A - (k_2 + k_4)C_B \quad [2]$$

In our case

$$\frac{dC_A}{dt} = 0; \quad \frac{dC_B}{dt} = 0$$

Appendix IV-B

The steady-state values C_A^* and C_B^* are thus obtained by solving the equations

$$0 = \frac{q}{M_A} - (k_1 + k_3)C_A^* + k_4 \frac{M_B}{M_A} C_B^* \quad [1']$$

$$0 = k_1 \frac{M_A}{M_B} C_A^* - (k_2 + k_4)C_B^* \quad [2']$$

8. Solution of equations [1'] and [2'] for C_A^* and C_B^*

From [2']

$$C_B^* = \frac{k_1 M_A}{M_B (k_2 + k_4)} C_A^* \quad [3]$$

∴ substitution in [1']

$$0 = \frac{q}{M_A} - C_A^* \left[k_1 + k_3 + \frac{k_4 M_B \cdot k_1 M_A}{M_A \cdot M_B (k_2 + k_4)} \right] \quad [4]$$

$$\frac{q}{M_A} = C_A^* \left[\frac{(k_1 + k_3)(k_2 + k_4) - k_1 k_4}{k_2 + k_4} \right] \quad [5]$$

$$\frac{C_A^*}{q} = \frac{k_2 + k_4}{\left[(k_1 + k_3)(k_2 + k_4) - k_1 k_4 \right] M_A} \quad [6]$$

= P_{SA} from equation [34] of Appendix IV-A

Appendix IV-B

Again from equation [2'] and substituting for C_A^* from equation [37]

$$C_B^* = \frac{k_1 M_A}{M_B (k_2 + k_4)} \cdot C_A^* \quad [7]$$

or

$$C_B^* = \frac{k_1 M_A}{M_B (k_2 + k_4)} \cdot \frac{q(k_2 + k_4)}{[(k_1 + k_3)(k_2 + k_4) - k_1 k_4] M_A} \quad [8]$$

i.e.

$$\frac{C_B^*}{q} = \frac{1}{M_B} \left[\frac{k_1}{(k_1 + k_3)(k_2 + k_4) - k_1 k_4} \right] \quad [9]$$

= P_{SB} from equation [35] of Appendix IV-A

Again

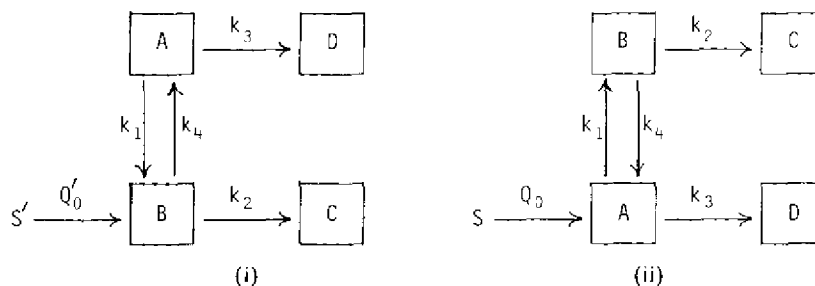
$$\begin{aligned} P_{AB} &= \frac{P_{SB}}{P_{SA}} \\ &= \frac{M_A}{M_B} \cdot \frac{k_1}{k_2 + k_4} \end{aligned} \quad [10]$$

Appendix IV-C

Kinetic analysis of model sequence 4b

Consider the case when the single pulse emission is to reservoir B rather than to reservoir A as above.

The system diagram is shown below, (i), and compared with the previous case, which is shown in (ii).



System (i) is structurally the same system as (ii). It only differs in the labels given to the corresponding reservoirs and the rate constants. Thus the results of the kinetic analysis can be readily obtained from the previous case by a suitable transformation of variables which is indicated below :

Case (i)	Case (ii)
A	B
B	A
<hr/>	
C	D
D	C
<hr/>	
k_1	k_4
k_2	k_3
k_3	k_2
k_4	k_1
<hr/>	
M_A	M_B
M_B	M_A
S'	S
Q'_0	Q_0

Appendix IV-C

Thus we can transform the results for the transfer coefficients from the previous case (IV-A, equations [34], [35] and [36]) to yield :

$$P_{S'B} = \frac{k_1 + k_3}{\left[(k_1 + k_3)(k_2 + k_4) - k_1 k_4 \right]} M_B \quad [1]$$

$$P_{S'A} = \frac{k_4}{\left[(k_1 + k_3)(k_2 + k_4) - k_1 k_4 \right]} M_A \quad [2]$$

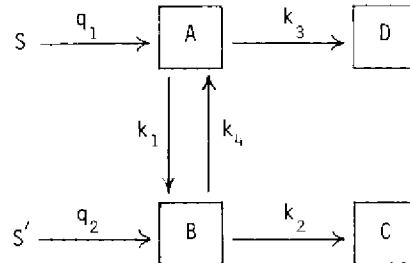
$$P_{AB} = \frac{(k_1 + k_3)}{k_4} \cdot \frac{M_A}{M_B} \quad [3]$$

$$P_{BA} = \frac{k_4}{(k_1 + k_3)} \cdot \frac{M_B}{M_A} \quad [4]$$

Appendix V

Model sequence 5 – steady state analysis – simultaneous releases to two reservoirs

1. System diagram



2. General assumptions

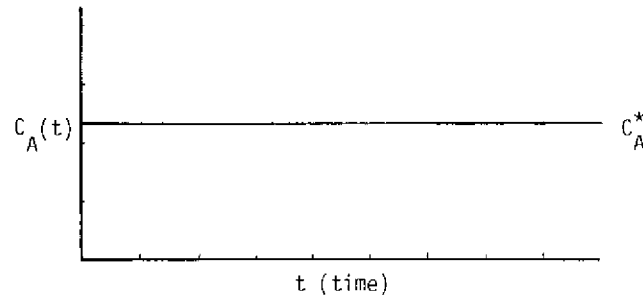
There are two sources of pollutants. S continually inputs to reservoir A at rate q_1 ; S' continually inputs to reservoir B at rate q_2 .

3. Initial conditions

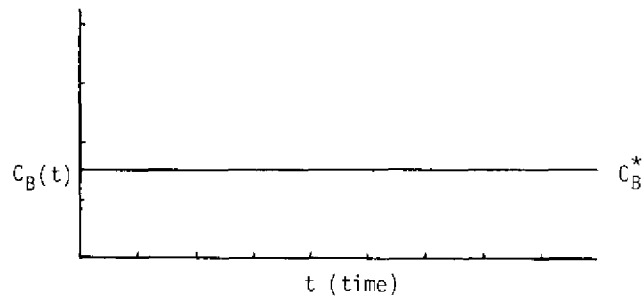
As this case concerns a steady-state situation, the relevant conditions are:

$$\frac{dC_A}{dt} = 0; \quad \frac{dC_B}{dt} = 0$$

4. Graphical description of solutions



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5. **Mass conservation relations** – as for Appendix IV-B except for additional simultaneous input to reservoir B
6. **Relations between parameters and variables** – as for Appendix I
7. **Applications of general relations to the system of interest**

$$\frac{dQ_A}{dt} = q_1 - k_1 Q_A - k_3 Q_A + k_4 Q_B$$

$$\frac{dQ_B}{dt} = q_2 + k_1 Q_A - k_2 Q_B - k_4 Q_B$$

or
$$\frac{dM_A C_A}{dt} = q_1 - (k_1 + k_3) M_A C_A + k_4 M_B C_B$$

and
$$\frac{dM_B C_B}{dt} = q_2 + k_1 M_A C_A - (k_2 + k_4) M_B C_B$$

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$$\frac{dC_A}{dt} = \frac{q_1}{M_A} - (k_1 + k_3)C_A + k_4 C_B \frac{M_B}{M_A} \quad [1]$$

$$\frac{dC_B}{dt} = \frac{q_2}{M_B} - (k_2 + k_4)C_B + k_1 C_A \frac{M_A}{M_B} \quad [2]$$

8. Solution of equations [1] and [2] to obtain steady-state concentrations C_A^* and C_B^*

In the steady state

$$\frac{dC_A}{dt} = 0 \quad \text{and} \quad \frac{dC_B}{dt} = 0$$

i.e.
$$0 = \frac{q_1}{M_A} - (k_1 + k_3)C_A^* + k_4 C_B^* \frac{M_B}{M_A} \quad [3]$$

$$0 = \frac{q_2}{M_B} - (k_2 + k_4)C_B^* + k_1 C_A^* \frac{M_A}{M_B} \quad [4]$$

Substituting from equation [4] for C_B^* into equation [3] we obtain :

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$$\text{or } C_A^* \left[\frac{(k_1 + k_3)}{1} - \frac{k_1 k_4}{(k_2 + k_4)} \right] = \frac{q_1}{M_A} + \frac{k_4 q_2}{(k_2 + k_4) M_A}$$

$$\therefore C_A^* \left[\frac{(k_1 + k_3)(k_2 + k_4) - k_1 k_4}{(k_2 + k_4)} \right] = \frac{1}{M_A} \cdot \frac{(k_2 + k_4) q_1 + k_4 q_2}{k_2 + k_4}$$

$$\therefore C_A^* = \frac{1}{M_A} \left[\frac{(k_2 + k_4) q_1 + k_4 q_2}{(k_1 + k_3)(k_2 + k_4) - k_1 k_4} \right] \quad [5]$$

Substituting this value of C_A^* into equation [4] above,

$$C_B^* = \frac{1}{(k_2 + k_4)} \left[\frac{q_2}{M_B} + \frac{k_1 M_A}{M_B} \cdot \frac{1}{M_A} \left(\frac{(k_2 + k_4) q_1 + k_4 q_2}{(k_1 + k_3)(k_2 + k_4) - k_1 k_4} \right) \right]$$

$$C_B^* = \frac{1}{(k_2 + k_4)} \cdot \frac{1}{M_B} \left[\frac{q_2 (k_1 + k_3)(k_2 + k_4) - q_2 k_1 k_4 + k_1 (k_2 + k_4) q_1 + k_1 k_4 q_2}{(k_1 + k_3)(k_2 + k_4) - k_1 k_4} \right]$$

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$$C_B^* = \frac{1}{M_B} \left[\frac{k_1 q_1 + (k_1 + k_3) q_2}{(k_1 + k_3)(k_2 + k_4) - k_1 k_4} \right] \quad [6]$$

9. Simplification of result by using the ratio of source strengths q_1 and q_2 .

Let $q_1 = Rq_2$

and $\phi = (k_1 + k_3)(k_2 + k_4) - k_1 k_4$

then equation [5] becomes :

$$C_A^* = \frac{1}{M_A} \left[\frac{(k_2 + k_4)Rq_2 + k_4 q_2}{\phi} \right]$$

or

$$C_A^* = \frac{q_2}{M_A} \left[\frac{k_4(1+R) + Rk_2}{\phi} \right] \quad [7]$$

Similarly from equation [6]

$$C_B^* = \frac{1}{M_B} \left[\frac{k_1 Rq_2 + (k_1 + k_3) q_2}{\phi} \right]$$

or

$$C_B^* = \frac{q_2}{M_B} \left[\frac{k_1(1+R) + k_3}{\phi} \right] \quad [8]$$

Let
$$q_T = q_1 + q_2$$

∴
$$q_T = Rq_2 + q_2 = q_2(1+R)$$

i.e.
$$q_2 = \frac{q_T}{(1+R)}$$

Then we can write equations [7] and [8] in the form :

$$C_A^* = \frac{q_T}{M_A(1+R)} \left[\frac{k_4(1+R) + Rk_2}{\phi} \right] \quad [9]$$

$$C_B^* = \frac{q_T}{M_B(1+R)} \left[\frac{k_1(1+R) + k_3}{\phi} \right] \quad [10]$$

10. Computation of total transfer coefficients from C_A^* and C_B^* accounting for all input fluxes (q_1 and q_2)

$$P_{S_T A} = \frac{C_A^*}{q_T} = \left[\frac{k_4(1+R) + Rk_2}{\phi} \right] \frac{1}{M_A(1+R)} \quad [11]$$

$$P_{S_T B} = \frac{C_B^*}{q_T} = \left[\frac{k_1(1+R) + k_3}{\phi} \right] \frac{1}{M_B(1+R)} \quad [12]$$

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$$T_{BA}^P = \frac{C_A^*}{C_B^*} = \frac{P_{S_T A}}{P_{S_T B}} = \left[\frac{k_4(1+R) + Rk_2}{k_1(1+R) + k_3} \right] \frac{M_B}{M_A} \quad [13]$$

$$T_{AB}^P = \frac{C_B^*}{C_A^*} = \frac{P_{S_T B}}{P_{S_T A}} = \left[\frac{k_1(1+R) + k_3}{k_4(1+R) + Rk_2} \right] \frac{M_A}{M_B} \quad [14]$$

Illustration of superposition principle

Equations [11] – [14] above could alternatively have been derived from the results obtained in Appendix IV-A and Appendix IV-C by invoking the superposition principle. This approach is illustrated below in the case of P_{SA} using exposure commitments (E_A, E'_A) and total inputs from sources (Q_0, Q'_0).

From Appendix IV-A, equation [34]

$$P_{SA} = \frac{E_A}{Q_0} = \frac{k_2 + k_4}{\phi} M_A$$

where

$$\phi = (k_1 + k_3)(k_2 + k_4) - k_1 k_4$$

$$E_A = \frac{Q_0(k_2 + k_4)}{\phi} M_A$$

From Appendix IV-C, equation [2]

$$P_{S'A} = \frac{E'_A}{Q'_0} = \frac{k_1}{\phi} M_A$$

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or
$$E'_A = \frac{Q'_0 k_4}{\phi M_A}$$

Thus:
$$E_A + E'_A = \frac{Q_0 (k_2 + k_4)}{\phi M_A} + \frac{Q'_0 k_4}{\phi M_A}$$

But: $R = Q_0/Q'_0$ so that $Q_0 = \frac{R Q_T}{(1+R)}$ and $Q'_0 = \frac{Q_T}{(1+R)}$

where $Q_T = Q_0 + Q'_0$

Therefore:
$$E_A + E'_A = \frac{Q_T}{\phi M_A} \left[\frac{R(k_2 + k_4)}{(1+R)} + \frac{k_4}{(1+R)} \right]$$

$$= \frac{Q_T}{\phi M_A} \left[\frac{k_4(1+R) + Rk_2}{(1+R)} \right]$$

But $P_{S_{TA}} = \frac{E_A + E'_A}{Q_T}$ by definition

Therefore
$$P_{S_{TA}} = \frac{k_4(1+R) + Rk_2}{\left[(k_1 + k_3)(k_2 + k_4) - k_1 k_4 \right] M_A (1+R)}$$

i.e. the same result as equation [11] above.

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This analysis shows how complex multiple source situations can be handled in the commitment framework as a set of situations each of which involves only one system of sources. The overall result is obtained by superposition.

11. Additional analyses: substitution for rate constants and application to the mercury case study

Using the results derived in the main text (p 21)

$$k_1 = \frac{V_d}{h}$$

$$k_2 = \frac{V_L + V_E}{Z} = \frac{V_\psi}{Z}$$

$$k_3 = k_1 = \frac{V_d}{h}$$

$$k_{i_4} = \frac{V_V}{Z}$$

A = continental atmosphere

B = soil

C = freshwater sediments

D = oceanic air

$$\phi = (k_1 + k_3)(k_2 + k_{i_4}) - k_1 k_{i_4}$$

or

$$\phi = \left(\frac{V_d}{h} + \frac{V_d}{h} \right) \left(\frac{V_\psi}{Z} + \frac{V_V}{Z} \right) - \frac{V_d}{h} \frac{V_V}{Z}$$

or

$$\phi = \frac{V_d}{hZ} (2V_\psi + V_V)$$

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∴ substituting into equation [11] we obtain :

$$\begin{aligned}
 P_{S_T A} &= \frac{1}{(1+R)M_A} \left[\frac{\frac{V_V}{Z} (1+R) + R \frac{V_\psi}{Z}}{\frac{V_d}{hZ} (2V_\psi + V_V)} \right] \\
 &= \frac{h}{V_d (1+R)M_A} \left[\frac{V_V (1+R) + R V_\psi}{2V_\psi + V_V} \right] \quad [15]
 \end{aligned}$$

Also substituting into equation [12] we obtain :

$$\begin{aligned}
 P_{S_T B} &= \frac{1}{(1+R)M_B} \left[\frac{\frac{V_d}{h} + \frac{V_d}{h} (1+R)}{\frac{V_d}{hZ} (2V_\psi + V_V)} \right] \\
 &= \frac{Z}{(1+R)M_B} \left[\frac{1 + 1 + R}{2V_\psi + V_V} \right] \\
 &= \frac{Z}{(1+R)M_B} \left[\frac{2 + R}{2V_\psi + V_V} \right] \quad [16]
 \end{aligned}$$

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Substituting into equation [13] we obtain :

$$\begin{aligned}
 T_{BA}^P &= \frac{C_A^*}{C_B^*} = \frac{M_B}{M_A} \left[\frac{\frac{V_v}{Z} (1+R) + R \frac{V_{vs}}{Z}}{\frac{V_d}{h} + \frac{V_{ds}}{h} (1+R)} \right] \\
 &= \frac{M_B}{M_A} \cdot \frac{h}{ZV_d} \left[\frac{V_v + V_v R + V_{vs} R}{1 + 1 + R} \right] \\
 &= \frac{M_B}{M_A} \cdot \frac{h}{ZV_d} \left[\frac{V_v + R(V_v + V_{vs})}{2 + R} \right] \quad [17]
 \end{aligned}$$

We identify A with the continental atmosphere, (ac), and B with soil, (s). The volume of the continental atmosphere is :

$$M_A = \sigma_c \cdot h$$

where σ_c is the area of the continents and h is the height of the atmospheric reservoir. This gives the proper dimensions for concentrations of pollutants in the atmosphere, i.e. amounts per unit volume.

The mass of the soil reservoir is

$$M_B = \sigma_c Z \rho_s$$

where Z is the depth of the soil reservoir and ρ_s is the density of soil. The concentration of pollutants in soil is measured in amounts per unit

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mass of soil. Substituting for M_A in equation [15] we obtain:

$$P_{S_{T^{ac}}} = \frac{1}{(1+R)V_d\sigma_c} \left[\frac{V_v + R(V_v + V_w)}{2V_w + V_v} \right] \quad [18]$$

Substituting for M_B in equation [16] we obtain

$$P_{S_{T^S}} = \frac{1}{(1+R)\sigma_c c_s} \left[\frac{2 + R}{2V_w + V_v} \right] \quad [19]$$

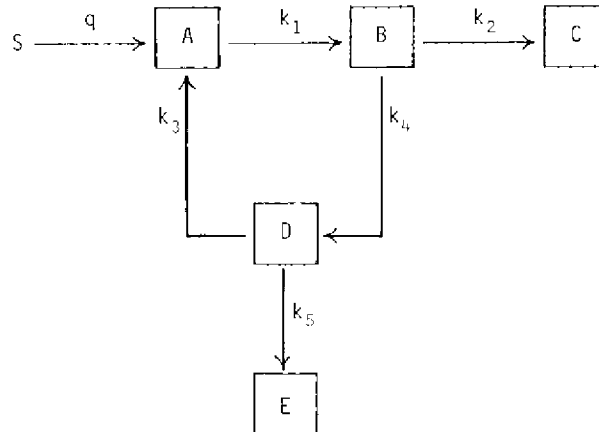
Finally, substituting for M_A and M_B in equation [17] we obtain:

$$\begin{aligned} T_{S,ac}^P &= \frac{\sigma_c Z_{p_s}}{\sigma_c h} \cdot \frac{h}{ZV_d} \left[\frac{V_v + R(V_v + V_w)}{2 + R} \right] \\ &= \frac{\rho_s}{V_d} \left[\frac{V_v + R(V_v + V_w)}{2 + R} \right] \end{aligned} \quad [20]$$

Appendix VI

Model sequence 6 – Steady state analysis

1. System diagram



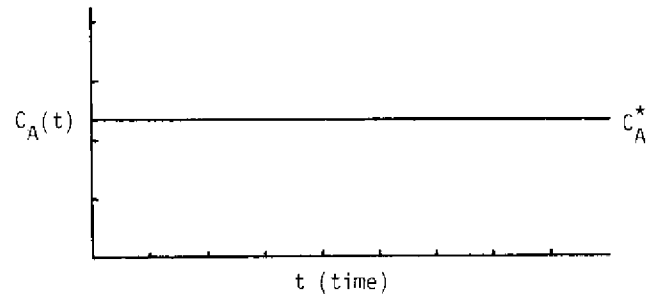
2. General assumptions – as for Appendix I

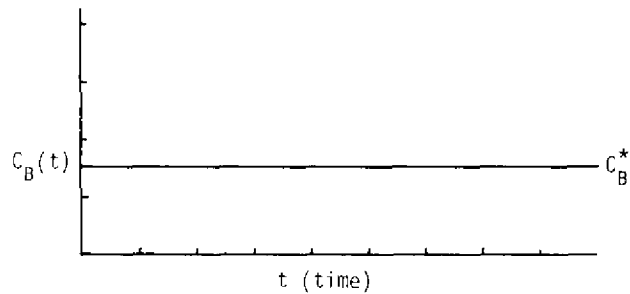
3. Initial conditions

The appropriate conditions for a steady-state situation are:

$$\frac{dC_A}{dt} = 0; \quad \frac{dC_B}{dt} = 0; \quad \frac{dC_C}{dt} = 0; \quad \frac{dC_D}{dt} = 0; \quad \frac{dC_E}{dt} = 0$$

4. Graphical description





5. Mass conservation relations

These are similar to those in other appendices. The recycling loop (B – D – A) means that reservoir A receives an additional input from reservoir D. The flow from D to E means that some of the net flux along the main pathway (A – B – C) is diverted through D to E.

6. Relations between parameters and variables – as for other Appendices.

7. Application of general relations to the system of interest

Flux conservation can be applied to reservoirs A, B and D to yield the following equations:

$$\frac{dQ_A}{dt} = q - k_1 Q_A + k_3 Q_D$$

$$\frac{dQ_B}{dt} = k_1 Q_A - k_2 Q_B - k_4 Q_B$$

$$\frac{dQ_D}{dt} = k_4 Q_B - k_3 Q_D - k_5 Q_D$$

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but since $Q_x = M_x C_x$, we may reorganize these equations into the following forms

$$\frac{dC_A}{dt} = \frac{q}{M_A} - k_1 C_A + k_3 C_D \frac{M_D}{M_A} \quad [1]$$

$$\frac{dC_B}{dt} = k_1 C_A \frac{M_A}{M_B} - k_2 C_B - k_4 C_B \quad [2]$$

$$\frac{dC_D}{dt} = k_4 C_B \frac{M_B}{M_D} - (k_3 + k_5) C_D \quad [3]$$

8. and 9. Solution of equations [1], [2] and [3] for the steady-state concentrations

From section 3 above $\frac{dC_x}{dt} = 0$ where $x = A, B, D$ equations [1] to [3] then become :

$$0 = \frac{q}{M_A} - k_1 C_A^* + k_3 C_D^* \frac{M_D}{M_A} \quad [4]$$

$$0 = k_1 C_A^* \frac{M_A}{M_B} - (k_2 + k_4) C_B^* \quad [5]$$

$$0 = k_4 C_B^* \frac{M_B}{M_D} - (k_3 + k_5) C_D^* \quad [6]$$

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from [4]

$$C_A^* = \left[\frac{q}{M_A} + k_3 C_D^* \frac{M_D}{M_A} \right] \frac{1}{k_1}$$

∴ substituting in [5]

$$k_1 \frac{M_A}{M_B} \cdot \frac{q}{M_A} + k_3 C_D^* \frac{M_D}{M_A} \cdot \frac{1}{k_1} = (k_2 + k_4) C_B^*$$

or

$$(q + k_3 C_D^* M_D) \frac{1}{M_B} = (k_2 + k_4) C_B^*$$

∴

$$C_B^* = \left[(k_2 + k_4) C_B^* - \frac{q}{M_B} \right] \frac{M_B}{k_3 M_D}$$

which on substitution in [6] yields :

$$k_4 C_B^* \frac{M_B}{M_D} = (k_3 + k_5) \left[(k_2 + k_4) C_B^* - \frac{q}{M_B} \right] \frac{M_B}{k_3 M_D}$$

or

$$k_4 C_B^* = \frac{(k_3 + k_5)(k_2 + k_4)}{k_3} C_B^* - (k_3 + k_5) \frac{q}{k_3 M_B}$$

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$$\therefore C_B^* = \left[\frac{(k_3 + k_5)(k_2 + k_4) - k_3 k_4}{k_3} \right] = \frac{(k_3 + k_5)q}{k_3 M_B}$$

$$\therefore C_B^* = \frac{(k_3 + k_5)}{\left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right]} \cdot \frac{q}{M_B} \quad [7]$$

Hence:

$$\begin{aligned} C_D^* &= \frac{(k_2 + k_4)M_B}{k_3 M_D} \left[\frac{(k_3 + k_5)}{\left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right]} \cdot \frac{q}{M_B} \right] - \frac{q}{k_3 M_D} \\ &= \frac{q}{k_3 M_D} \left[\frac{(k_2 + k_4)(k_3 + k_5) - (k_3 + k_5)(k_2 + k_4) + k_3 k_4}{(k_3 + k_5)(k_2 + k_4) - k_3 k_4} \right] \end{aligned}$$

$$= \frac{q}{k_3 M_D} \left[\frac{k_3 k_4}{(k_3 + k_5)(k_2 + k_4) - k_3 k_4} \right]$$

$$C_D^* = \frac{k_4}{\left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right]} \cdot \frac{q}{M_D} \quad [8]$$

and

$$\begin{aligned}
 C_A^* &= \frac{q}{k_1 M_A} + \frac{k_3 M_D}{k_1 M_A} \cdot \frac{k_4}{\left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right]} \cdot \frac{q}{M_D} \\
 &= \frac{q}{M_A} \left[\frac{(k_3 + k_5)(k_2 + k_4) - k_3 k_4 + k_3 k_4}{k_1 \left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right]} \right] \\
 C_A^* &= \frac{(k_3 + k_5)(k_2 + k_4)}{k_1 \left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right]} \cdot \frac{q}{M_A} \quad [9]
 \end{aligned}$$

10. Computation of transfer coefficients

$$P_{SA} = \frac{C_A^*}{q} = \frac{(k_3 + k_5)(k_2 + k_4)}{k_1 \left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right] M_A} \quad [10]$$

$$P_{AB} = \frac{C_B^*}{C_A^*} = \frac{k_1 M_A}{(k_2 + k_4) M_B} \quad [11]$$

$$P_{SB} = \frac{C_B^*}{q} = \frac{(k_3 + k_5)}{\left[(k_3 + k_5)(k_2 + k_4) - k_3 k_4 \right] M_B} \quad [12]$$

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