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Modeling Exposure Routes to Man of Trace Metals Associated with Acid Precipitation

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Pollutant metals released to the environment disperse and interact in various ways before arriving at sensitive receptors. Modeling of pollutant behavior may be by time-dependent or time-independent means. The time-independent, exposure commitment method requires a less extensive data base and can begin with general associations between environmental concentrations or fluxes. Such assessments for representative background conditions have been performed for most of the metals associated with acid precipitation. Examples are given here for cadmium and mercury. These overviews are only the beginning stage of relating pollutant releases to environmental effects.

Introduction

Metals are released to the environment from both natural and anthropogenic sources. Wind-blown dusts and volcanoes are important natural sources of metals. Industrial processing of metals and various combustion processes are major anthropogenic sources. The sources may be to air, as the above examples, or the releases may be to water in industrial liquid effluents or to soil in waste dumps or in sludge and fertilizer applications.

In addition to these direct discharges, secondary sources may be considered to arise from increased availability of metals already present in the environment. This occurs from altered environmental conditions. Particularly in the context of the present discussions, increased acidity of soils and waters from acid deposition affects mobility and availability of metals to organisms and to man.

Metals associated with acid deposition include mercury, with enhanced release from sediments in acidic lakes and increased uptake by fish, and aluminum which, from a greater rate of leaching from soils, has been implicated in toxic effects in trees and fish. Other metals which may have enhanced uptake from slightly increased acidic environments or greater leaching to runoff or to groundwater include cadmium, copper, lead, manganese, nickel, vanadium, zinc, and the metalloids arsenic and selenium. The predominant route of transfer of metals to man is via ingestion of foods or drinking water. Some additional transfer may occur from dusts on hands or from contact with processing or delivery materials (e.g., water pipes). Inhalation of particulates in air is an additional route of entry, but this is generally of relatively less importance.

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Modeling of exposure routes implies the formulation of a simplified arrangement of system components and the expression of relationships between concentrations and exposures in the environment and in the receptor. There are two basic approaches to modeling. One may use either a time-dependent or a time-independent method. The method of choice is determined by the underlying data base.

A critical point in modeling is the assignment of model parameters. For this, reliance is placed on measurements. There are obvious difficulties if these have not been made under the conditions of interest. There are always limitations but, if models can provide even relatively broad connections between environmental components, there is a basis for increasing detail and understanding at later stages.

Time-Dependent Modeling

If sufficient information is available on the distribution and rates of transfer of a pollutant in the environment, a time-dependent model may be formulated. This gives the most complete description of environmental behavior. The pollutant amounts are specified at each location of interest and at each moment of time.

The time-dependent or kinetic model requires a complete and accurate formulation of transfer pathways. Generally, first-order, linear kinetics are assumed. In each instance, a constant fractional portion of a compartment's contents is transferred to subsequent compartments in the pathway chain. This is expressed as

$$dA/dt = -kA$$

where A is the pollutant amount in a defined environmental region (e.g., in air or in surface soil). The amount may be estimated from measurements of the concen-

tration of the pollutant in the medium and from estimates of the volume or mass of the compartment. The constant of proportionality k, the rate constant, may be estimated from the ratio of output rate to instantaneous amount. The reciprocal of the rate constant is the mean residence time.

In practice, one must distinguish the various separate inputs and outputs to and from each compartment and to each of the various other compartments which define the transfer pathways. The rate of change of the pollutant contents of a compartment is the sum for inputs or difference for outputs of rate constants times the relevant compartment contents. A series of differential equations is formed to describe the system dynamics. The equations are generally too complicated for direct solutions, but system analysis procedures may be used. An example of kinetic modeling to help design and interpret multimedia monitoring projects was recently published by Wiersma et al. (*1*). Of course, there are many other illustrations of the applications of this method.

It is important that the model of the environmental system be correctly formulated. If important pathways are omitted, the values inferred for the other rate constants will be compensating, and although observed values may be matched, the solution gives a false balance which may be inappropriate in further applications to varied sets of conditions. The time-dependent method must be supported by an extensive and complete data base.

Time-Independent Modeling

The alternative approach to pollutant modeling is the time-independent method. In this case, expressions are given of the partitioning of pathway transfer and of the amounts of pollutant which reach compartments of interest. The method is particularly convenient in steady-state conditions, when concentrations in various media maintain fixed ratios. The ratios are called concentration factors and the assessment method is called the concentration factor method. A wider application of the time-dependent method involving cumulative transfer per unit input is called the exposure commitment method.

Exposure is defined here as the time integral of concentration in an environmental compartment. This combination of concentration and duration of presence is a useful expression in pathway assessments. When the time integral is for the entire period of duration from a specified release of the pollutant, the expression is termed the exposure commitment.

Exposure and exposure commitment have units of concentration times time (e.g., μg-yr/m^3). Multiplying the initial concentration of a pollutant in a compartment by the mean residence time evaluates the exposure commitment. This follows from first-order kinetics. The amount (concentration) present in the compartment at any one time is the initial amount (concentration) times the exponential function. The infinite time integral of the exponential function is the reciprocal of the rate constant which is, in fact, the mean residence time:

$$\int_0^\infty e^{-kt} = 1/k = \overline{T}$$

Ratios of exposure commitments to pathway compartments have the same numerical value as the ratio of steady-rate concentrations. An exposure commitment may be seen as the cumulative effect (concentration-days) from a single release (i.e., μg-day/g per gram released). The steady-state concentration is the cumulative effect at a single time of the residual effects (remaining amounts) of all previous releases (e.g., μg/g per g/day continuing releases). This may be demonstrated in diagrams (*2,3*). The main point is that in associating steady-state fluxes with concentrations (x μg/day giving y μg/g in medium of interest), as is the usual approach, one can immediately say what the effect of increased release will be (i.e., y μg-day/g additional exposure for each x μg released; at re-established equilibrium there will be ny μg/g concentration in the medium of interest from nx μg/day continued release).

The general expression "transfer factor" may be used for the various ratios evaluated in the time-independent modeling method. The ratios may involve steady-state concentrations or fluxes, cumulative transfers, exposure commitments. Many frequently used concepts in pollutant assessment, such as the deposition velocity, concentration factor, fractional absorption, are ratios of time-dependent or integral quantities and are thus transfer factors in the general sense.

Exposure Commitment Assessments

It can be easily recognized that the release of a pollutant to the environment commits exposure to a receptor at some future time and perhaps over prolonged periods. The evaluation of the exposure in terms of cumulative transfer or expressed as a new equilibrium concentration if the releases continue is the exposure commitment or time-integrated method. There is no question of the validity of the method. That would be the same as questioning the ability of the environment to know how to disperse a pollutant released into it. It is necessary only to make proper observations and to make relevant associations. Concentrations and fluxes will not be related except at steady-state and in direct pathway chains.

It would be hoped that observed associations (i.e., defined transfer factors) would be somewhat generalizable. This may be so, but widely different conditions (e.g., soil type, fish species, acidity level) will require different values of the transfer factor.

The exposure commitment assessment method has been applied to a series of metals which are generally encountered pollutants. The results have been published in a series of MARC reports entitled "Exposure

Table 1. Exposure commitment assessments.

Pollutant	Reference[a]
PB, Cd, As	Vol. 1 No. 1 (1981)
Hg, Ni, Sn	Vol. 1 No. 2 (1981)
PCBs, Se, Cr	Vol. 2 (1982)
Cu, V, Sb	Vol. 3 (1983)
PAH, Zn, Al	Vol. 4 (1985)

[a] MARC Reports (*4–7*).

Commitment Assessments of Environmental Pollutants" (*4–7*). The metals as well as a few organic compounds thus far considered are listed in Table 1. The representative background values are suggested, and comparisons of exposure pathways are made. The endpoint receptor in these examples is man; however, the procedure would be similar for other organisms of interest.

The results of "representative" evaluations will be of interest, but the specially altered conditions caused by acid precipitation require that new values be assigned to transfer factors. Enhanced mobility and uptake may be expected, but important interaction effects must also be taken into account. The general procedures are valid, however, of relating concentrations or fluxes at steady-state to define transfer factors for specified conditions.

Environmental Cadmium

Only few examples may be given here of pollutant assessments. For cadmium, the general relationships along the ingestion pathway may be expressed as follows:

$$\overset{\text{Air}}{1\ \text{ng/m}^3} \rightarrow \overset{\text{Soil}}{0.2\ \mu\text{g/g}} \rightarrow \overset{\text{Diet}}{15\ \mu\text{g/day}} \rightarrow \overset{\text{Kidneys}}{9\ \mu\text{g/g}}$$

These values have been selected from a wider review of measurements reported for unpolluted background conditions (*4*). Combinations of parameters may be introduced to make more quantitative associations between corresponding values.

Cadmium in air is deposited on soil by wet and dry deposition processes. A representative value of the total deposition velocity for ambient aerosols to which cadmium and other metals are attached is 0.5 cm/sec (1.6×10^{-5} m/yr). From a concentration of cadmium in air of 1 ng/m^3, the deposition rate to soil is 160 μg/m^2-yr. For assumed mixing to a depth of 20 cm (the plough layer), the concentration in soil is increased by 60×10^{-5} μg/g per year:

$$\frac{160\ \mu\text{g/m}^2\text{-yr}}{20\ \text{cm} \times 1.4\ \text{g/cm}^3} \times 10^{-4}\ \text{m}^2/\text{cm}^2 = 60 \times 10^{-5}\ \mu\text{g/g-yr}$$

A soil density of 1.4 g/cm^3 has been assumed.

To maintain the background concentration of cadmium in soil at the equilibrium level of 0.2 μg/g, balancing removal by leaching or other removal processes, a mean retention time of cadmium in soil of 300 years is inferred.

$$60 \times 10^{-5}\ \mu\text{g/g-yr} \times 300\ \text{yr} = 0.2\ \mu\text{g/g}$$

The various parameters may be adjusted over perhaps considerable ranges, depending on the specific local conditions. The values selected are only a first approximation to associate air and soil cadmium concentrations in a reasonable way.

The association between soil and diet (terrestrial foods) reflects only very broad observations of typical background soil levels and dietary intake. This could be made specific for particular soil conditions and a particular food if required and if data are available.

The further association between dietary intake and concentrations of cadmium in kidneys (cortex) assumes gastrointestinal absorption of 5%, distribution to kidneys of 30% of the body content, mean residence time in the kidneys of about 25 years, and mass of kidney cortex of approximately 220 g. Some of these factors are the same as the cadmium metabolic model of Kjellström and Nordberg (*8*). The mass of the kidney cortex has been taken to be 70% of the 310 g total kidney mass (*9*). The calculations is as follows:

$$15\ \mu\text{g/day} \times 0.05\ \mu\text{g/}\mu\text{g} \times 0.3\ \mu\text{g/}\mu\text{g} \times 25\ \text{yr}/220\ \text{g}\ (365\ \text{day/yr}) = 9\ \mu\text{g/g}$$

For comparison, the contribution to exposure from inhalation of cadmium may also be evaluated. Estimates are available for the breathing rate (15 m^3/day) and the fractional retention in the lungs of ambient aerosols and absorption to the blood (of the order of 25% of the intake amount). The distribution to kidneys and retention is as mentioned above. The result is:

$$1\ \text{ng/m}^3 \times 15\ \text{m}^3/\text{day} \times 0.25\ \text{ng/ng} \times 0.3\ \text{ng/ng} \times 25\ \text{yr}/220\ \text{g}\ (365\ \text{day/yr}) = 50\ \text{ng/g}$$

From these general considerations, it is seen that inhalation of cadmium is less important by over two orders of magnitude than ingestion of cadmium in diet originating from cadmium in air. Additional direct sources of cadmium to soil via fertilizer applications increase the cadmium levels in soil and can increase dietary intake, possibly in a significant way, and this should also be considered. With the long residence time of cadmium in soil, altered inputs are reflected in new equilibrium levels only after very long time periods.

Environmental Mercury

For mercury, similar relationships could be formulated for important pathways, e.g., air → deposition → run-off → lakes → fish → man (*10*). The chain may be initiated at any point at which information is available. For example, new conditions of acidity in a lake may

call for a revised estimate of mercury concentrations in the water. This in turn will affect the eventual mercury levels in fish. It is often the case that fish are sampled directly. They are easily obtained and show directly the cumulative effect of interacting factors. To understand the chain of events, however, attempts must be made to formulate the relationships along the complete chains of transfer.

Once the associations are made between representative concentrations or fluxes (e.g., air → lake water → fish) for stable background conditions, these may be scaled up or down to determine the relationships for new values (e.g., higher concentrations of mercury in air). This cannot be taken too far, as other determining factors are likely to be changing as well.

It may at times be necessary to make relatively wide associations in the pathways, overstepping intermediate considerations if information is not available. For example, it may be noted that the background concentration of mercury in continental air is 4 ng/m^3 (*11*), and the concentration in fish in a fresh water lake is 0.5 μg/g. If it can be assumed that mercury in air (primarily in inorganic form) is an important determining factor for mercury in fish (primarily in organic form), then any increase in the air concentration would be expected to increase deposition, lake water concentrations and, ultimately, the mercury concentrations in the fish in a similar proportion.

While the procedure of associating background concentrations, i.e., defining transfer factors, is straightforward, it is, of course, essential that the associaton is relevant and that the effect is directly transferable to the end compartment of interest.

These general observations may give some guidance, but more extensive data from local areas are required to allow more theoretical relationships to be formulated and understanding to be obtained of the mechanisms which are responsible for the observed or anticipated environmental effects of pollutant releases.

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