CHAPTER 4

Models for Total Transport

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4.1. GENERAL

This chapter deals with the problem of setting up a quantitative and predictive mathematical model for pollutant distribution. It will be based on information of the type discussed in the previous chapters and should make possible the dose calculations described in the chapter to follow.

First, let us make clear that we mean to address the broad question of how a pollutant is partitioned in various parts of the environment, how this partition changes with time, and how the pollutant may be converted to different chemical forms as part of the process. When we use the word distribution we imply a description involving all these facets.

It seems (Goodall, 1974)* that there are four principal factors that must be considered. While they are all interrelated, we can try to separate them for simplicity. The first is geographical; different pollutants are typically transported over different distances, and local, regional, and global movements usually involve different combinations of transport mechanisms.

^{*}There are many references describing the process of modelling in an ecological context; for general treatments see Jeffers (1972), Smith (1974), or Waide and Webster (1976). References dealing with pollutant transport in general terms are rather fewer, although the field is well developed for radionuclide transport and gross pollution of potentially potable water supplies (for review see Argentisi *et al.*, 1973; for the most recent general treatment see Holcomb Research Institute, 1976). Most other references cited in this chapter deal specifically with pollutant movement.

The second is time scale. It is clear that movement of a pollutant over a time scale of years is quite different from that over a scale of minutes or hours; also it involves different distance scales. In fact, distances and time are so interrelated that they need to be discussed together (Goodall, 1974), as they are in what follows.

The third important thing to be described is distribution of a pollutant among trophic levels and species (Goodman, 1974). Much work has been devoted to this subject; if a certain amount of aggregation is permitted, a reasonable description can often be put together on the basis of information on uptake of pollutants by individual species, accumulation in the different trophic levels and so forth. Much of the material presented later in this volume relates to this step.

The fourth aspect is the chemical form of the pollutant. This aspect is all-pervasive, and strongly influences the other three (Wood, 1974). A dominant consideration is that the chemical form may change in various ways during movement of the pollutant, both by physical mechanisms, particularly in the atmosphere, and in association with biota, by various processes of biotransformation and biodegradation. Thus this aspect has profound importance both for mechanisms of transport and for influence on uptake, retention, and toxicity in biota. These have been the main subjects addressed in the preceding two chapters; our approach here is not to duplicate what has been said, but only to restate some of it in the form most suitable for use in the discussion of model formulation to follow.

Before we proceed, we should admit that any such approach is bound to be a simplification. This, of course, is true of any scientific approach; no experimental or theoretical analysis ever includes every possible interaction between elements of the system (Rapoport, 1972). As applied to this discussion, it means that not every possible interaction can be included in the models presented. The whole idea of modelling involves identification not of every possible pathway but only of those that account for the largest part of the phenomena observed (Smith, 1974). The reader will undoubtedly notice that some interconnections have been omitted; it should not be assumed that they have been forgotten or ignored.

Connected with this point is another aspect, or purpose, of mathematical models, namely their use in identifying pathways for which our understanding is relatively imprecise (relative, that is, to their importance in the system) as well as those which, although they may be biologically or chemically interesting, are not worthy of further refinement for the quantitative study of pollutant transfer under consideration. Indeed, it may well be said that at the present stage of development of the modelling art, the main advantage of formulating a mathematical model is not the making of precise predictions of the future state of the system. Rather, the value lies in the very exercise of stating precisely how much is really known about each pathway, and in the possibility of allocating future research effort in such a way as to contribute most effectively to quantitative knowledge of the overall behaviour of the system (Miller *et al.*, 1976).

4.2. GEOGRAPHICAL TRANSPORT

The continuum of distances over which a pollutant can be transported is traditionally, if somewhat arbitrarily, divided into levels such as local, regional, and global. By these we mean, respectively, distances of a few kilometres, of a hundred to perhaps a thousand kilometres, and of many thousands of kilometres. In most cases, geographical transport by physical factors greatly dominates that due to movement of or by biota (Bolin, 1976). Atmospheric transport is involved in all three, but with different time scales: minutes for local, hours to days for regional, and many weeks or more for global distribution. General oceanic circulation may be significant for global transport, but only over a time scale of years (Wollast et al., 1974). Transport by water (rivers) can be important for regional distribution, while surface run-off and subsurface water must sometimes be considered for local pollutant distribution (transport of dust by air, or of sediment by water, is considered to be included). It should be specifically mentioned that although a general mixing and dilution occurs in most cases, there can also be situations involving surprisingly little general dispersion or dilution. Atmospheric transport may be confined to a relatively narrow plume immediately downwind of a source (e.g. Kao, 1974); even in oceans or large lakes, pollutants may remain in the top few metres of water for some time, taking many years before mixing is truly complete (Robinson, 1973). Another complicating factor is that each of these processes may occur several times, such as when dust is resuspended by wind or when sediment is moved downstream in a river by successive spring floods.

It is true that each particular mode of movement is a part of the overall global circulation of a pollutant. However, movement on scales of different time and distance may often be thought of as essentially decoupled. The study of transport of a chemical in a river, for example, will typically require that exchange to and from the atmosphere be considered; this does not, however, require that global atmospheric movement be considered simultaneously, for a particular river will contribute negligible amounts to the atmosphere, and the latter can be considered a fixed reservoir of large size for the purpose of studying the river (Bolin, 1976).

Concerning actual transport rates, approaches differ for each class of problem. Predicting airborne transport at local distances depends very much on having information on vertical structure of the atmosphere as well as current wind conditions. The techniques of Pasquill (1974) and others are quite well developed for this sort of problem, and one variant or another of this approach is in wide use today.

For regional atmospheric transport, these methods fail since the weather pattern itself will typically change in a time comparable to that taken by the pollutant to travel a few hundred kilometres, and knowledge of wind conditions at the source provides an inadequate basis. Here, one must use either the as-yet-underdeveloped general circulation models, or trust to the simpler but justly criticized approach of

Trajectory Analysis, which also requires more detailed wind and weather data than are easily accessible (Nordo *et al.*, 1974). Global transport may be even more difficult, and only general large-scale mixing and transfer rates are normally used (Bolin, 1976).

Transfer from atmosphere to ground level is by absorption into, or adsorption onto, ground-based substances, or by wet or dry deposition. Rates at which these take place are moderately well understood when airborne pollutants are attached to large particles which settle out rapidly (dry deposition), in which case one can speak of deposition velocities estimated on the basis of laboratory and field experiments. For removal from the atmosphere by rain or snow, less is known, but some guidelines are available; one needs to estimate the fraction of the pollutant contained in the air column up to the height at which the precipitation forms, and to use a fractional clearance factor based on the degree of precipitation (Slade, 1968). Some substances, such as radioactive noble gases, may be assumed to be uniformly mixed so that concentrations may be calculated directly. (In all these estimates, many further details must be considered, such as the fact that pollutants do not normally rise above the tropopause in local- or regional-scale problems; see Slade, 1968; Nordo *et al.*, 1974; Pasquill, 1974.)

Movements in the reverse direction, i.e. movements into the atmosphere by resuspension, volatilization, etc., are much less well understood. At this time, few generalizations are available and the phenomena must be investigated separately for each pollutant examined.

Transport by water (normally fresh water) over local and regional distances, has been extensively studied. Generally, polluting materials will dissolve (phosphates, oxides of sulphur) or be attached to particulates (heavy metals, water-insoluble hydrocarbons) (Goodman, 1974). In the latter case, transport is determined by the behaviour of the particulates in the water itself, and the characteristics of the river will determine whether the pollutants move only during movement of bed sediment, or whether a significant amount is bound to particles small enough to remain in suspension. Typically, most of the pollutant is at any time bound to larger bed sediment particles, but the suspended materials account for most of the transport (De Groot and Allersma, 1975).

When a pollutant comes into contact with ground or water, most of it adsorbs or binds chemically to soil or sediment particles. Here, complicated chemical and biological reactions may take place which again have been the subject of large amounts of research but permit few generalizations (Wood, 1974). Typically, the soil or sediment constitutes a large reservoir of relatively unavailable polluting material, while chemical equilibria or biologically mediated transformations keep small but significant amounts available for transport or uptake by biota; particularly for heavy metals, these amounts may be in much more toxic chemical forms (Krenkel, 1973).

In general, then, pathways are many and varied. Each of the mechanisms

mentioned is under active study by many scientists, whose work we clearly cannot hope to summarize in the space available. However, once a particular pollutant release is identified for consideration, it becomes clear that only a few of the pathways are important. We hope to illustrate this with the examples to follow.

4.3. TROPHIC-LEVEL AND SPECIES DISTRIBUTION

There is no end to the discussion about subdividing an ecosystem into compartments. Many biologists point out (correctly!) that inter-species, inter-age, and inter-sex differences are great and that there is no possibility of discussing how 'an invertebrate', for example, processes or reacts to any given substance. Nonetheless, the concept of energy, mass, and nutrient transfer between trophic levels in an ecosystem has proved extremely useful in many studies, and can certainly be applied to pollutant transfer problems (Rigler, 1975). Furthermore, the alternative of studying all species in sufficient detail to be able to predict their responses to a given pollutant is simply not practicable and we are forced to imagine the ecosystem as subdivided into rather large and internally heterogeneous compartments, and to describe each in overall terms only.

One saving feature of this approach is that the individual scientist can frequently add to the information about a compartment by using his own more detailed understanding of it. Thus, for example, if in an aquatic ecosystem it were known that the average concentration of a particular heavy metal in fish was of a certain value, the biologist would typically expect this concentration to be higher in larger and in older fish, and certainly higher in piscivorous species (Bligh, 1971).

The greatest advantage of the trophic-level approach is that pollutants typically move from one species to another, either through the environment or along the food chain, and the latter is precisely what the energy and nutrient cycling studies are concerned with. If one knows the food intake and gut absorption, as well as the body retention function for that particular combination of animal and pollutant, then the resulting body levels can be calculated (Fagerstrom and Asell, 1973).

It is here that we encounter again the importance of the chemical form of the pollutant since absorption, retention, and toxicity (not to mention solubility and other physical variables) change as a pollutant takes different chemical forms (Goodman, 1974). This happens, for example, when a heavy metal is changed from inorganic to organic form or the reverse.

Because of these features of the problem, it may be necessary either to restrict one's consideration to the form of the substance that is most toxic, or to consider simultaneously several 'superimposed' diagrams of the system, one for each chemical form, with interconnections at (and only at) those points where chemical conversion may take place (see the example of mercury, below). The rate of transfer due to chemical change, especially in respect of biologically mediated transformations but to a lesser extent in those governed by chemical equilibria,

remains one of the areas of greatest ignorance. Nonetheless, such transfer must be quantified since we need to know the total toxicity of the forms present, not just the amount of the substance, if ecotoxicity is to be made a subject of prediction and precise analysis (Truhaut, 1974).

4.4. MODEL CONSTRUCTION: GENERAL

To the word 'model' different writers attach quite different meanings, sometimes with unfavourable connotations. Let us begin, therefore, by saying that we do not use the word to describe something different from or unrelated to the actual ecosystem under study. To us, a 'model' is simply a quantitative summary statement of what is known about the important processes going on in the system. It can be no more elaborate than knowledge of the various real processes permits – failure to accept this limitation has caused difficulties for many modellers – but it can provide quantitative information that intuition could not (Holcomb, 1976).

There are still many types of models, and for the present purposes we choose to identify three (Smith, 1974). To begin with, one can talk about simple calculations designed to elucidate, for example, the relation between biomasses and energy transfers or perhaps to point out how simple the bioaccumulation of a pollutant really is. It is this type of mathematics that the field biologist or other scientist understands most easily, and the kind that is generally taken most seriously.

A second type of model involves overall balances of inputs and outputs of a given substance to and from a system (Odum, 1971). While not designed to predict future history or to address mechanisms by which pollutants move, this type is critical for an understanding of the relative importance of different pathways, and the exercise of producing the appropriate numerical estimates sometimes leads to the realization that what had previously been regarded as a dominant pathway is not the most important at all. This sort of formulation has the added advantage of helping to identify mechanisms for which understanding is lacking, and focuses our attention on pathways that merit closer attention and further research (Fagerstrom and Asell, 1973).

A third and quite different kind of 'model' is one that might conceivably be used where no idea of overall performance is available, and is designed to simulate future history in a descriptive and predictive way, rather than to expose the simplicity of its structure or its overall balance. This type of 'model' has many good and bad (mainly bad) characteristics: it is not accessible to people most competent to criticize its reality; a cumbersome process of computer programming is required before its predictions can begin to be examined; and its verification and validation require techniques for which the basic methodology, not to mention general confidence in them, has not been developed (Mar, 1974). Nonetheless, it is the only type that can provide information totally inaccessible by intuitive approaches (Robinson, 1973).

So far, in using the word 'model' we have been referring to the third type. This is deliberate; highly simplified calculations will never have sufficient predictive value, reliability or subtlety to support the complex decisions involved in setting environmental standards. However, it might help if an example or two of the simpler concepts were given before the more complicated one is attacked.

Consider a substance that passes unchanged through several predator-prey interactions, and for which retention in the body of the predator is rather long. Specifically, assume that each day a predator, with body weight b_1 , eats a_1 g of prey which contains a concentration x_0 of pollutant. Assume further that the predator absorbs a fraction f_1 of the pollutant taken in, and clears it at a fractional rate per day of k_1 . Then the equilibrium concentration of pollutant in the body of the predator will be

$$x_1 = \frac{a_1 f_1}{b_1 k_1} x_0$$

If this predator is a prey for some higher organism, then the equilibrium level for pollutant in its flesh will be in turn

$$x_2 = \frac{a_2 f_2}{b_2 k_2} \frac{a_1 f_1}{b_1 k_1} x_0$$

and this may be repeated several more times. Since the k_i are typically small (k = 0.01 for a biological half-life of 70 days), a many-fold magnification can take place at each level.

It is perhaps worth saying explicitly that this is the end of the example; the calculations are meant to clarify the mechanism rather than to predict future history.

Sometimes mechanisms can be greatly clarified on the basis of simple calculations. As an example of this, consider the situation with the highly toxic monomethylmercury, as opposed to less toxic inorganic mercury compounds, and the observation that the fraction of mercury in the organic form increases sharply as it moves up the food chain, independent of the total mercury concentration. Typical values for mercury in the organic form (Miller, 1977) are the following:

invertebrates	25-30%
fish	65-75%
fish (piscivorous)	85-95%

The suggestion has often been made, based largely on these numbers, that fish must be able to convert inorganic mercury to the organic form.

However, organic mercury is much more efficiently absorbed through the intestine; experiments demonstrate that perhaps 95% of organic mercury is

absorbed, compared to perhaps 15% for the inorganic form (de Freitas, 1977). Suppose that the ratio of organic to inorganic mercury in invertebrates is 3:7 (i.e. 30% organic, 70% inorganic), then the corresponding ratio for the mercury actually absorbed by their predator is

$$\frac{3}{7} \times \frac{0.95}{0.15} = 2.7$$

which is equivalent to 73% organic. A second trophic level increases this to a ratio of 17: 1, or a percentage of 94% organic. These are close enough to observed values to make it clear not only that we do not need to postulate a methylating mechanism, but that in fact if such a mechanism were present, we would be hard pressed to explain why levels of organic mercury are not even higher. (In fact, the fraction in organic form is higher than this, since inorganic mercury undergoes faster clearance.)

Many other examples could be given, each describing a single mechanism, generally a simple one, by which one can explain most or all of some observations on a system. Such examples are satisfying; however this situation is not what one encounters in environmental questions. The ecotoxicologist is forced to consider the problem of describing many interacting processes. Naturally, we lose the ready appeal and clarity of simple models, and must proceed cautiously; however we may not avoid a problem or a solution simply because it is complex.

The next section deals with the overall cycling or movement of a pollutant, using mercury as an example.

4.5. COMPARTMENT MODELS

One begins by dividing the ecosystem into a collection of separate (mutually exclusive) compartments, generally numbering around 10 or fewer (Smith, 1974). This leads, admittedly, to a very rough description, but the larger the number of compartments the more interactions must be investigated; in fact the number of interactions increases roughly with the square of the number of compartments (Miller, 1977). One must make some sort of trade-off between a model so simple that it can provide no answers, and one so complex that more interactions are involved than one can possibly quantify.* Probably this figure of 10 is fairly close to the optimum at present, although more complex models are feasible where research resources are plentiful (Patten, 1971).

For each compartment one identifies a small number of key quantities adequate to describe it. Examples are total amount of pollutant it contains, and total mass or biomass (or energy or carbon equivalent). Normally these are regarded as varying in

^{*}There does exist a school of thought which holds that these constraints can never be satisfied together, and any model simple enough to calibrate will be too simple to be meaningful. The author does not subscribe to this point of view but cannot disprove it.

time, with steady-state values considered as a special (simplified) case. Procedures for working with a time-dependent model are important.

One must always bear in mind that the describing variables (often called State Variables) chosen at this point represent everything that the model will ever be able to tell the user about the system; it is at this stage, not later, that one must decide on the level of detail of the questions that the model will be expected to answer. Thus, for example, if only total biomass is considered for some compartment, it is not meaningful to ask later whether shifts in age or species distribution might or might not be predicted by the mathematical formulation.

Since each of these variables changes over time, one must describe how their values are to be calculated, normally as a time-dependent differential equation. If the variables represent quantities that are conserved, e.g. persistent chemicals, or mass or energy, then any change in a compartmental level must be explained by input from or output to interconnected compartments. In these other compartments, one also knows the level of the same substance, and it is only a matter of choosing an appropriate form for the 'rate equation' and numerical value for the 'rate constant' (as well as deciding how the rate constant is to be assumed to vary with time, weather, temperature, and a variety of other physical and chemical factors).

In many cases, it is reasonable to assume that the rate of transfer of material out of some compartment is proportional to the instantaneous amount present (a constant death rate, for example, or a radioactive decay). Then, one can write the governing equations in the form often referred to as 'first-order kinetics' or, more simply, as a linear equation. In the (very unlikely) case in which it was reasonable to approximate *all* such interactions with linear terms, one would have a fully linear system; the mathematical properties of such systems have been extensively investigated. Indeed, some workers deliberately choose a fully linear formulation, not because they are convinced that it properly describes all interactions, but because the added analytical power of a linear model may make up for some inaccuracies (Waide and Webster, 1976).

In general, there are compelling reasons for believing that not all interactions can be described by linear terms, and some non-linear expressions will generally be incorporated in the system model (Burns, 1975). In principle, this does not alter the ability of a reasonably sized computer to predict the future from the model. It does, however, make life difficult for the analyst or theoretician who wishes to make generalizations about model behaviour and its response to disturbances.

We should insert a comment about the relative difficulty of the various steps in model formulation, namely the comment that the mathematics is not the problem. Complex formulations involving sophisticated mathematical notation abound; what is missing in most cases is a rational consideration of what forms the various interactions may take and, even more important, estimates of the numerical value of the rate constants and how they vary with environmental conditions. Since it is immediately clear that these questions can occupy years of effort for each

interaction, it follows that any formulation requiring the determination of many such coefficients is unlikely to be implemented or to yield useful results (Holcomb Research Institute, 1976).

4.6. AN EXAMPLE: MERCURY IN WATER

The basic qualitative information about mercury behaviour in water has been known for some time (Goldwater, 1972). Generally, mercury enters a river in a moderately harmful chemical form, sinks, and resides in the sediments for lengthy periods. For the most part, what geographical transport does take place is desorption into the water column coupled with some movement of the sediment itself (Krenkel, 1973).

The hazard resulting from sedimentary mercury became evident when it was observed that fish were contaminated with low, but toxicologically significant, levels of monomethylmercury (Fimreite, 1970), a form causing a variety of neurological symptoms through poorly understood mechanisms (Bidstrup, 1964). Subsequent experiments showed that this methylmercury can be synthesized *in situ* by bacterial action, probably in the sediment (Jensen and Jernelov, 1969), or perhaps photochemically in the water column itself (Akagi and Takabatake, 1973).

In accordance with what was said earlier, we must be careful to subdivide the system into a minimum number of compartments consistent with the known transport and transfer processes. At the very least, it seems clear that water and sediment (suspended and deposited) must be separated; in general we know that the nature and amount of suspended material in the water greatly affects its binding capacity for heavy metals. For overall transport of the bulk of the mercury, probably nothing else needs to be considered (Miller, 1977).

From the standpoint of ecotoxicology, however, biota must be considered, especially fish, since fish serve as a bioaccumulator and the vector to man, and since the vanishing of fish is an observed ecological effect of mercury contamination (Fimreite, 1970). In order to describe the pathways of mercury to fish, it would seem that compartments for fish, higher plants, and invertebrates are needed.

Further subdivisions could be considered. Piscivorous fish are observed to contain higher mercury levels than others (Bligh, 1971), and could be modelled separately; also, it might well be worthwhile to subdivide further both suspended materials and sediments into organic and inorganic fractions.

Finally, as was emphasized earlier, the chemical form of the mercury must be considered. In the present case monomethylmercury must obviously be singled out for special consideration because of its much greater toxicity (Bidstrup, 1964), and for simplicity we may hope to include all other forms in some compartment such as 'inorganic mercury', since our interest is only to describe the transfer through fish to man.

In most presentations, one sees a diagram much like that in Figure 4.1, in which are shown the compartments and the important interactions (Miller, 1977).



Figure 4.1 Pollutant transport model: mercury in an aquatic ecosystem

However, such a diagram is misleading. It does not make clear whether each box represents amount of pollutant, amount of biomass, or some combination; nor is it clear whether arrows represent transfer of mass but not necessarily pollutant (as from fish to sediment) or pollutant but not biomass (water to fish), etc. It must be remembered that pollutant moves in several ways; it is carried along by biomass transfer but also moves by adsorption, desorption, etc., which have no associated biomass movement. Thus such transport phenomena must be considered separately.

To be consistent with what was said earlier, we might model the system at several levels simultaneously, presumably having one set of variables for biomasses and another for each of the critical chemical species. In these terms, it would seem that the 'minimum resolution' model would involve six compartments, within each of which we keep track of biomass and two kinds of mercury, and would require 18 descriptive variables and interactions which, if not further restricted, would number approximately 80.

However, further consideration shows that some of the compartments and many of the interactions may be omitted. For example, we have agreed that biota play little part in the movement of total mercury, and are little affected by it, so three compartments may be ignored in the second level. Similarly the various arrows often indicate transfers that are clearly not real (such as movement of biomass from water to fish) or have been demonstrated to be negligible in studies undertaken for the specific purpose (e.g. uptake of mercury by plants directly from sediment). Detailed considerations of this type produce the much-simplified version shown in Figure 4.2 (in which no arrows have been omitted). Now, the number of compartments is reduced to 15 and the number of interactions to around 40. These numbers are still high; and we are forced to resist the temptation to subdivide further in such ways as mentioned above.



Figure 4.2 The dynamics of methylmercury production

We now assign symbols x_1 to x_{15} shown in Figure 4.2 to represent the masses of each compartment. Notice that these are all in units of mass, but represent masses of different substances, and will be greatly different in magnitude, ranging from millions of kilograms (x_1, x_2) to one gram or less $(x_{12}$ to $x_{15})$. (This may also lead to numerical difficulties but such computational problems will not be discussed here.)

Each mass must next be made the subject of a rate-of-change equation of the form

 $\frac{\mathrm{d}x_i}{\mathrm{d}t} = \begin{array}{c} \text{Sum of several terms, each} \\ \text{representing one interaction} \end{array}$

and the remaining task is to decide on the form of each term. The symbol $k_{i,j}$ conventionally represents the rate constant for the transfer from x_j to x_i . Thus, for example, $k_{7,9}$ would be involved in the term describing movement of total mercury

in the suspended-solid compartment (x_9) to mercury associated with water (x_7) , i.e. a process of desorption and solubilization (Miller, 1977).

Finally, we can address the actual terms. For obvious reasons, we do not include an exhaustive listing of them all, but rather select just one as an example. Somewhat arbitrarily, let us consider x_{12} .

For x_{12} , there are three mechanisms: uptake of methylmercury from water, clearance into water, and browsing by invertebrates. Remembering that x_{12} represents the methylmercury content of the suspended solids, not their mass or any such quantity, we can conjure up an expression for each providing that we know the dynamics of the mass itself, which is the subject of the equation for x_3 , not discussed here.

Coefficient	Numerical value	Units
k _{2,3}	0 Summer 0.077 (May only)	fraction/day
k2,4	0.001-0.003	fraction/day
k2,5	0.0 Winter-summer 0.006 (Aug. to Nov.)	fraction/day
$k_{2,6}$ $k_{3,3}$ $k_{4,2}$ $k_{4,3}$ $k_{5,5}$ $k_{6,4}$ $k_{6,5}$ $k_{6,6}$ $k_{8,7}$ $k_{12,11}$ $k_{14,11}$ $k_{14,11}$ $k_{16,111}$ $k_{16,114}$	0.002 Average 0.05 0.100 0.05 0.005-0.03 (May to July) 0.056-0.063 0.02 (June to mid-Sept.) 2.0 $\times 10^{-7}$ 5.545 0.00016 16.6 0.224 5.545 0.00049 16.6 4.0 $\times 10^{-5}$ 0.009 1.0 0.014 52.04 0.85 81.0 96.0 0.85	fraction/day fraction/day kg sed/kg invertebrate/day kg/kg inv/day fraction/day kg/kg fish/day kg/kg fish/day fractional desorption/day fractional sorption/day fractional sorption/day fractional desorption/day fractional desorption/day fractional desorption/day fractional sorption/day fractional sorption/day fractional desorption/day fractional desorption/day fractional clearance/day excretion efficiency fractional clearance/day kg water cleared/kg invertebrate/day digestion efficiency (MeHg) kg water cleared/kg fish/day digestion efficiency of MeHg

Table 4.1 Coefficients for the Mercury Transport Model (Partial List)

Uptake rate of methylmercury from water will be proportional to the concentration (not the mass) of methylmercury in water, which is x_{10}/x_1 . It will also be proportional to the mass of the solids, i.e. to x_{12} , but will be limited by the concentration present. Thus when we include a rate constant which is to be determined, we have a form like

$$\frac{\mathrm{d}x_{12}}{\mathrm{d}t} = +k_{12,10}x_{10}x_{12}(C_{12,\max} - x_{12}/x_3)x_1$$

(a non-linear term). For clearance to water, a term of the form

 $-k_{10,12}(x_{12}/x_3)(C_{10,\max}-x_{10}/x_1)$

may be appropriate. Removal by invertebrates is equal to the browsing rate of the equation for x_3 multiplied by the concentration of methylmercury; the term might have a form like

$$-k_{13,12}(k_{4,3}x_4x_3/x_{3,avg})(x_{12}/x_3)$$



Figure 4.3 Behaviour of mercury in an aquatic system. W = total mass of water;SS = mass of suspended material; TMW = total mercury associated with water; TMS = total mercury associated with sediment. Spring floods cause violent fluctuations in all but the final quantity, which decreases smoothly with time

with the constant $k_{13,12}$ now representing an efficiency of ingestion of methylmercury when contained in food particles, i.e. a gut uptake coefficient determined in the laboratory. These terms would be combined with an overall transport term, also determined by measurement.

We need go no further to observe how terms are constructed (or how much uncertainty there is in the actual mechanisms). The next step is to summarize numerical values for the various $k_{i,j}$ (leaving it to the reader to surmise the functional form of the term). This is done in Table 4.1.

Finally, we display the results of a two-year run in Figure 4.3. It can be seen that overall mercury levels in sediment are predicted to decrease substantially each year and concentration of mercury in fish lags noticeably behind. We will comment further on this model in section 4.7.

4.7. USES OF MODELS

There are many uses for models formulated in this fashion. Roughly in temporal sequence rather than in order of importance, the main ones would seem to be the following (Naylor *et al.*, 1968):

- 1. to force participtants to agree on clear definitions of compartments and pathways;
- 2. to clarify the extent to which each mechanism of transport or transfer can be described in quantitative terms;
- 3. to make numerical predictions of future behaviour;
- 4. to estimate the uncertainties in those predictions;
- 5. to assist in research planning and resource allocation by identifying critical and poorly understood mechanisms;
- 6. to allow the scientist to test the response of the simulated system to specified disturbances; and ultimately
- 7. to predict the response of the system to various management scenarios.

There are other purposes, of course, including such things as suggesting validation experiments and procedures. However, those listed above seem to be the most important to the ultimate user or decision-maker as opposed to the analyst. The main point is that many uses exist for such a formulation; it is unfortunate that so much attention has been devoted to the third and so little to those that follow it (Frenkiel and Goodall, 1977).

The first two probably do not need to be discussed further since they have been illustrated by this chapter. Of course, it is always worthwhile emphasizing that, in the actual research process, these stages may involve substantial personal and professional conflict. The resolution of this conflict early in the course of the work is essential for acceptance, if not success, of the steps to follow (Holcomb Research Institute, 1976).

The third, prediction of the future state of the system, is the one most of us are most aware of. It is necessary to repeat that what is predicted is only the value of those describing variables that have been defined explicitly in the model formulation. Generally, this constitutes *less* information than the ecologist could gain by the most cursory of on-site inspections (although it may be more quantitative) and in most cases the biologist can and should interpret and extend the model predictions in the light of his more detailed understanding of the system.

Estimation of uncertainty, or probable error level, in model prediction, is a relatively simple procedure which has only recently begun to attract as much attention as it deserves (Burns, 1975). Essentially, error arises because of our lack of knowledge about both the functional form of the interactions and the numerical values (and variations) of the parameters, or rate constants, involved. The latter are more important over the short term, the former over the long.

For parameter values, the procedure for error estimation depends on the linearity or non-linearity of the model. One asserts that the output variables depend on the input parameters in some way,

$$x_i(t) = f(p_1, p_2, \dots, p_m)$$

and identifies the 'best estimate', say $x_j^0(t)$, as that sequence of values produced by the 'best' parameter values (say p_i^0) so that

$$x_i^0(t) = f(p_1^0, p_2^0, \dots, p_m^0).$$

If this dependence is linear, the changes in the x_j will be proportional to the changes in the p_i , so that changing any number of the parameters p_i will change the output in a way that may be calculated as

$$x_j - x_j^0 = \Sigma_i \frac{\partial f}{\partial p_i} (p_i - p_i^0).$$

(In practice, these coefficients $\partial f/\partial p_i$ are simple to calculate numerically.) Next, one estimates how uncertain the actual values used for p_i^0 really are, and uses this formula to produce an estimate of the uncertainty in the x_i .

If the behaviour of the system is non-linear, the same answers can be obtained without using a linear formula. To do this, one again estimates the probable range within which each 'true' parameter value is thought to lie, and solves the model many times (i.e. uses the computer to generate many future behaviours), each time using for the parameters values chosen at random from somewhere within the appropriate range (the Monte Carlo technique). Finally, one observes the magnitudes of run-to-run differences in output variables and uses these as estimates of real uncertainties.*

*This description of a Monte Carlo process has been kept very general largely because of space limitations and in the hope that this work may appeal to a wide audience. The technical details have been discussed elsewhere (Miller, 1974; Burns, 1975).

The technique of Sensitivity Analysis is closely allied to these ideas. In that approach, one tries to identify some measure of disturbance, or some other effect on the ecosystem, which depends in a simple way on the describing variables. For example, one might use the sum of squares of the differences between the disturbed output variables and those for the 'best' run, integrated over time.

$$D = \int_0^T \Sigma_j [x_j(t) - x_j^0(t)]^2 dt$$

Next, usually by solving the computer model again with a single parameter altered, one calculates the change produced in D by a unit change in that parameter. This is the Sensitivity Coefficient for that parameter:

$$S_i = \frac{\partial D}{\partial p_i}$$

In most practical cases, these coefficients differ from one parameter to another by orders of magnitude. By observing their relative sizes one can then consider allocating greater research effort to the investigation of those mechanisms to which model behaviour is particularly sensitive. The approach has been rather widely used to guide data gathering efforts in, for example, geophysical exploration (Meyer, 1971); its use in assignment of research priorities is more recent.

In some cases it may be observed that all the sensitivity coefficients are small, so that model performance and predictions are relatively stable over a range of parameter variations and other disturbances. Such a model is referred to as 'robust', and one has some confidence that its predictions represent the real performance of the system. That is to say, one can argue that it is likely to be a valid representation of reality.

The concept of validity is, naturally, of great concern to modellers; any use of a model depends ultimately on the assumption that its performance does correspond to the actual behaviour of the system, and the process of demonstrating this, the so-called validation process, is a vital part of model development (Miller, 1977). Unfortunately, there is no general procedure for carrying it out, any more than there is a general procedure for verifying any scientific theory. The best that one can do is to demonstrate that the behaviour of the universe is consistent with the model over a certain range of conditions, subject to the limited predictive abilities of the model and a recognized level of uncertainty. The validation process is often thought of as the demonstration that the model is able successfully to predict the state of the actual system. Actually, validation should be regarded as a continuing effort or at least as an iterative process.

4.8. FINAL THOUGHTS

Ultimately, the purpose of this or any model is to provide information on which judgments of ecotoxicology can be based. For this purpose, the final product is the

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time course of exposure of some target organism to a polluting substance. For the case of effects of methylmercury on man, for example, the critical pathway is through consumption of contaminated fish. The level of contamination at any time is the quantity $x_{15}(t)$ in the model described. Total exposure will then be given by

$$E = \int_0^\infty C(t) x_{15}(t) \, \mathrm{d}t$$

where C(t) describes rate of fish consumption, and $x_{15}(t)$ may result from any specified combination of environmental inputs. Once this function and the resulting integral are specified (along with the likely errors), the environmental transport model has done its work; the rest is a matter of assessing responses and effects, as described in the chapters to follow.

4.9. CONCLUSIONS

- (i) No single type of model can be useful for all pollutant transport problems; particular situations must be characterized in terms of time, distance, and the nature of the ecosystem.
- (ii) The fundamental issue in specific model formulation is identification of the different chemical forms of the pollutant and their interconversions, together with the persistence and toxicology of each.
- (iii) For specific chemicals, the geographical transport is typically less well understood than sources, bioaccumulation, or toxicology.
- (iv) In given cases, models can be formulated which will contribute materially to the prediction of pollutant movement and the making of policy decisions. However, more attention needs to be paid to credibility of models, and more work devoted to verification and validation procedures. In particular, model predictions should not be quoted unless some measure or estimate of the uncertainty in those predictions is included.

4.10. REFERENCES

- Akagi, H. and Takabatake, E., 1973. Photochemical formation of methylmercuric compounds from mercuric acetate. *Chemosphere*, 2, 131–3.
- Argentisi, F., DiCola, G., and Verkeyden, N., 1973. Biosystems Modeling: A Preliminary Bibliographic Survey, Commission of the European Communities EUR 4966 e, Luxembourg.
- Bidstrup, P. L., 1964. Toxicity of Mercury and its Compounds, Elsevier, New York, 112 pp.
- Bligh, E. G., 1971. Mercury levels in Canadian fish. In Proceedings of the Symposium on Mercury in Man's Environment, Feb. 15-16, 1971, Royal Society of Canada, Ottawa, pp. 73-90.

- Bolin, B., 1976. Transfer processes and time scales in biogeochemical cycles. In Nitrogen, Phosphorus, and Sulphur-Global Cycles (Eds. B. H. Svensson and R. Söderlund), SCOPE Report 7, Ecol. Bull. (Stockholm), 22, 17-22.
- Burns, J., 1975. Error analysis of nonlinear simulations. *IEEE Trans. Sys. Man. Cyb.*, SMC-5, 331-40.
- de Freitas, A. S. W., 1977. Uptake and retention of mercury by fish. In Miller, D. R., op. cit.
- De Groot, A. J. and Allersma, E., 1975. Field observations in the transport of heavy metals in sediments. In *Heavy Metals in the Aquatic Environment* (Ed. P. A. Krenkel), Pergamon Press, pp. 85-96.
- Fagerstrom, T. and Asell, B., 1973. Methyl mercury accumulation in an aquatic food chain. Model and some implications for research planning. *Ambio*, 2, 164-71.
- Fimreite, N. 1970. Mercury uses in Canada and their possible hazards as sources of mercury contamination. *Environ. Pollut.*, 1, 1.
- Frenkiel, F. and Goodall, D. W. (Eds.), 1977. Simulation Modelling, Report of SCOPE Project 5, in press.
- Goldwater, L. J., 1972. Mercury: A History of Quicksilver, York Press, Baltimore.
- Goodall, D. W., 1974. Problems of scale and detail in ecological modelling. J. Environ. Management, 2, 149-57.
- Goodman, G. T., 1974. How do chemical substances affect the environment? *Proc. Roy. Soc. Lond.*, B185, 127-48.
- Holcomb Research Institute, 1976. Environmental Modelling and Decision Making, Report for the Scientific Committee on Problems of the Environment, Praeger Publishers, 111 Fourth Avenue, New York.
- Jeffers, J. N. R. (Ed.), 1972. *Mathematical Models in Ecology*, The 12th Symposium of the British Ecological Society, Grange-over-Sands, Lancashire, 23–26 March 1971, Blackwell, Oxford.
- Jensen, S. and Jernelov, A., 1969. Biological methylation of mercury in aquatic organisms. *Nature*, 223, 753-4.
- Kao, S. K., 1974. Basic characteristics of global scale diffusion in the troposphere. Adv. Geophys., 18B, 15-32.
- Krenkel, P. A., 1973. Mercury: environmental consideration. CRC Critical Reviews in Environmental Control, May 1973, pp. 303-73 and August 1974, pp. 251-339.
- Mar, B. W., 1974. Problems encountered in multidisciplinary resources and environmental simulation models development. J. Environ. Management, 2, 83-100.
- Meyer, C. F., 1971. Using experimental models to guide data gathering. J. Hydraul. Div., Amer. Soc. Civil Eng., 97, 1681-97.
- Miller, D. R., 1974. Sensitivity analysis and validation of computer simulation models. J. Theor. Biol., 48, 345-60.
- Miller, D. R. (Ed.), 1977. Distribution and Transport of Pollutants in Flowing Water Ecosystems, Final Report of the Ottawa River Project, National Research Council, Ottawa, Canada, May 1977.
- Miller, D. R., Butler, G. and Bramall, L., 1976. Validation of ecological system models. J. Environ. Management, 4, 383-401.
- Naylor, T. H., Balintfy, J. L., Burdick, D. S., and Chu, K., 1968. Computer Simulation Techniques, Wiley, New York.
- Nordo, J., Elaissen, A., and Saltbones, J., 1974. Large-scale transport of air pollutants. Adv. Geophys., 18B, 137-50.

Odum, E. P., 1971. Fundamentals of Ecology, 3rd edn., Saunders, Philadelphia.

Pasquill, F., 1974. Atmospheric Diffusion, 2nd edn., Wiley, New York.

- Patten, B. C., 1971. A primer for ecological modelling. In Systems Analysis and Simulation in Ecology (Ed. B. C. Patten), Vol. I, Academic Press, New York, pp. 1-122.
- Rapoport, A., 1972. Explanatory power and explanatory appeal of theories. Synthese, 24, 321-42.
- Rigler, F. H., 1975. The concept of energy flow and nutrient flow between trophic levels. In Unifying Concepts in Ecology (Eds. W. H. van Dobben and R. H. Lowe-McConnell), Report of the Plenary Sessions, First International Congress of Ecology, The Hague, the Netherlands, Sept. 8–14, 1974. B. V. Junk Publishers, The Hague, pp. 15–26.
- Robinson, J., 1973. Dynamics of pesticide residues in the environment. In *Environmental Pollution by Pesticides* (Ed. C. A. Edwards), Plenum Press, London.
- Slade, D. H. (Ed.), 1968. Meteorology and Atomic Energy, U.S. Atomic Energy Commission TID-24190, National Technical Information Service, U.S. Dept. of Commerce, Springfield, Virginia.

Smith, J. M., 1974. Models in Ecology, The University Press, Cambridge.

- Truhaut, R., 1974. Ecotoxicology A New Branch of Toxicology: A General Survey of its Aims, Methods and Prospects. In Ecological Toxicology Research: Proceedings of the NATO Science Committee Conference on Ecotoxicology held at Mt. Gabriel, Quebec, Canada, May 6–10, 1974. Plenum Press, New York, 1975.
- Waide, J. B. and Webster, J. R., 1976. Theory in Ecosystem Analysis. In Systems Analysis and Simulation in Ecology, Vol. 4, Ed. B. C. Patten. Academic Press.
- Wollast, R., Billen, G. and Mackenzie, F. T., 1974. Behaviour of Mercury in Natural Systems and its Global Cycle. In Ecological Toxicology Research: Proceedings of the NATO Science Committee Conference on Ecotoxicology held at Mt. Gabriel, Quebec, Canada, May 6-10, 1974. Plenum Press, New York, 1975.
- Wood, J. M., 1974. Biological cycles for toxic elements in the environment. Science, 183, 1049-52.