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**Estimating Environmental
Concentrations of Chemicals Using
Fate and Exposure Models**

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ESTIMATING ENVIRONMENTAL CONCENTRATIONS OF CHEMICALS USING FATE AND EXPOSURE MODELS.

SUMMARY

Fate and exposure modelling of chemicals in the environment is becoming increasingly important. Models can be used for initial exposure assessments to evaluate the potential distribution of new and existing chemicals in the environment. More detailed models can help to quantify the expected concentrations under different conditions and are often useful for interpreting field observations and accompanying monitoring programmes and for assessing the relative importance of different processes. This report provides details of the processes that determine environmental fate and exposure, a discussion of selected models and their appropriate use and limitations, and guidance on quality assurance and validation of modelling.

Numerous models exist for a variety of purposes. In this report they are categorised according to the media for which they are intended to be used, i.e. air, water, soil and multi-media models. Within these categories there may be models that are designed for various time and spatial scales, depending on what processes are incorporated within the model and how they are formulated.

Selection of an appropriate model requires an understanding of the basic transport and transformation processes by which a chemical moves and reacts in the environment. Such knowledge of the underlying principles is essential for ensuring that models are used appropriately. Thus attention has been paid to describing the processes that occur in the environment and their relative importance in different situations.

The practical application of models is described and examples of models are given. No one model is preferred to another, however the appropriate use and limitations of the models is emphasised. The aim is to provide an overview of models currently being used, particularly within the chemical industry, and to encourage the use of models, but in their proper context with consideration to all the underlying principles and limitations.

The report considers various aspects of quality assurance in modelling and principles for good modelling practice, both in terms of model development and from a users standpoint. The question of model validation is addressed in some detail. This has many aspects; the model processes and assumptions must be valid for the modelling purpose, the input data must be scientifically sound and the computer code must be validated. Comparison with field observations is the last stage of the validation process and is essential for gaining confidence in their predictive power. However, it is emphasised that no matter how good a model may be, models are only an

approximation of reality and the complexity of the environment is such that no model will ever reproduce it precisely.

SECTION 1. INTRODUCTION

It is becoming increasingly necessary to characterise the hazard that new and existing chemicals may pose to man and the environment. Part of the procedure of hazard assessment involves establishing the chemical concentrations to be found in the environment. This has led to the development of many so-called fate and exposure models which are made to mimic reality. These are generally mathematical models frequently using computer programs. They may vary greatly in complexity and sophistication and thus in the extent to which they represent the real environment.

Many mathematical models have been developed for different applications. Every-day examples of such models are the weather forecast models. To those first addressing the topic of fate and exposure modelling, considerable confusion exists over which model to use and why. To address this problem ECETOC formed a task force with the following terms of reference:

- review the models used by ECETOC member companies for estimating exposure concentrations in the environment;
- provide a critical analysis of current models/modelling techniques used in the chemical industry;
- provide guidance on the appropriate use and limitations of exposure assessment modelling including advice on approaches to validation.

This report summarises a selection of the fate and exposure models used within the chemical industry. Such models consist of three main components, input, calculation and output.

Usually, three different types of input data are required, that is chemical, environmental and load or discharge data. Specific requirements are indicated for the models discussed in this report.

Practical experience shows that for many chemicals reliable, critically evaluated chemical data are lacking. A further complicating factor is the difficulty of translating laboratory derived reaction constants into environmental reaction constants. Environmental parameters usually show large temporal and spatial variations. For practical purposes, averaged values are used in most model calculations. Data on the load or discharge into the different environmental compartments are often not known accurately. In many cases loading is not constant and may be discontinuous or diffuse. Again for practical purposes, averaged values are normally used.

The calculation component in computer models contains the mathematical relationships describing the fate process, sometimes referred to as the "black box". In part, this is because in many models data on variable parameters, notably on environmental parameters, have been

incorporated in the calculation component as constants and, therefore, can not or not easily be changed or even inspected by the user. This component often includes Quantitative Structure Activity Relationships (QSARs) and ecokinetic models as building blocks.

The output of computer models can be graphical and/or numerical. Currently, there is a tendency to develop computer models that provide solely graphical output where different concentration ranges are characterised by different colours. Such graphical output is useful as simple and conveniently arranged summary of the model results. Nevertheless, to allow full use of the modelling exercise and to encourage simple checks that the model output is sensible, quantitative numerical output should not be omitted.

The scope or applicability of fate and exposure models varies from evaluative to predictive, from comparative to absolute.

The purely evaluative or comparative models can be fairly simple, such as Mackay's fugacity models. In these models a skeletal environment, a so-called generic environment, is usually defined. These models should be used only to obtain an idea about the global fate and behaviour of chemical. They can be used to compare compounds and to reach conclusions as to the acceptability of production and use of these compounds at a regional scale.

Predictive or absolute models, the so-called site-specific models, are developed to predict chemical concentrations in a specific area resulting from a defined discharge. These models may be highly complicated and require a large amount of input data.

Environmental fate and exposure models can be subdivided in various ways on the basis of load or discharge characteristics of the chemical, steady state or dynamic models, calculation procedures, analytical or numerical models, or applicability of the model. In this report the latter subdivision has been adopted incorporating:

- multimedia models,
- air models,
- surface water models,
- soil and groundwater models.

Human exposure and food chain models are excluded.

SECTION 2. BACKGROUND

There are many ways in which a chemical can enter the environment and many pathways along which it can travel and react, depending on the nature of the chemical, environment and release pattern. Consequently, environmental fate and exposure models are often developed only for specific media, such as air, water and soil. Moreover, there are often different mathematical descriptions of the transport and transformation processes that can be used, and various numerical techniques for formulating these mathematics.

Companies faced with the task of predicting the fate and behaviour of chemicals have a wide range of models at their disposal. Literally hundreds of models have been developed for a variety of reasons and many are available commercially or even free of charge. Many of the most comprehensive models come from the US Environmental Protection Agency (US EPA).

The choice of model is difficult. It is easy to misinterpret model results if the underlying principles are not properly understood. Worse still, it is possible to apply models to situations where they are not valid. It is thus essential to understand the basic mechanisms which control the behaviour of chemicals after release into the environment in order to choose the appropriate model for a given situation. Section 3 provides details of the processes that can be included in fate and exposure models.

The task force has attempted to address the problem of choosing the right model for a particular situation. This has been done by reviewing the environmental fate and exposure models currently used by ECETOC member companies. Questionnaires were sent out to all members to establish what models were being used; approximately 50% of the companies responded indicating some 40 models used for a variety of purposes. The information obtained was used to select those models which were most widely used. The selected models are further described and reviewed in Section 4 and the Compendium. For practical purposes those models used by one Company only were generally not further considered, unless they were judged to be of particular importance.

Few models have been extensively validated in field studies. It is thus difficult to comment on the predictions of the model and how well they represent concentrations in the environment. The task force is concerned that during the development of the computer programs new versions are issued and the changes brought about in the predicted environmental concentrations are rarely considered in terms of validation. Some basic aspects and recommendations for model validation are made in Section 5.

A definition of specialist expressions used in this report is given in the glossary.

SECTION 3. ENVIRONMENTAL TRANSPORT AND TRANSFORMATION PROCESSES

There are numerous processes that take place in the environment, many of which may affect fate and behaviour of a chemical. The effect of these processes on chemical concentrations in the environment depends on chemical properties, environmental parameters and load or discharge patterns. Different mechanisms can become dominant as the chemical moves through space and time. Therefore, it is essential to have an understanding of the environmental processes and the parameters that influence their rate (C W to send reference). The following section describes the main processes incorporated in fate and exposure models.

3.1. TRANSPORT PROCESSES

Transport processes determine the distribution of a chemical in the environment in space and time. For example, in surface water models these may be advection, dispersion, particle settling, resuspension, sedimentation, sediment mixing and diffusion processes. The main problem is to obtain representative data for the rate of these processes to be included in the overall modelling framework. For still waters and slow flowing rivers it is often possible to obtain reasonable estimates, for estuarine and coastal waters this may not be possible. Definition of the transfer mechanisms can be difficult and may be critical to the evaluation. Many of the transport mechanisms which may occur in air, water and soil are essentially similar although their magnitude will be different. The main transport processes are discussed in the following sections.

3.1.1. Advection

In all environmental media, advection can play an important role in determining the movement of chemicals. They may be transported in dissolved, gaseous, condensed or particulate phases.

In surface water models, advective currents are specified as part of the environmental data set. They may be computed from a hydrodynamic model or interpolated from a set of current measurements. Alternatively, they may be defined as gross volumes of water entering and leaving the model elements, where the flows are computed on the basis of the law of conservation of mass.

The situation in the atmosphere is very similar to that in tidal waters, with the advective currents being driven by pressure gradients. Flow fields in air or tidal water may be computed from interpolated current measurements or by solving the equations for air or water motion.

In soil, advective water or air currents are much smaller, never the less they still determine the displacement of chemicals that partition in air and water. Most models compute advective water flows in the saturated zone hydrodynamically. Calculation of air and water flows in the unsaturated zone are more complicated and most models tend to use a simplified layer approach where soil properties are considered constant for each layer. Advection of gaseous and dissolved chemicals generally is controlled by up- and downward fluxes of air and water through the soil layers.

3.1.2. Dispersion

Dispersion is an important process determining dilution of chemicals in the environment. It is the result of turbulence which, under environmental conditions, usually is far more important than molecular diffusion. The rate of dispersion is dependant on the relative sizes of turbulent eddies and the plume within which most of the chemical is present. Any velocity shear in the advective flow field may also contribute if the plume crosses the shear boundary. In models, dispersion may be calculated in different ways depending on the environmental medium.

Dispersion is described mathematically using Fick's diffusion law stating that the flow of a chemical, J , is proportional to its concentration gradient, C .

Thus: $J = -D \cdot \Delta C$

and then: $\frac{dC}{dt} = \frac{d}{d_i} \left(D_i \cdot \frac{dC}{d_i} \right)$

where D_i = the coefficient of dispersion in directions x, y, z, (m^2/sec).

This equation can be rigorously integrated by a numerical method but in most cases more simple equations are used.

In surface water, dispersion is usually expressed as mixing coefficients which are characteristic for a water body. The transfer rate, r_p , of material through dispersion may then be quantified as:

$$r_i = \frac{\Delta C \cdot D_i \cdot A_i}{l_i}$$

where

r_i = transfer rate (mol/sec)

i = x, y, z, (the 3 spatial dimensions)

A_i = cross sectional areas for dispersive exchanges, (m²)

l_i = characteristic length scales for eddies, (m)

ΔC = concentration gradient over length l_i in directions x, y, z, (mol/m³)

For groundwater, dispersion may be defined in the same way although mixing coefficients will be much smaller.

Because of the inherent random character of the wind in the atmosphere it is not possible to predict dispersion of a chemical in air with certainty. Although basic equations to describe dispersion are available, no single mathematical model exists that can be used as a practical means of computing atmospheric concentrations over all ranges of conditions. In practice, the vertical and horizontal concentration distributions perpendicular to the mean wind direction is described as a Gaussian normal distribution, the standard deviations of which are functions of distance from the source and meteorological conditions.

3.1.3. Volatilisation

Air-Water Transfer: Transfer between air and water has been widely studied. Although the thermodynamic aspect of equilibrium is well known the kinetics are still only moderately understood. At equilibrium, the concentration of a chemical in water is related to its concentration in air by Henry's law:

$$C_{air} = H \cdot C_{wat} \quad \text{or} \quad P_{air} = H' \cdot C_{wat}$$

where:

C_{wat} = water phase concentration, (mol/m³)

C_{air} = air phase concentration, (mol/m³)

P_{air} = partial vapour pressure, (Pa)

H = Henry's constant, (dimensionless)

H' = Henry's constant, (Pa.m³/mol)

Henry's law constant can be measured directly or estimated with reasonable accuracy using the ratio between the vapour pressure and the aqueous solubility of a chemical.

The rate of evaporation in the environment depends not only on chemical properties but also on environmental parameters, mainly turbulence in water and air.

Several theories have been published, but the two-film theory of Whitman (1923), which was originally developed for engineering purposes, is the most widely used. This theory assumes the existence of two stagnant boundary layers at the air/water interface. Chemicals pass across the boundary layers by molecular diffusion, while the bulk of water and air is assumed to be homogeneously mixed. This leads to a first-order function of the concentration gradient in the two phases. The transfer coefficient depends on molecular diffusivity of the chemical in water and air, and the thickness of the boundary layers.

The transfer coefficient can also be derived from comparison between the compound of interest and reference compounds, such as water and oxygen for which volatilisation in the environment is extensively studied. Numerous investigations have been performed and various empirical equations relating the transfer coefficient to indicators of the turbulence in water and air, such as current speed and wind velocity have been presented (Isnard, 1990).

Soil-Air Transfer: Transfer between soil and air (the atmosphere) is a much more complicated process and no satisfactory mathematical description is available. It depends on partitioning of the compound between solids, air and water within the soil, and its rate of diffusion from soil-air to the atmosphere.

When the water content of the soil is sufficient to cover all soil particles, partitioning between air and solids in soil can be described as two processes, that is between air and water and between water and solids:

$$C_{air} = H \cdot C_{wat} \quad \text{and} \quad C_{sol} = K_d \cdot C_{wat}$$

As a result the partition coefficient for equilibrium conditions between air and solids is equal to the ratio between Henry's Law constant and the adsorption coefficient:

$$C_{air} = \frac{H}{K_d} \cdot C_{sol}$$

where:

C_{sol} = solid phase concentration, (mmol/kg)

K_d = adsorption coefficient between solids and water, (l/kg)

No simple equation is available to describe the rate of partitioning in soil, equilibrium is generally assumed. It should be noted that the rate of transfer between the atmosphere and air in soil is strongly influenced by wind speed, and soil temperature and porosity.

3.1.4. Adsorption on Soils and Sediments

Hydrophobic Organic Chemicals: The adsorption of hydrophobic organic chemicals onto solids has been reviewed by several workers (Lyman, 1983; Elzerman and Coates, 1987; US EPA, 1989; ECETOC, 1990a). The adsorption mechanism for these substances is believed to be partitioning in or onto soil organic matter. The distribution of such chemical between water and soil is given by the absorption coefficient, K_d (cf Section 3.1.3.).

The organic carbon (oc) related adsorption coefficient, K_{oc} , can be used as a standardised value which can be applied to other soils with known organic carbon or organic matter (om) content (median conversion factors are: $oc = om \times 0.58$ or $K_{oc} = K_{om} \times 1.72$). K_{oc} is related to the soil adsorption coefficient, K_d , by the following formula:

$$K_{oc} = \frac{K_d \cdot 100}{\%_{oc}}$$

where:

$\%_{oc}$ = percentage organic carbon.

Although measured values of K_d (and hence K_{oc}) are available for some chemicals, notably pesticides, this does not apply to the majority of substances. Consequently, most models incorporate formulae to calculate K_{oc} from chemical properties such as the octanol/water partition coefficient, K_{ow} , and solubility (Lyman, 1983). For soils with low organic carbon or high clay content adsorption to inorganic matter may become important and the K_{oc} approach is not valid.

The kinetics of transfer between solids and water are poorly understood. The above equations assume instantaneous equilibrium. It is possible to consider the kinetics of

adsorption using a first-order function of the concentration difference between the sorbent and the solution. However, this model does not provide a good fit with experimental data which generally show a rapid initial uptake, within a few hours) followed by a slow approach to equilibrium (ECETOC, 1990a).

Ionisable compounds: Because ionisable compounds include environmentally important chemicals such as phenols and certain pesticides, as well as metals, some comment is necessary on their partitioning behaviour although the situation is even less clear than for hydrophobic substances. Both pH and salinity will have an effect on the partitioning of ionisable compounds but relationships are unclear. The situation with regard to the adsorption of ionic chemicals has led the statement in a recent report (US EPA, 1989) that "for ionic organic chemicals there is as yet no comprehensive partitioning theory that identifies the normalisation quantities and provides the parameters to predict free dissolved concentration." It is necessary to be aware of these limitations when modelling the fate of ionisable compounds.

3.1.5. Bioaccumulation

Bioaccumulation is characterised by an enrichment of a compound in biota compared to its concentration in the surrounding environmental compartment. It can be caused by bioconcentration, uptake from the media, or by biomagnification, uptake via the food chain. Experimental determination of bioaccumulation expressed as the bioconcentration factor, *BCF*, is mainly performed for aquatic organisms.

$$BCF = \frac{C_{biota}}{C_{wat}}$$

where:

C_{biota} = concentration in the biota, (mmol/kg)

For non-ionisable substances the BCF can be estimated from the octanol-water partition coefficient, $\log K_{ow}$ (Lyman, 1983), however BCF will be over estimated for compounds that are metabolised and for those compounds with high molecular weight (>700 g/mol).

3.1.6. Water Phase Heterogeneous Transport

Sediment transport: The dynamics of sediment transport are extremely complicated, particularly for cohesive sediments. Most fate and exposure models do not include sediment associated processes dynamically due to the complexity and inter-dependence of the processes, and basic lack of suitable data. It is recognised that sediment-water

exchange processes can provide an important contribution in determining chemical fate and thus some understanding of these mechanisms is essential. Where sediments are considered potentially important, the problem is usually simplified to looking at gross fluxes of chemicals associated with sediment due to particle settling, resuspension and sedimentation (burial).

Particle Settling: Particle settling is an important mechanism for transporting sorbed chemical to the sediment bed. Some models effectively incorporate a single term to represent an overall mass flux of suspended sediment to the bed, e.g. EXAMS, MACKAY 2 & 3. More complex models may allow more than one different particle type and some models allow for several different sizes with different organic carbon content. The choice of model will depend very much on the problem at hand and the availability of settling velocities and the size distribution of the suspended particles. Estimates of particle settling may be obtained in several ways. The three most common methods are the use of sediment traps, laboratory bench scale tests or calculation using Stoke's Law.

Resuspension: Sediment resuspension is an important mechanism for re-introducing chemicals into the water column. Particles at the sediment-water interface may be lifted into the water column if sufficient energy is available. This energy may be transferred from advecting water, internal waves and other sources such as dredging and fishing. Unfortunately, resuspension is extremely difficult to measure (US EPA, 1986) and estimates are usually made with sediment traps providing the source of the material can be determined. If the sedimentation rate is known, the resuspension flux may be estimated as the difference between settling and sedimentation (US EPA, 1986; ten Hulscher *et al*, 1989). This is a common approach for lakes and slow flowing rivers. In fast flowing rivers and estuaries resuspension can be represented as a function of the shear stress exerted on the bed.

Sedimentation: Sedimentation is the net result of settling and resuspension. Its rate can be determined fairly accurately although values are usually very small (mm/yr). The most commonly used methods are sediment dating (Eadie and Robbins, 1987; US EPA, 1986) or direct field measurements using benchmarks with marked survey stakes (US EPA, 1986).

Sediment Mixing: The sediment top layer may be mixed through bioturbation (Fowler, 1982; Eadie and Robbins, 1987; ECETOC, 1990a). This process may be important since chemicals within the mixed layer can be re-introduced into the water column after a period of time, depending on the extent of the biological activity in the sediment. This is