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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

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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: $J = -D.\Delta C$

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

where D_i = the coefficient of dispersion in directions x, y, z, (m²/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_i, of material through dispersion may then be quantified as:

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

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:

$$C_{air} = H . C_{wat} \qquad \text{or} \qquad P_{air} = H' . C_{wat}$$

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:

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

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 x 0.58 or K_{oc} = K_{om} x 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

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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 compunds that are metabolised and for those compunds 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

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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

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especially significant if there is a net sedimentation since chemicals may be mistakenly assumed to be buried if sediment mixing is not taken into account.

3.1.7. Air Phase Heterogeneous Transport

Chemicals are removed from the atmosphere by wet deposition (absorption into droplets followed by precipitation), and dry deposition (adsorption at the earth's surface to soil, water or vegetation).

Wet Deposition: When a droplet moves through air it may collect aerosols and gases. Three mechanisms can be identified whereby particles in the air reach the surface of the falling droplet. Small particles undergo Brownian diffusion that may bring them in contact with the droplet due to their random motion. Interception may take place when a particle, following the streamlines of flow around the droplet, is sufficiently large that its surface comes into contact with that of the droplet. Inertial impaction may occur when the particle is unable to follow the rapidly curving streamlines around the droplet and continues to move toward it. Atmospheric gases may dissolve in droplets or may be adsorbed on the droplet surface without undergoing further reaction. For these processes the rate of transfer of gas molecules to the surface of a stationary or falling droplet has to be calculated. Difficulties in predicting gas scavenging rates arise when the gas has an appreciable vapour pressure around the surface of the droplet and thus the composition of the droplet must be known in order to predict the net rate of transfer of material to the droplet.

Wet deposition can be assumed to be a first-order process and is commonly characterised by a washout coefficient which is proportional to rainfall intensity. Values of the washout coefficient presented in the literature vary over several orders of magnitude (Slinn and Hales, 1970; Hales et al., 1973).

Dry Deposition: Dry deposition can occur in two basically different ways. Firstly, particles may separate under the forces of gravity and follow Stoke's law. Turbulent diffusion represents an opposing force. Secondly, loss of material by absorption at the earth's surface creates a low concentration at the surface setting up a concentration gradient in air creating a downward flux of material. This flux is expressed as the product of a deposition velocity and the concentration of the substance at a reference height.

Deposition velocities of particles are a function of particle size and vary over a large range (McMahon and Denison, 1979; Sehmel, 1980). Particles smaller than 10μ which are not effectively removed by gravitational settling can undergo dry deposition, also particles may be removed from the atmosphere by deposition on vegetation or other

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surfaces. Due to turbulent mixing, a downward flux is then established, which may be expressed in terms of a deposition velocity similar to that of sedimentation. For particles greater than 10μ, the deposition rate is given essentially by the gravitational settling. At higher wind speeds, deposition is enhanced due to increased atmospheric turbulence. High vegetation may be more effective at collecting aerosol particles, in that stems and leaves of bushes and trees act as filters, intercepting particles by impaction. Field data that quantify the effect are vailable from pesticide-spray experimentation.

3.2. TRANSFORMATION PROCESSES

Transformation is of major importance in determining the persistence of a chemical in the environment and is an essential element in fate and exposure models. Transformation processes are modelled using rate constants for the individual processes or, in certain cases, combined processes. The main processes are discussed below.

3.2.1. Biodegradation

Microbial degradation of organic chemicals is the major metabolic process in many situations. As a general rule, if biodegradation of a chemical has been demonstrated the laboratory it is expected to occur also in the environment. However, process kinetics are not well understood. Rate constants determined in the laboratory are not necessarily applicable in the field. Most fate and exposure models either allow the user to specify a rate constant, r_b, or use the following equation:

$$r_b = \frac{\mu_{max} \cdot C_i x_i}{k_s + C_i}$$

where:

r_b = rate constant, (mol/m³/sec)

μ_{max} = maximum growth rate, (mol/sec/cell)

k_s = half-saturation rate, defined as the chemical concentration at one-half of the maximum growth rate, (mol/m³)

x_i = microbial population, (cell/m³)

C_i = chemical concentration in the aqueous phase, (mol/m³)

In the environment the concentration C_i usually is very low and the equation can be simplified as:

$$r_b = k_b \cdot C_i$$

where:

k_b =   pseudo-first order rate constant for biodegradation, (sec^{-1})

Biodegradation is the most important degradation pathway in water, soil and sediment for many organic chemicals. The rate of biodegradation is related to the structure of the chemical, microbial numbers, organic carbon content and temperature and moisture in the case of soil. These properties generally vary spatially and an accurate estimate of the rate of biodegradation is very difficult even if laboratory or field data are available. In fate and exposure models, kinetics are normally assumed to be pseudo-first order. A more detailed discussion can be found in ECETOC (1991).

In deeper soils or sediment layers or under special conditions in surface water the oxygen content can be very low. In this case anaerobic biodegradation can become an important process. Microorganisms which grow under anaerobic conditions can use nitrate or sulphate as an oxygen source. The kinetics of this process in the environment are not well understood. A similar approach as for aerobic biodegradation can be followed.

3.2.2.   Hydrolysis

Hydrolysis is defined as the cleavage of organic molecules by reaction with water according to the generalised reaction:

$$RX + H_2O = ROH + HX$$
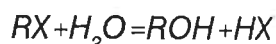
Typical compound classes which may hydrolyse are: alkylhalogenids, amides, amines, carbamates, nitriles, epoxides and esters.

In hydrolysis three different processes can be distinguished, that is neutral, and acid and alkali catalysed reactions. Substances like humic compounds, metal ions and Bronsted acids and bases can also catalyse hydrolysis. In soils and sediments hydrolysis can be affected by sorption on solid surfaces. As hydrolysis can be pH dependent kinetic data at different pH values are required. The pH values observed in the environment range from 4.5 to 8.5 for surface waters and from 7.5 to 8.5 for seawater. For most soils it is in the range 4.5 to 6.5 although soils with extreme pH values as low as 3 and as high as 10 may occur at some locations.

3.2.3.   Phototransformation

Phototransformation, sometimes called photodegradation or photolysis, can be divided into direct and indirect phototransformation reactions. In direct phototransformation, a compound absorbs solar radiation (wavelength > 295nm) and reacts from the excited state. In indirect phototransformation, solar energy initiates reactive species, mostly transient oxidants like OH• radicals, which then react with the compound.

Different phototransformation reactions will occur in different parts of the environment and at varying rates. In the troposphere, where indirect phototransformation is the most important process, reaction with OH• radicals is dominant. The OH• reactivity of a great number of organic chemicals has been determined. Missing data can be estimated using a method developed by Atkinson (1988). O_3 and NO_3• may also be important reactive species but reaction rate constants are less easily available.

In water, direct phototransformation may be important (ECETOC, 1984). Its rate may depend on pH, chemical concentration, oxygen content and above all on the light absorbance of the water which is a function of depth, suspended matter and colouring of the water column. The direct phototransformation rate in water, r_p, is usually expressed as:

$$r_p = k_p . C_i$$

where:

r_p = rate constant for phototransformation, (mol/m³/sec)

k_p = pseudo-first order rate constant for phototransformation, (sec⁻¹)

C_i = chemical concentration in the aqueous phase, (mol/m³)

Direct phototransformation in water can be an important process for compounds which absorb sunlight and react in water with a sufficient quantum yield.

For special compound classes, such as sulphur containing compounds which can react with singlet oxygen, indirect phototransformation can be important. The reactive transients in water are mostly formed in photochemical reactions of dissolved humic substances. Singlet oxygen, hydrated electrons, peroxides, H_2O_2 and OH• radicals are the main transients. OH• radicals can also be formed during irradiation of aqueous nitrate or nitrite solutions or by metal catalysis.

In soil, phototransformation reactions are of minor importance because they occur only at the surface. Both direct and indirect phototransformation can occur.

3.2.4. Speciation

Metal ions and inorganic or organic ligands may interact in water to form complexes. Many chemicals contain functional groups that dissociate in water to yield charged species. The distribution of a chemical among its different forms is described as speciation. For example, copper occurs as Cu^{2+}, $CuOH^+$, $CuHCO_3^-$, $CuSO_4$, Cu-humic acid complex and other compounds depending upon the pH of the water and the presence of other substances. Speciation determines the biological availability of a chemical and its physico-chemical behaviour, such as adsorption to suspended matter. It is a function of the chemicals concentration, pH, ionic strength, temperature, redox potential etc. (Morel et al, 1973).

Chemical speciation in complex aqueous solutions, such as natural waters, can be calculated using speciation models. They apply, in most cases, the 'equilibrium constant' approach, using stability constants for the species considered, or the 'free energy minimisation' method, using Gibbs energies for the formation of the different complexes. Speciation reactions in the models include dissociation, hydrolysis, redox equilibria, complex formation and phase transfer phenomena, such as precipitation, adsorption, ion-exchange and formation of gaseous compounds. All these reactions are considered to be at equilibrium, i.e. there are no kinetic calculations.

Nordstrom et al (1979) and Nordstrom and Ball (1984) provide an overview of speciation models designed for river water, groundwater and sea water and they give several modelling examples. Models differ generally in their computational approach, in their sets of chosen species and often in the way that activity coefficients are calculated. The latter is particularly significant for modelling of sea water with a high ionic strength. Sposito (1984) reviewed models that are suitable for soil solutions and described different approaches to modelling adsorption onto soil particles beyond the simple adsorption isotherm method.

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No.2	Joint Assessment of Commodity Chemicals, 1,4-Dioxane
No.3	Joint Assessment of Commodity Chemicals, Methyl Ethyl Ketone
No.4	Joint Assessment of Commodity Chemicals, Methylene Chloride
No.5	Joint Assessment of Commodity Chemicals, Vinylidene Chloride
No.6	Joint Assessment of Commodity Chemicals, Xylenes
No.7	Joint Assessment of Commodity Chemicals, Ethylbenzene
No.8	Joint Assessment of Commodity Chemicals, Methyl Isobutyl Ketone
No.9	Joint Assessment of Commodity Chemicals, Chlorodifluoromethane
No.10	Joint Assessment of Commodity Chemicals, Isophorone
No.11	Joint Assessment of Commodity Chemicals, (HFA-132b) 1,2-Dichloro-1,1-Difluoroethane
No.12	Joint Assessment of Commodity Chemicals, (HFA-124) 1-Chloro-1,2,2,2-Tetrafluoroethane
No.13	Joint Assessment of Commodity Chemicals, (HFA-123) 1,1-Dichloro-2,2,2-Trifluoroethane
No.14	Joint Assessment of Commodity Chemicals, (HFA-133a) 1-Chloro-2,2,2-Trifluoromethane
No.15	Joint Assessment of Commodity Chemicals, (HFA-141B) 1-Fluoro 1,1-Dichloroethane
No.16	Joint Assessment of Commodity Chemicals, (HCFC-21) Dichlorofluoromethane
No.17	Joint Assessment of Commodity Chemicals, (HFA-142b) 1-Chloro-1,1,Difluoroethane
No.18	Joint Assessment of Commodity Chemicals, Vinylacetate
No.19	Joint Assessment of Commodity Chemicals, Dicyclopentadiene
No.20	Joint Assessment of Commodity Chemicals, Tris-/Bis-/Mono-(2-ethylhexyl)phosphate
No.21	Joint Assessment of Commodity Chemicals, Tris-(2-butoxyethyl)-phosphate

SECTION 4.   ENVIRONMENTAL MATHEMATICAL MODELS

4.1. MULTI MEDIA MODELS

4.1.1. General Aspects

Objectives and structure of Multi-Media models: Multi-media models have been developed to estimate fate and behaviour of a chemical in the environment on a large (regional) scale. They give an idea of the mass balance of a chemical and identify the compartment(s) in which it tends to partition. They have been introduced for evaluative purposes. They do not exactly represent the real but rather a generic environment which may help to improve understanding of the fate and behaviour of a substance.

Depending on their level of sophistication, they may also give an indication of the relative importance of the various transfer and transformation processes and lead to an estimation of the distribution of a chemical between environmental compartments.

Multi-media models assume an 'unit world' which is supposed to represent the actual environment on a large scale. This unit world is divided in several compartments with specified volumes. Most models consider six compartments: air, water, soil, sediment, suspended solids and aquatic biota, but this may vary. Some models, for example, consider only the first four of these compartments being the most important in volume. Other models include more compartments, such as atmospheric particles and terrestrial biota. Within each compartment, the chemical is assumed to be evenly distributed. In other words, each compartment is homogenous.

Once the unit world is defined, the models take into account different phenomena which may affect the fate of the chemical. Each of these phenomena is quantified and the set of equations obtained, together with a description of the discharge, constitutes the structure of the model.

Classification of models: Multi-media models are generally classified as follows:

Conservative or non-conservative models: a chemical released in the environment may be transformed. To simplify matters, in particular when the kinetics of degradation are not well known, some models consider the chemicals to be persistent or conservative and thus do not make any allowance for degradation.

Equilibrium or non-equilibrium models: the concentration of a chemical in the different compartments islinked by thermodynamic equilibrium laws, such as Henry's law for

partitioning between water and air. Equilibrium is rarely achieved and the kinetics of transfer processes between compartments may be taken into account.

Steady-state or non-steady-state models: the concentration of a chemical in any compartment may be assumed to be constant, steady-state, or to vary with time depending on the discharge rate, non-steady-state.

Based on the above listed criteria, Mackay and Paterson (1979) have introduced the following model classification:

- Level 1: equilibrium, conservative and steady-state models,
- Level 2: equilibrium, non-conservative and steady-state models,
- Level 3: non-equilibrium, non-conservative and steady-state models,
- Level 4: non-equilibrium, non-conservative and non-steady-state models.

4.1.2. Basic Models

Level 1 Models:

In Level 1 models, equilibrium and steady-state are assumed and transformation of the chemical is not taken into account. Based on thermodynamic equilibrium laws, the Level 1 model simply calculates a theoretical distribution of the chemical between compartments. The distribution is computed from equilibrium partition coefficients and the volumes of each compartment. Level 1 models help in identifying the "target" compartment(s) which may have to be studied more extensively.

Level 2 Models:

Level 2 models also assume equilibrium and steady-state but take into account transformation and advection. In addition to distribution, they calculate the environmental life-time of a chemical based on the different concentrations in each compartment and the amount of product released. As for Level 1 models, Level 2 models assume that equilibrium is achieved between compartments, consequently, the distribution of the chemical is the same as that obtained at Level 1. Therefore, the use of Level 2 models is not essential since the only extra information that is obtained compared to Level 1 models is the computed life-time which is far from the reality since the kinetics of the transfer processes are not taken into account.

Level 3 Models:

Level 3 models give the same type of results as Level 2 models, but with a greater precision, since rates of transfer between compartments are taken into account. Thus, not equilibrium but only steady-state is assumed. Level 3 models are built around a system of equations, one for each compartment, which describe all inputs and outputs for each compartment. Level 3 models present a more accurate estimate of chemical quantities and concentrations in each environmental compartment and its life-time. Level 3 models lead to a more accurate distribution of the chemical in the environment and its lifetime.

Level 4 Models:

Level 4 models assume non-steady-state. They allow prediction of the time required for the chemical to disappear from the environment once its use has ceased or, alternatively, the time needed to reach steady-state when chemical releases are continuing. Level 4 models are built around the same set of equations as Level 3 models but, because they assume non-steady-state, solving this set becomes more complicated, especially, if the variability in the release with time is complex.

4.1.3.   Data Requirements

The data required for Level 1 models are: Henry's law constant, the adsorption coefficients for soil and sediment and the bioconcentration factor, if the biota is included in the model. For common hydrophobic chemicals, only data on solubility and vapour pressure would suffice as the other parameters may be calculated from these data. However, the use of experimentally determined partition coefficients should be preferred.

In addition to the data required for Level 1 models, Level 2 models require data on transformation rate constants and load or discharge rates.

For Level 3 models the same data are used as for Level 2 models but discharges are defined for each compartment and not globally as in the earlier models. In addition, Level 3 models require data on rates of transfer between compartments, which are generally estimated.

Level 4 models use the same data set as Level 3 models but the way the data is handled differs.

4.1.4. Examples of Models and Guidance for Their Use

The concept of modelling an ecosystem including different compartments by quantifying transfer and transformation was introduced by Blau *et al* (1975). Baughman and Lassiter (1978) subsequently introduced the use of such models for evaluative purposes, so that details of the behaviour of a chemical in the environment were predicted. The application of this idea on a large scale was promoted by Mackay who published the first comprehensive descriptions of Level 1 (Mackay, 1979), Level 2 (Mackay and Paterson, 1981) and Levels 3 and 4 models (Mackay *et al*, 1985a). Mackay published articles on the application of Level 3 models for 2,3,7,8-tetrachlorodioxine and linear alkyl benzene sulphonate (LAS) (Mackay *et al*, 1985b; Holysh *et al*, 1986).

Several other authors have published papers on Level 1 and 2 models which are slightly different from the Mackay version (Zitko and McLeese, 1980; Neely, 1982; Yoshida *et al*, 1983; McCall *et al*, 1983; Buckhard *et al*, 1985; Calamari *et al*, 1987; Burridge and Haya, 1988; Ryan and Cohen, 1986; Cohen and Ryan, 1985; Yoshida *et al*, 1987; 1988). The various models differ mainly in the definition of the "unit world" and the manner in which the partition and transfer coefficients are estimated.

The number of compartments, and their size and characteristics, such as density or organic carbon content, may vary between models. Even in the publications of Mackay sizes and characteristics of the compartments and the way of estimating transfer rates vary. In more sophisticated models the concept of a spatial gradient in the compartments has been introduced (Cohen and Ryan, 1985).

It is important to strike a balance between simple models which do not represent reality and models which are difficult to use. Level 2 models usually are of minor interest while Level 4 models should be used only for estimating disappearance of chemicals from the environment. Level 1 and Level 3 models are very useful simple models.

Level 1 models with an air/water/solids "unit world" present, on the basis of a limited number of data, the major feature of the environmental fate and behaviour of chemicals, i.e. the "target" compartment(s) where they are expected to accumulate. Level 3 models are of value to assess the distribution of a chemical in the environment in a more realistic manner.

However, representing the environment in the form of these unit world models constitutes a large simplification. An important drawback is that these models compute only one concentration value for each compartment whereas measurements indicate that actual concentrations in the environment may range over several orders of magnitude

(ECETOC, 1988). These models are only suited to provide an indication of concentrations in places far away from the source, i.e. background or average levels. The quantitative results of the models, therefore, must be used with care. But apart from that, these models may prove useful for assessing the fate behaviour of chemicals in the environment.

Multi-media models provide estimates with varying degrees of accuracy. This depends on whether it is possible to account for all phenomena that may be involved and to obtain realistic data, especially rate constants. The problem can be partially overcome by performing a sensitivity analysis and, or, by using a statistical approach. The models may be further improved by adapting the unit world to the region of interest. This has been done for various countries, such as Sweden, Canada, Japan and France (OECD, 1991).

European governmental authorities are developing models for priority setting among existing chemicals and hazard/risk assessment for new and existing chemicals. For the Dutch authorities the National Institute of Public Health and Environmental Protection (RIVM) is developing two models, DRANC, Dutch Risk Assessment system for New Chemicals (Toet *et al*, 1991), and PRISEC, Dutch PRIority Setting system for Existing Chemicals (Meent and Toet, 1992). The basis for these models, which are largely similar, is a multi-media model tailored for the Netherlands to calculate predicted environmental concentrations (PEC's). Further, these systems include modules for air emissions and a waste water treatment plant which provide the input for the multi-media model. Its output is used to evaluate potential hazard for man and the environment with an intake module to calculate uptake of the chemical by man, and aquatic and terrestrial organisms and an effect module to estimate predicted no-effect concentrations (PNEC's). Currently, the results of the multi-media module of PRISEC are being evaluated and compared with the results of a recently published Mackay Level 3 model (Mackay *et al*, 1992) by further ECETOC Task Forces.

4.2. AIR MODELS

4.2.1. General Aspects

Air acts as a medium for transport, dilution and physical and chemical transformation of chemicals. Advection and dispersion are undoubtedly the most important process in atmospheric modelling. Air dispersion models are used to calculate concentrations at given receptor points resulting from given discharges. Concentrations may be expressed as hourly, daily, monthly or yearly averages or frequency distributions.

There are two basic ways of describing dispersion, the so-called eulerian and lagrangian approaches (Seinfeld, 1975; Pasquill, 1974). Each of the two approaches represents a valid mathematical description of dispersion but both have inherently associated difficulties. For the purpose of practical computation, several approximations are developed which form the basis for common dispersion models.

4.2.2. Basic Models

Gaussian Plume Models: Gaussian plume formulae are common expressions for the concentration distribution in space and time based on the fundamental lagrangian approach. They describe dispersion in stationary homogeneous turbulence. The Gaussian Model is discussed in more detail in Section 4.2.4.

Box Models: In a box model, the atmosphere is subdivided in a number of boxes for which the dimensions are defined. In each box the chemical is assumed to be homogeneously mixed. For each box a mass balance equation is solved for each time step taking into account sources, sinks and fluxes of material across the boundaries. The model is simple to formulate and handle.

Eulerian Grid Models: Eulerian grid models solve the dispersion equation numerically. Concentrations are calculated for the grid points as averages in time and space. The computational effort involved in this modelling is substantial.

Random Walk Models: In lagrangian models particles move randomly within the grid space with prescribed transition probabilities. These models describe the dispersion of a passive tracer in a turbulent flow (Ashok and Britter, 1989). Individual air parcels are followed and the concentration of the tracer is computed for each parcel. Large computer storage and time is needed.

4.2.3. Data Requirements

The ability to perform dispersion calculations depends on the availability of appropriate input data, representative dispersion parameters and sufficient meteorological information relevant for the dispersion process. The amount and type of data required for an air model depends upon its sophistication. The minimum set of data which is always required are load or discharge data and wind speed. The data requirements are described below in more detail.

Chemical Data: More complicated models may require information on direct and indirect phototransformation. Chemical data is not required for simple models.

Environmental Data.

Terrain data: Most models assume flat terrain. Only the geographical coordinates of the receptor point are needed. Some models are capable of handling rough terrain (e.g. hills and urban areas) and require data on surface height, roughness length and the influence of the topography on wind direction and wind speed.

Meteorological data: These data include average wind speed, direction and profile, air temperature, a description of the turbulence, usually in the form of stability classes (Gifford, 1961; Pasquill, 1961; Turner, 1964; Klug, 1969; Manier, 1971; TA LUFT, 1986; Pasquill, 1971), height of the inversion layer, i.e. the ceiling height. In many cases the meteorological data will be insufficient in space and time. Generally only surface values are available and turbulence characteristics have to be estimated.

Load or Discharge data: These include geographical coordinates of the source, its height and exit diameter, chemical mass flow, volumetric flow of the total exhaust gas and its temperature. In the case of line, area or volume sources their dimensions are required. Usually the emission data are not detailed enough in space and time. This applies especially for accidental releases when source data are likely to be inaccurate.

4.2.4. Examples of Models and Guidance for Their Use

Gaussian Models: Chemical concentrations are described as a two-dimensional Gaussian distribution perpendicular to the mean wind direction. This implies the transfer of chemicals by advection to be greater than dispersion and hence can only be applied when the wind speed is greater than zero. Conventionally a minimum velocity of 1 m/s is used (Manier, 1978).

The model assumes fixed time steps which can be defined as, for example 0.5 or 1 hour. All other variables are regarded as constant during each time step. They may be changed for subsequent time steps.

On the basis of the data discussed in Section 4.2.3. the model calculates:

Effective source height: This is the sum of the release height and the plume rise. The plume rise is influenced by temperature differences, initial momentum, wind speed and stability of the atmosphere (Briggs, 1969, 1971).

Dispersion parameters: These are functions of the downwind distance from the emission source, stability of the atmosphere, release height and surface roughness.

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Several sets of dispersion parameters exist (Gifford, 1961; TA LUFT, 1986; Pasquill, 1971). For regulatory use in some countries these sets are defined by the authorities.

Dispersion parameters have been determined experimentally for distances greater than 100m but less than 10km. The model should not be applied outside this range.

The Gaussian Plume equation is applied to calculate concentrations at specified points. The Gaussian Plume formula should only be applied for flat terrain and a homogeneous atmosphere. For hilly terrain and urban areas, correction of wind speed and direction is needed. By incorporating statistical meteorological data the model can be used to calculate frequency distribution of concentrations for different receptor points. Most widely used are the Gaussian puff and plume models.

Simple Gaussian models are used for primary screening of single stacks in flat terrain. Only maximum concentrations from point and area sources are estimated. If the results indicate a potential air quality problem a more detailed screening is warranted. Simple screening can be performed using the so-called R91 Report (Clarke, 1979) (cf. Compendium A).

An example of an extended screening model for regular releases is the PTPLU model (Pierce *et al*, 1982). An improved screening model for accidental releases is VDI 3783, Part I (VDI, 1987) (cf. Compendium B).

The model most commonly used for regulatory purposes is the ISC model (cf. Compendium C). It is used to perform refined modelling analysis for stationary sources on flat terrain such as for stack design studies, regulatory compliance, evaluation and studies of gas releases.

An example of a model for calculating frequency distributions is the TA-LUFT model (TA LUFT, 1986) (cf. Compendium D). This model is required to be used in Germany to obtain emission permits and to demonstrate compliance with ambient air quality standards.

Advanced Models: Advanced models are used for special situations, for example turbulent dispersion in complex terrain, long-range atmospheric dispersion and chemically reactive plumes. The physical basis of all these models is a detailed description of the entire flow field including local effects of of buildings and other terrain perturbations on the turbulence and thus the rate of dispersion. The mean and turbulent wind fields taken from such numerical models are needed for random walk dispersion calculations.

Complex Terrain Models: Random walk models, also called Lagrangian stochastic models, are increasingly being used to model atmospheric dispersion for complex terrain. The advantages of these models are their simplicity, flexibility and ability to produce relatively accurate results. An example of this type of models is the Atmospheric Dispersion Modelling System ADMS, which can be applied for flat and hilly terrain, coastal transitions and to evaluate the local effect of building (cf. Compendium E). Applications of this model to calculate chemical concentrations in urban air are given by Rao *et al* (1989) and to assess turbulent dispersion in complex terrain by Etling *et al* (1986). A multi-scale model combining urban and regional modelling is described by Odman and Russel (1991).

Long Range Dispersion Models: Regional and global scale dispersion models and global transport and reactivity models are valuable tools to assess the global impact of local and regional emissions in air. Several box and grid models, are used to assess transport of air borne chemicals over long distances. Acid deposition in Norway has been investigated with a box model, as has quantification of long-range transport of sulphur over Europe (Eliassen, 1978). Typical applications using the box model ENAMAP have been described by Johnson (1983). The MESOS model was developed to simulate transport, dispersion and removal of chemicals released from point sources for distances up to 2,000km (Apsimon *et al*, 1985). This model calculates trajectories of discrete puffs from a given source taking into account statistical meteorological data along these trajectories. The Chernobyl reactor accident provided the opportunity to validate long-range dispersion models (Albergel *et al*, 1988; Hass *et al*, 1990).

Chemically Reactive Plume Models: The dependence of chemical reactions on turbulent mixing is of importance for many applications. For example, the reactions between air constituents like ozone and nitrogen oxide is of importance with respect to air quality (Seinfeld, 1986; Chang *et al*, 1987). For slow chemical reactions, turbulence succeeds in mixing the constituents before the chemical reactions become effective. Such situations can be described by box models. When the time scales of the chemical reaction are of the same order as the turbulent mixing time the reaction rates may be controlled by turbulence to bring the chemical species together (Janssen *et al*, 1990). A model to assess chemical concentrations in urban air incorporating photochemical reactions, turbulent dispersion and surface removal processes has been developed and evaluated by McRae *et al* (1982). A review of models for chemically reactive plumes can be found in Georgopoulos and Seinfeld (1986). The model CRPM incorporating mixing on both small and large scales has been validated for different emissions and meteorological conditions (De Arellano *et al*, 1990).

Combined Models: A model combining long-range transport and chemical reactivities has been developed (TREND) and applied successfully for SO and NO_x (van Jaarsveld and Onderdelinden, 1991). This model describes both short and long distance transport and average concentrations and deposition for time-scales from 1 day to more than 10 years. Later the model was adapted to describe the atmospheric behaviour of NH_x (Asman and van Jaarsveld, 1992).

Heavy Gas Dispersion Models: Models to asses the dispersion of heavy gases have been developed primarily to evaluate safe designs and operating procedures for transport, production and storage of flammable and toxic materials. Heavy gases usually form low, flat clouds which spread because of their density. Even gases with molecular weights less than air appear to behave in this way, e.g. ammonia, due to their low temperatures and/or the presence of aerosols. This process cannot be described by using normal Gaussian Models (Van Ulden, 1974).

Current heavy gas models assume that mass transfer occurs by entrainment of air across the cloud boundaries and that internal mixing is fast enough for the concentration within the cloud to be uniform, a so-called slab model (van Ulden, 1983). Air entrainment velocities are calculated as a function of turbulence levels, density differences and cloud speed. These functions are derived from laboratory experiments and field experiments.

As a heavy gas cloud dilutes its density approaches that of the surrounding air. At this stage the subsequent dispersion of the cloud is modelled using conventional Gaussian Models.

A variety of heavy gas dispersion models exist (Hanna and Drivas, 1987). In some cases the models include modules for estimating source strength of accidentally released chemicals. There may be four major phases included in hazardous gas modelling: source emission, initial dispersion, heavy gas dispersion and neutral density dispersion.

All model results have low predictive value due to uncertainty of the release data in an emergency situation and the variability of local weather situations. A number of dense gas dispersion experiments have been performed in laboratory wind tunnels and water channels (Puttock et al, 1982; Puttock and Colenbrander, 1985). This field of modelling is still in its early stage and further developments are expected.

Examples of heavy gas dispersion models are the numerical grid models CHARM (RADIAN, 1986) and FEM3 (Chan, 1983) and the slab models DEGADIS (Havens and Spicer, 1985) (cf. Compendium F) and WHAZAN (Kayes, 1985). More recently models

have been developed based on experimental situations, e.g. VDI 3783, Part 2 (VDI, 1990; Koenig, 1987; Koenig-Langlo and Schatzmann, 1988) which take into account effects of topography and obstacles. A Lagrangian model predicting drift of agricultural sprays has been developed which provides good agreement with field dispersion data (Hashem and Parkin, 1991).

Risk Assessment Models: Various model packages have been developed for risk assessment at chemical and petrochemical facilities involving manufacture, storage and transport. These are integrated sets of computer programs often coupled with an on-site weather station for automatic calculation of chemical concentrations in air in case of an emergency. An example is SAFETI (Lonsdale, 1975) (cf. Compendium G) which includes models for dense gas dispersion, passive atmospheric dispersion, free turbulent jet behaviour and evaporation from pools. Dispersion is calculated using box or Gaussian models.

4.3. SURFACE WATER MODELS

4.3.1. General Aspects

Surface water models simulate the fate and behaviour of chemicals which enter the environment via domestic or industrial, treated or untreated sewage outfalls, surface runoff and atmospheric deposition. Many models are designed to assess only discharges from sewage outfalls. This is because other sources often have a low contribution to the overall input and are more difficult to assess. The models described are frequently used by the chemical industry for assessing municipal discharges of household and trade chemicals and of chemicals in the effluent of industrial production sites. Some of the models are also used by authorities for the assessment of fate and behaviour of both new and existing high volume chemicals.

4.3.2. Basic Models

This chapter differentiates between large-scale dilution models which operate in a regional, e.g. a whole river, or national mode, and site-specific models which require a more detailed characterisation of the projected site. Spill models are treated separately although they may also be regarded as site-specific models. In practice, this distinction is not strictly valid because a dilution model can be used for site-specific assessment and a spill model can be considered as a dilution model. The distinction between the different models in the following subsections is therefore according to their main modelling purpose.

Simple dilution models assume a homogenous distribution of chemicals in a water body, i.e. for one given set of water current, sewage treatment and discharge conditions one average concentration is calculated. Site-specific models may also calculate the concentration profile of a chemical in the water body. Apart from simple river dilution models, all models take into account advection and dispersion of chemicals in water and one or more compound specific transport or transformation processes, such as evaporation, sediment adsorption and biodegradation.

Concentrations of chemicals released at many points into rivers through almost continuous sewage outfalls, municipal or industrial, can be estimated by river dilution modelling. The simulation comprises a relatively large region, typically a whole country and can be conducted at different levels of accuracy. The basic type calculates one average concentration for one given dilution factor. When more detailed data about dilution factors are available, chemical exposure can be expressed in the form of a frequency distribution of concentrations in the rivers considered.

4.3.3. Data Requirements

The data required to run a surface water model can be summarised as data on the chemical, the simulated environmental area and the load or discharge pattern.

Chemical data: These are in particular molecular weight, melting and boiling point, water solubility, ionisation constant, parameters to calculate sorption to sediment and biomass, volatilisation, phototransformation, hydrolysis, oxidation and biodegradation reactions.

Environmental Data: These vary according to the complexity of the model. Dilution type models require data on the stream dilution factor (SDF). Several approaches to define the SDF exist. It can be only a rough estimation in the form of one figure for a whole region or a more sophisticated estimation which needs data on the number and discharge flows of sewage treatment plants, and the river flow in different seasons. A frequency distribution of SDF is calculated with data on river flow and velocity at average and critically low river flow conditions, the discharge flow of tributary rivers and data on location and effluent discharge volumes of sewage treatment plants along these rivers.

Additional site specific input data may include system geometry and hydrology, such as width of river or estuary, depth of water column, water volumes, entering stream and non-point-source flows and sediment loads, salinity distribution, tidal currents and freshwater flow rate in estuaries, rainfall, evaporation rates, wind speed, amount of biomass, pH,

temperature, suspended sediment concentration, ion exchange capacities of the sediment, dissolved organic carbon, oxygen content, and advective and dispersive transport parameters.

Load and Discharge Data: Dilution models require data on the yearly quantity of the chemical on the market, the fraction of the chemical disposed of to the drain (for most household chemicals this fraction is 1.0) and its removal in different types of sewage treatment, i.e. mechanical, biological, physico-chemical. Site specific models require data on chemical loading for each simulated compartment. For spill models volume and density of the spill are needed.

4.3.4. Examples of Models and Guidance for Their Use.

Basic River Dilution Model: The simplest type of river dilution model is used for initial exposure assessments, e.g. by authorities for a first screening of chemical notifications. It usually simulates worst-case conditions of sewage outfalls in receiving waters and results in crude exposure estimations.

The model is a mass balance calculation estimating dilution of chemicals in a receiving stream. Chemicals are assumed to be non-reactive and to remain in the dissolved state (Holman, 1981; De Henau *et al*, 1986). For consumer product chemicals the concentration in the receiving surface water, C_{sw}, is calculated using the basic equation:

$$C_{sw} = \frac{M.F.(1-f.T)}{P.W.SDF}$$

where:

M	=	quantity of chemical sold/year, (tonnes)
F	=	fraction of chemical to drain, (1 for most consumer product chemicals)
f	=	removal in different steps of sewage treatment,
T	=	fraction of population served by sewage treatment,
P	=	population number,
W	=	flow of waste water/capita/year, (m^3/capita/year)
SDF	=	stream dilution factor.

This type of model uses one dilution factor for the region to be simulated. This can be an average or median value, a 90 or 95% percentile or a worst-case value, depending on the purpose of the prediction. Dilution factors may be different in different countries.

Simple river dilution models provide one single concentration value for a chosen dilution factor.

This method is used widely by industry and authorities and has been proven to provide useful approximations of exposure concentrations. However, as simple river dilution models use only one dilution factor for a whole region, often a rather low value is chosen. Thus, exposure concentrations are usually overestimated also because transfer and degradation processes are not taken into account. Seasonal changes of stream flow and variations in the chemical discharges are not taken into account either.

Advanced River Dilution Models: A better approximation of exposure concentrations can be obtained by using a distribution of stream dilution factors. These can be derived from a statistical evaluation of a comprehensive data base on stream and waste water flows at all discharge points along the rivers of the simulated area including seasonal changes. The concept was first developed in the US and is used in an US EPA river dilution model PDM3, Probabilistic Dilution Model Version 3 (US EPA, 1987) (cf. Compendium H). A model developed particularly for the assessment of household chemicals uses dilution factors for activated sludge, trickling filter and primary treatment as a function of sewage discharge volume and total number of treatment plants (Rapaport, 1988).

In Europe such a database exists in the Netherlands based on publications from the RIVM, National Institute of Public Health and Environmental Protection, which give details of sewage treatment plants (de Greef and de Nijs, 1990) and the RIZA, National Institute for Sewage Treatment, which defines the type of sewage treatment applied, i.e. mechanical, biological and physico-chemical (RIZA, 1989). The former includes information on effluent discharge volumes and type of receiving water, e.g. canals, rivers and polders, with details on depth, width and flow. The latter provides data on the number of inhabitants and industrial equivalents served by each type of sewage treatment. This information has been combined to calculate dilution factors for the discharge into canals, large and smaller rivers, tributaries, polder outlets and polder ditches (Versteeg et al, 1992). A similar data base has been developed for two large river basins in France (Crouzet, 1990). There is a need for similar information to be developed throughout the whole of Europe.

The more refined model PG ROUT (cf. Compendium I) takes into account advection, dispersion, adsorption and degradation in the receiving water body (Rapaport and Caprara, 1988; Caprara and Rapaport, 1991). It thus allows the calculation of chemical concentrations along the stream flow downstream of sewage outfalls.

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River dilution models using an advanced approximation of dilution factors result in a frequency distribution of exposure concentrations in the simulated area. The calculations can be conducted for varying stream flow conditions. The PDM3 model allows an estimation of how frequently a specified concentration, e.g. concentration of concern, could be exceeded within the whole registered area or at a specific site. PG ROUT provides, in addition, the possibility to model a selected river where concentrations can be predicted above and below each sewage treatment plant, at each drinking water intake or at any other location thus providing an approximate site-specific assessment.

Advanced river dilution modelling was applied to NTA, nitrilotriacetic acid, in US streams (Rapaport, 1988) and to DTDMAC, Ditallow dimethyl ammonium chloride, and LAS, linear alkyl benzene sulphonate, in Dutch surface waters (Versteeg et al, 1992). The latter includes a validation exercise in the river Dommel. The PDM3 model is frequently used by the US EPA for an initial exposure assessment for new chemicals in many product categories.

The PG ROUT model algorithms were applied to the river Rhine and validated with in-stream LAS concentrations (Hennes and Rapaport, 1989). The model predicts the concentration values and trends with reasonable accuracy, within a factor of 2. It was also applied to predict LAS concentrations throughout all routed US streams and was validated for several streams (Caprara and Rapaport, 1991).

Site Specific Models: Site specific models are designed to predict concentrations in well defined environments following known emissions. Such models are usually characterised by the use of extensive data describing the simulated site and a complex mathematical framework which subdivides the environment into several geometric elements (box or grid models).

River and Lake Models: The best models in this category are EXAMS, Exposure Analysis Modelling System (Burns et al, 1982; Burns and Cline, 1985), and WASP4, Water Analysis Simulation Programme (Ambro et al, 1987), (cf. Compendium J and K).

The box model EXAMS was developed by the US EPA as a first attempt to combine all relevant transport and transformation processes governing fate and behaviour of a chemical in surface waters in one model.

Although developed separately, WASP4 is largely similar to EXAMS. But, in addition it can simulate time-varying flows, estuaries and coastal waters and it contains its own sediment transport module which allows for sediment resuspension.

Due to the complexity of these models a considerable amount of data is needed. The required dataset may change with the purpose of the calculations (OECD, 1989).

Estuarine Models: In coastal areas, most of the industrial and municipal waste water is ultimately discharged into estuaries. Estuaries have several characteristics which are different from rivers and which are important in determining the fate of chemicals. The influence of the tide in estuarine waters results in large quantities of water being made available for dilution which subsequently gets flushed out to sea as the tide ebbs.

It is possible to obtain estimates of dilutions and residence times in estuaries using a steady state model such as that described by Ketchum (1951) and Pearson and Pearson (1965). This type of model is quite simple and estimates chemical concentrations in different "segments" along the estuary, on the basis of intertidal water volumes. The data required for this sort of model are the depths and widths in the estuary between the tidal limit and the estuary mouth, and the freshwater flow.

An estuary model predicting the fate of household chemicals is described by Lung *et al* (1990). It is a tidally-averaged, steady-state fate and transport model which enables one-dimensional and two-dimensional, longitudinal and vertical simulations. Estuaries are characterised by their hydraulic geometry, salinity distribution and freshwater flow rate. For discharging waste water treatment plants their location, water flow and treatment parameters are given. The model is readily available and can be operated on a personal computer. The results from such a model will give a broad indication of likely concentrations of a non-reactive substance at different distances from a point source.

The flow patterns which result from the tidal motions are often complex and will rarely be reproduced with sufficient accuracy using a steady state model, unlike rivers and still waters. The different densities associated with the salt/freshwater interface can also give rise to a density-driven circulation producing significant currents, especially in stratified and partially mixed estuaries. Where there is vertical stratification in the water column, mixing may be inhibited, causing chemicals to remain in the bottom or surface layer for considerable periods. If the estuary is wide the rotation of the earth can induce a horizontal circulation, the Coriolis effect, which can cause chemicals to travel along one side or another of the estuary, rather than being transported toward the estuary centreline and out to sea. The above features of estuaries need to be considered in relation to the estuary of concern.

There are several techniques for modelling tidal effects and numerous hydrodynamic models, some of which are readily available, e.g. WASP4 and others which have been

developed and used by consultants. These models can be extremely useful in assessing optimum discharge locations and in undertaking reviews of existing and proposed discharges for environmental impact assessments. They are generally site-specific and require fairly comprehensive data sets and modelling expertise to set up and interpret the results.

Spill Models: Spill models are designed to calculate distribution and concentration of chemicals following accidental releases into the environment. Depending on the time taken to run the model they may be used to determine the appropriate course of action in the case of an emergency. They may also help to plan storage and handling of a chemical in any given situation. By their nature, they are generally concerned with short time scales and acute toxic effects.

The processes that are most important in a spill situation depend mainly on the solubility, vapour pressure and the density of the chemical. These key parameters will determine whether the substance will evaporate, dissolve and be mixed throughout the water column, and whether it will float on the surface or sink to the bottom.

For soluble compounds the most important processes in the short term are those that determine the dilution, namely advection and dispersion. As time progresses other processes may become important although their removal rate has usually less effect than that due to the dilution. Consequently, many spill models that are designed for soluble compounds require extensive data sets to describe the dilution characteristics of the receiving water. Two-dimensional and three-dimensional models can be distinguished, with the latter incorporating vertical mixing. Plumes of higher concentration develop as a result of relatively fast vertical mixing while cross mixing occurs considerably slowly. One example of such a model is the ICI SPILL model (cf. Compendium L).

Poorly soluble chemicals that float will gradually spread over the surface forming a thin layer. They may eventually cover extremely large areas. The rate of spreading depends on the density of the chemical and net surface tension or spreading coefficient. For such chemicals volatilisation may be an important process, especially if the vapour pressure is high, otherwise there may be a balance between the rate of dissolution and the rate of volatilisation (Wolff and Poels, 1986). The Shell model CHEMSPIL (cf. Compendium M) is one example of a spill model for buoyant chemicals. For poorly water soluble chemicals that sink, adsorption to solids and biota will be an important consideration, however their dissolution may become important over time. For a review of the hazard assessment of floating chemicals after accidental spill at sea refer to ECETOC (1990b).

4.4. SOIL AND GROUNDWATER MODELS

4.4.1. General Aspects

Chemicals in soil and groundwater generally arise from agricultural or industrial activities. In these areas the main problems in recent years were related to the application of pesticides and the assessment and remediation of contaminated sites. Historically, modelling efforts in these two subject areas have been quite separate, probably due to different groups of workers being involved in two different, relatively new fields of environmental concern. There are similarities between the two areas.

4.4.2. Basic Models

There are two main types of model which are used to assess chemical concentrations in soil, those that simulate chemical movement in the unsaturated zone, from the soil surface down to the water table, and those that simulate chemical movement in the saturated zone, in the groundwater below the water table. Most unsaturated zone models, hereafter called soil models, are one dimensional and simulate vertical movement only. The output from these models is often used as input for saturated zone models, hereafter called groundwater models.

For most chemicals the two most important factors which influence their behaviour in the unsaturated soil zone are sorption and biodegradation. As a result of its relatively high carbon content and large amount of microorganisms the soil top layer is the most effective barrier preventing chemicals from leaching to groundwater. Deeper soil layers usually contain less carbon and biomass and retain most chemicals less effectively. Leaching depends on physico-chemical properties of the chemical and the soil water flux. The latter varies with climate, vegetation and soil properties. Special soil conditions such as water blocking layers or fissures are not normally included in models but can strongly influence leaching of chemicals.

Groundwater models usually evaluate two dimensional horizontal transport in groundwater, although some are three dimensional also including vertical movement. Organic chemicals can reach the groundwater zone either dissolved in water or, in case of an accidental spill, as organic liquids which may be immiscible with water. Groundwater moves from higher to lower water levels along the so called hydraulic gradient. Compared to flow rates of surface water such as rivers flow rates of groundwater are very low, ranging from 1 to 1,000m per year. If the permeability of soil is low and/or adsorption is important, then advective transport of chemicals may be reduced dramatically. Dispersion will result in dilution of dissolved chemicals in the

groundwater. Dispersion can occur by molecular diffusion and mechanical mixing. Due to lack of soil biota degradation processes are normally very slow in the groundwater, however there are exceptions. In the case of severe contamination on industrial sites microorganisms may accumulate on the soil particles forming a biofilm which can enhance biodegradation (ECETOC, 1990c)

4.4.3. Data Requirements

Different data may be required for soil models than for groundwater models. In the following subsections these data are described in more detail.

Chemical Data: Most compound specific data models are similar to those used in other model systems. These are discussed above. Additional data that may be required are diffusion and adsorption coefficients. For spill models bulk mass density and viscosity are required.

Environmental Data: For soil models the type, number and complexity of the environmental data are characteristic for each model. The differences between models tend to reflect the complexity of the soil matrix and the number of different processes which are included in the model.

To simulate the behaviour of an organic chemical in soil with sufficient accuracy the soil is divided into horizontal layers. The layers can differ considerably with respect to their sorption and biodegradation potential. Soil texture refers to the particle size distribution and has to be known for each soil layer. To simulate a worst-case situation soil types containing large portions of sand and low organic carbon content should be used for modelling.

The porosity and density of the soil may influence up and downward transport of chemicals via soil-water and air. Chemical transport to groundwater by water flow can be very rapid in soil with a very high porosity, especially if there are gaps and fissures in the soil/rock structure. Under dry soil conditions dissolved chemicals can move upwards induced by plant transpiration and evaporation of soil-water.

Climate data are important for soil simulation models such as the amount of rain (leaching), the temperature (evaporation, biodegradation and hydrolysis), the wind speed (evaporation) and the sunlight intensity (photodegradation).

Erosion processes will influence transport of compounds as well as the amount of water which will be available for vertical movement. In this context the slope of the modelled soil area is important.

For groundwater models the following aquifer data are required, transmissivity, storage factors, recharge factors, hydraulic conductivity, permeability, withdrawal rates, e.g. pumping rates, and well locations.

Load and Discharge data: Load and discharge to soil can be continuous or discontinuous, point source or diffuse. Deposition may be due to pesticide application but airborne chemicals can also reach the soil by dry and wet deposition. Quantitative data for wet and dry deposition are rare and highly dependent on local meteorological conditions.

For groundwater models data on the location and the concentration at the source are required.

4.4.4. Examples of Models and Guidance for Their Use

Soil Models: PRZM, Pesticide Root Zone Model, (cf. Compendium N) is the most widely used soil model and is discussed as an example. It is a soil leaching model developed for the assessment of pesticide leaching and is widely used by authorities, universities and industry. It has been validated by comparison with field data (Jones and Estes, 1987; Hegg *et al*, 1988; Smith *et al*, 1990).

Other models are available, e.g. SESOIL - which is a soil leaching model capable of predicting the migration of organic chemicals and metals through the unsaturated soil zone. The model predicts partitioning of the chemical between the dissolved, gaseous and sorbed phases. Output data is limited to average monthly values. The model cannot be applied to sites showing large vertical variations in soil properties (cf. Compendium O).

Groundwater Models: The ILLINOIS STATE Random Walk Model (cf. Compendium P) is an example of a groundwater model. It is also available under an alternative name PLASM. This model is designed to simulate one- or two-dimensional solute transport, including the effects of advection and dispersion, on chemical concentrations.

The model has a limited capability to simulate chemical reactions and adsorption processes. These processes are not modelled explicitly but are generally inferred by use

of a retardation factor. Although the model is designed to deal with two-dimensional problems the flow model can be made quasi three-dimensional by the use of layers.

Combined Soil and Groundwater Models: A combined soil and groundwater model termed RUSTIC is available (cf. Compendium Q). It is essentially a combination of the soil model PRZM and the groundwater model SAFTMOD, a saturated zone flow and transport model. The model, available from the US EPA, has not been extensively used or validated.

Non-Aqueous Phase Models: Non aqueous phase liquids (NAPL's) are poorly soluble compounds that will remain in the free phase either floating on top of the groundwater table or at the bottom of the aquifer. Chemicals commonly found in groundwater such as hydrocarbons fall into this category.

The viscosity of a substance will affect permeation and also the effective storage capacity of the soil. Schwille (1981) has shown that depending on viscosity chemiclas tend to be retained in the soil in amounts of about 0.3% to 5% by volume of soil, following the passage of the organic liquid. This points to the possibility that large quantities of immiscible liquid are retained as droplets dispersed within the pores of the aquifer, Even if the bulk of the NAPL is removed these droplets may remain and dissolve over time in groundwater.

The solute transport described in the above paragraphs may well be important for some NAPL's where certain components may dissolve in groundwater. However, transport of the bulk of the NAPL itself is much more important and is generally governed by bulk density and its viscosity. For buoyant substances density differences of 1% between the substance and the surrounding water are known to influence fluid movement significantly and in most cases the densities of organic liquids differ from that of water by more than 10%. For dense substances, transport has a strong vertical component and upon reaching the bottom of the aquifer, the aquitard, they will tend to flow along the physical gradient under the force of gravity. This transport may be relatively unaffected by the actual groundwater flow.

During dissolution of such products equilibrium is rarely achieved. This implies that the volume of groundwater that could be contaminated by a NAPL is much larger than that calculated by assuming dissolution to the solubility limit (Mackay and Roberts, 1985). If the bulk of the compound then lies on top of the water table or at the bottom of the aquifer it can become a much larger area source for soluble components to dissolve into the groundwater.

There are only a few models to predict the behaviour of NAPL's. One example is the model MOFAT-2D (also called MOTRANS) available through the Scientific Software Group (cf. Compendium R).

SECTION 5. QUALITY ASSURANCE AND VALIDATION IN ENVIRONMENTAL MODELLING

Originally, environmental computer models have been (and are still being) developed and used as research tools. The potential usefulness of these models is recognised by decision makers, such as governmental authorities and industry, who have to make decisions on permits, hazard assessments and monitoring strategies.

While developing and using models, researchers improve understanding of environmental processes and usually improve the models accordingly. They are aware of the limitations of the model and the uncertainties of the results. Decision makers, however, use models solely as management tools without having to understand the environmental and other processes and they may not be sufficiently aware of the limitations of the model and uncertainties of the results.

Since currently an increasing number of models are being developed especially for decision makers it is timely to define criteria to ensure the quality and performance of the models by applying good modelling practice and performing proper model validation.

5.1. GOOD MODELLING PRACTICE

Several aspects are of importance in relation to good modelling practice, that is provision of proper documentation, peer review of the model code and documentation, and updating of the model when appropriate.

Proper documentation for a model should include at least a user guide and a functional specification. Furthermore, documentation could cover a discussion of the (environmental) processes that are incorporated in the model including a rationale for their selection and a report of (field) validation exercises.

Papers in scientific journals have to pass exacting tests such as peer review before being accepted for publication and, after publication, other scientists have the opportunity to react, usually in the same journal. For peer reviewing of computer models distinction has to be made between the documentation for the model and the computer code itself. Many models have been insufficiently documented or the documentation is not readily available. Thus, the documentation for these models has not been peer reviewed or scrutinised by other scientists. With respect to computer codes the situation is even worse. For computer codes simply no system of peer review exists. Apart from that, in most cases computer codes can not be scrutinised since source codes normally are not made available.

Finally, no systematic approach exists for updating of computer models. Environmental science is multi-disciplinary and developing rapidly. Environmental computer models usually are made by one or a small group of scientists, often specialised in one or a small number of disciplines. It is frequently the case that models, even in the development stage, are not up to date with current scientific knowledge in all relevant disciplines. Furthermore, after the model has been issued updating usually ceases completely. Thus both the users of models and the decision makers using the results of the models, may be misled by the data generated due to mistakes, obselesence or ignorance of the steps taken by the mathematical modeller.

The equations used in the calculations are often empirical. Some of these equations have been validated extensively by experiment and are highly reliable. Others, however, may be based on a small data set and have a low reliability. Many of these equations are valid only for a specific group of chemicals and sometimes they are applied inappropriately. Since knowledge in this area is developing rapidly, new and improved equations and correlations regularly become available. It should be possible for the user to incorporate these improvements into the model.

When considering quality assurance of environmental computer models, this should start with a widely accepted systematic approach of peer reviewing and updating of these models. Ideally, (potential) users should combine resources for instance at an inter-industry level to set-up such a systematic approach, to define the type of models that are required and subsequently to peer review and update these models.

In peer reviewing a model the following aspects should be addressed.

Documentation:

- scientific quality and completeness of the total documentation,
- user friendliness of the user manuals.

Computer code:

- does the model operate as described in the documentation,
- there should be no hidden (fixed) input data in the model, it should be simple for users to change all chemical and environmental parameters that are variable,
- all potential relevant processes should be represented,
- all processes and correlations should be clearly distinguished,
- calculation procedures should be defined.

Model operation:

- general availability of required hardware and software,
- user friendliness of the model,
- input and output structures should be specified.

Procedures to update the model require that in the computer code the descriptions of processes and correlations are clearly separated. Subsequently, the validity of each process and correlation equation can be assessed and updated regularly.

In this way, a limited number of environmental computer models would become available, for which the quality is defined and guaranteed. This will lead to a reduction of the large number of currently available models for which the authors claim equal suitability for the same job to a relatively small number for which confidence can be established. For commercial applications, there is a tendency to try to develop models which can be used by laymen. If models are to be made into powerful tools it is clearly time to start developing models on a professional basis with high quality specifications. Once these models become available it is still questionable whether they should be used by laymen rather than by specialists who are aware of their characteristics and limitations.

5.2. MODEL VALIDATION

Model validation in terms of comparing model output with field observations is the last stage in assuring the quality of environmental computer models. It is only after the quality of the computer model code has been assessed and found to be satisfactory, should one embark on field validation exercises.

The major problem in field validation of environmental computer models is the large spatial and temporal variability of experimental data measured in the field. It is not abnormal for the concentration of a chemical in sediment samples taken from within the same square metre to vary by more than a factor of 10 or even 100. Thus when the field validation of an environmental computer model consists of comparing the computer calculations with a limited number of field measurements, which may be lacking sufficient information on the essential environmental conditions, the exercise is bound to fail.

An adequate field validation exercise would require an extensive set of field observations which would allow a full statistical evaluation of the data. Moreover, for each data point the relevant environmental information should also be available to ensure that calculations based on one set of environmental conditions are not compared with field observations obtained under a different set of conditions.

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It must be kept in mind that all the models described earlier predict the mean concentration, whereas a single experimental observation constitutes only one sample from the hypothetically infinite range of observations from that identical experiment. Thus, it is not to be expected that single observations agree precisely with the predicted mean concentration. Nevertheless, because it is practically impossible to repeat an experiment under identical environmental conditions, one must be content with at most a few experimental data points when testing any available model.

SECTION 6.   CONCLUSION

Estimating environmental concentrations of chemicals is a key process in hazard assessment which compares the predicted environmental concentrations (PECs) to the no-effect concentrations (NECs). Fate and exposure models are useful tools for estimating environmental concentrations and are increasingly applied in many different situations.

Considering the great number of models available, potential users need guidance on the choice of the model to meet their specific problem. The type and sophistication of modelling required will vary according to the situation. Even for a specific purpose there may be several suitable models from which to choose.

Before selecting a model, the fundamental problem is to define precisely the question a model is intended to answer and the level of accuracy required. Once, this has been decided, it will be possible to select a model which includes all the relevant processes and which is designed for the appropriate spatial and temporal scales of the problem at hand. Once having chosen a suitable model and obtained data it is still easy to misinterpret the model results if the underlying principles are not properly understood. Very often, the problem does not lie in the model itself but in the way that it is used and in the selection of the input data. It is thus essential to understand the assumptions and limitations of the different modelling approaches. For this reason models should be used only by specialists and it is essential to have good documentation describing the use of the model and the input data required.

When presenting model results all assumptions and data used should be reported. In this way the model results can be used by others to examine results applying different input data.

In practice, modelling tends to be done in two main areas. The first is the assessment of the fate of chemicals at a specific location, the purpose being to predict concentrations resulting from the emission to a known environment. The second is the screening and regulatory control of new and existing chemicals where the purpose is to evaluate the potential exposure, typically on a much larger regional or global scale. These two areas of modelling require rather different approaches. The former requires suitable relevant data and model processes applicable to the site. In most, if not all cases, local situations are highly complicated and knowledge about the fate and behaviour of chemical compounds in the local environment is limited. The results of these site-specific models must be considered as an approximation of real concentrations. The second case requires definition of a more generic environment which will be representative of the typical use of the chemical. This can be conducted at a screening or more advanced level.

At a screening level an "average" environment is envisaged. Multi-media models are of particular interest at this level. Simple air, water and soil models can be used on the basis of a "median" or "worst-case" assumption. For the latter the main problem is to define the situation: it is always possible to define a "worst-case" scenario but this can be very unrealistic especially if the "worst-case" assumptions are accumulated.

At an advanced level the same simple, or more sophisticated air, water or soil models, can be used but with more comprehensive input data representing the frequency distribution and which will represent all the possible cases. This will lead to a statistical distribution of the predicted concentrations. This approach is commonly used for river discharge and air releases but is not used to the same extent for the soil situation.

Traditionally validation means comparing predicted results with field observations. Only in the case of site specific modelling is a strict validation of a model possible. For screening modelling it is not possible to ensure a proper model validation since no specific situation is available as a reference. Validation of probabilistic approaches to modelling is possible but this requires a great amount of measured environmental concentrations in different locations which allow the computation of a statistical distribution of the analytical results. Model validation has many aspects: the model processes and assumptions must be valid for the modelling purpose, the input data must be well established and the computer code must be validated. Comparison with field observations is the last stage of the validation process.

In conclusion it is important to note that environmental fate and exposure models can be powerful tools for evaluating the potential hazard of chemicals released in the environment; (hazard is being defined as a function of environmental concentration and toxicity). They can save time and allow complicated calculations. Models are instrumental in highlighting areas of particular importance, indicating sensitivities and identifying gaps in knowledge. Nevertheless, proper validation procedures should be developed to ensure the scientific quality of the models.

COMPENDIUM ON THE MORE COMMONLY USED MODELS.

COMPENDIUM A. R91 REPORT

The U.K. Pollution Inspectorate (HMIP) use the so-called R91 report (Clarke, 1979), written by the National Radiological Protection Board (NRPB) as the basis for simple predictions of the behaviour of radioactive releases to the atmosphere. This report deals with the estimation of dispersion in the short and medium range, that is from about 100m to a few tens of kilometres from the source, and is based upon a Gaussian plume model. A scheme is presented for categorising atmospheric conditions and values for the associated dispersion parameters are given. The report deals with specific meteorological conditions and considers releases of up to 24 hours duration. It also considers longer term average concentrations, typically annual average concentrations.

Data requirements: The minimum data requirements are the basic Gaussian formulation data (release rate, wind speed, standard deviations of the vertical and horizontal Gaussian parameters, effective source height).

Output: The output is simply the chemical concentration, expressed either as the annual average or the amount present based on a unidirectional wind speed at specified distances from the source up to a maximum of 100km.

Experience/Validation: The R91 scheme was developed by the NRPB for modelling the dispersion of radioactive gases. Although it is used mainly by the nuclear industries, it is also used by several other organisations in government and industry since the dispersion problem is exactly the same. No major validation exercises have been reported.

Limitations: The R91 modelling scheme is limited by the general applicability of the Gaussian plume approach which is only applicable to buoyant gases. No account can be taken of radioactive or chemical transformations and no ground deposition can be taken into account.

COMPENDIUM B. VDI 3783. DISPERSION OF EMISSIONS BY ACCIDENTAL RELEASES

VDI 3783 presents a computation method to estimate the dispersion of emissions by accidental releases on the basis of the Gaussian dispersion equation. The concentrations calculated cover a mean dispersion situation as well as the worst possible dispersion within the frame of the model.

On the basis of the spatial structure and the temporal variation of the strength of the source, the ambient air concentration with its spatial and temporal variation is calculated by the superposition of the concentration of instantaneous point sources which emit in succession.

Data requirements: The source configuration and the temporal variation of source strength, volume flow rate and temperature of the release as well as the height of the source are required. In the worst case situation the wind speed is set at the lowest value, viz 1m/sec. The wind speed for the mean dispersion situation is equal to the most frequent wind speed at neutral atmospheric stability, measured at a representative station.

Experience / Validation: ask G.H. to provide

Output: The maximum concentration value and the temporal variation of concentration is calculated for the dispersion situations mentioned.

Limitations: Calculations are only made for standardised meteorological situations in connection with safety studies according to administrative regulations. The method should not be used for calculating acute industrial accidents or for reconstructing past accidents.

COMPENDIUM C. INDUSTRIAL SOURCE COMPLEX DISPERSION MODEL (ISC)

The Industrial Source Complex Dispersion Model (ISC) is an example of an advanced Gaussian Plume model. It contains a number of options that are designed to consider atmospheric turbulence and gravitational settling (dry deposition), complicated source configurations and special atmospheric effects. The model accepts various source types such as point, line, area and volume sources. Additional options include site-specific wind profiles, vertical temperature gradients, stack tip downwash, building eddy effects, plume rise calculated as a function of downwind distance, and time dependent exponential decay of chemicals (Wagner 1987).

> **Data requirements:** ISC requires locations of the source, emission rate, stack height and inside diameter, stack gas exit velocity and temperature. Optional inputs are source elevation, building dimensions, particle size distribution with corresponding settling velocities, and surface reflection coefficients. The ISC-short-term model requires hourly surface weather data including hourly stability class, wind direction, wind speed, temperature and mixing height. The ISC-long-term model requires stability wind rose data, average afternoon and morning mixing heights, and average air temperature. For each receptor point coordinates and optimal ground elevation are required.

> **Output:** Average concentrations or total deposition are calculated at each receptor point for any desired combination of sources. Tables of highest and second highest concentration at each receptor point for each specified time period.

> **Experience/Validation:** The ISC model is widely used within and outside the US Environmental Protection Agency (EPA) in regulatory applications. The model has undergone an extensive review and peer revision to correct and improve the technical features of the model.

> **Limitations:** Sources are modelled as continuous. Complex terrain is not addressed.

COMPENDIUM D. TA-LUFT - AUSBREITUNGSMODEL

The TA-LUFT model is a climatological Gaussian plume model which estimates annual average concentrations and percentiles of the annual frequency distributions of concentrations downwind from a point source for given receptor points or averages in space (TA LUFT, 1986). The model has been applied in order to calculate the ground level concentration of gases, particles and chemicals emitted from a point source or several emission sources by summing up their contributions. Removal processes such as dry deposition are included. Plume rise is calculated as a function of downwind distance, according the Briggs-formulas (Briggs, 1969).

Data requirements: The TA-LUFT model requires location, and height of the point-source, emission rate, exhaust volume rate and temperature at source. Optional input is the particle size distribution. Meteorological input are the frequencies of the joint occurrences of wind speed, wind direction and stability classes, corresponding to the scheme of Klug/Manier. For each receptor point the geographical coordinates are required.

Output: The annual average concentration and the cumulative frequency distribution of concentrations at each receptor point or for specific averages in space (so called areas of estimation) are calculated.

Experience/Validation: The TA-LUFT model is widely used according to the technical guidance of the German Air Pollution Control Act in the context of air quality control. The results of calculations, especially the annual averages, are in fairly good agreement with values actually measured (long-term value by factor 2, short-term value by factor 4 (Biniaris and Wilhelm 1988)).

Limitations: The TA-LUFT model is an empirically derived model. The calculations are based on meteorological data which are monitored during a ten year period. Specific and incidental emission conditions cannot be considered. Complex terrain is not addressed.

COMPENDIUM E. ADMS - ATMOSPHERIC DISPERSION MODELLING SYSTEM

The ADMS system is being developed by Cambridge Environment Research Consultants in the UK. The aim is to produce a quality assured computer code to predict mean variance, and related statistical information for air concentrations, time integrated air concentrations and ground level deposits. The model is applicable to flat or hilly terrain, coastal situations and local building effects. The model provides estimates of uncertainty in its predictions.

Data Requirements: As well as source data and meteorological data, the model requires specific information on the site buildings, surface (roughness) characteristics and the topography of the surrounding land. Data files are supplied with the model which define standard constants, parameters and default values.

Output: The output is provided in the following forms:

■   configuration, version, parameter and run log,

■   warnings, limitations and uncertainty log, tabulated printer output on a user specified grid, and data files for subsequent graphical output.

No graphical output is provided although input and output are possible at intermediate stages, so that linkage with other user software is possible.

Experience/Validation: The ADMS package was completed in March 1991 and followed by a six month trial period prior to final acceptance by the sponsoring organisations. Certain parts of the model are available. ICI Group Environmental Laboratory have used the computational flow module to generate three dimensional wind fields in the Grangemouth area in Scotland and have used the results as input to an random walk transport model.

For validation the model performance will be assessed against selected data sets as part of the project development. The theory is well cited and peer reviewed (Carruthers *et al*, 1988, Hunt *et al*, 1988, Belcher *et al*, 1990).

Limitations: The model represents steady state and is not designed to handle dense gases. The flow equations are good at dealing with flow over a hill but are not as good at representing the flow in the lee of a hill. Although the model handles buildings, these are represented as simple rectangular blocks and may not reproduce very accurately the effects of some structures. The meteorological data need to be in a specific detailed format which

may be difficult to generate. In the UK the Meteorological Office has the appropriate extensive data sets that are needed.

COMPENDIUM F. DEGADIS

The Dense Gas Dispersion Model DEGADIS was developed by Havens and Spicer (1985) and is an adaptation of the Shell HEGADAS model described by Colenbrander (1980). It is designed to model atmospheric dispersion of ground level source dense gas clouds released with zero initial momentum into an atmospheric boundary layer over flat terrain. The model deals with situations in which a blanket of gas which is denser than air spreads laterally by density driven forces which entrain air at the top of the blanket by wind shear and also at the advancing front. The blanket centre is assumed to remain stationary over the source.

It describes the dispersion processes which accompany the ensuing gravity driven flow and the entrainment of the gas into surrounding atmospheric boundary layer. If the gas release does not exceed the potential atmospheric rate of uptake gas is taken up directly by the atmospheric flow and dispersed downwind. If the gas release exceeds the potential atmospheric uptake rate a dense gas blanket is formed over the primary source which is modelled to incorporate air entrainment at the gravity spreading front. Downwind dispersion is modelled with a power law concentration distribution in the vertical direction and a modified Gaussian profile in the horizontal direction with a power law specification for the wind profile.

> **Data requirements**: The model requires the release rate and physical properties of the chemical such as molecular weight, initial temperature, and heat capacity constant. The ambient meteorological conditions are described by wind speed, Pasquill stability class, air pressure and humidity.

> **Output**: Calculated are the centreline concentration, the mixture density and the mixture temperature of the cloud. Optional are ground level iso-contours for given concentration levels.

> **Experience/Validation**: The DEGADIS model has been compared with observations in several experiments. Compared with other models of similar type the DEGADIS model predictions are closest to the observations.

> **Limitations**: Complex terrain, building wake effects, buoyant cloud, concentration fluctuations and dry and wet deposition are not handled.

COMPENDIUM G. SAFETI

The SAFETI package is an integrated set of computer programs for automatic and continuous risk assessment of chemical and petrochemical facilities involving manufacture, storage and transport. The modelling sequence includes models of dense gas dispersion, passive atmospheric dispersion, free turbulent jet behaviour and evaporation from pools. The dispersion models used are box models and Gaussian models.

Data requirements: SAFETI needs information describing the plant, i.e. the inventories of hazardous substances, details of piping lengths and interconnections between vessels, to calculate the inventory available for release in the event of a rupture or leak. Information on the failure frequency of process piping and vessels is required. The weather data needed are wind direction, wind speed and atmospheric stability. Also the distribution of the surrounding population must be supplied in order to calculate the overall impact of releases.

Output: The risk contour plot is the standard method of presenting the overall results of risk assessment. It consists of a series of contours which indicate the level of risk to a person at a particular location, that is the frequency of fatality for individuals from causes associated with the releases in question. Another output is the F-N curve, which indicates the level of risk to the population in general, but gives no information on the location of this risk. The graph plots frequency against number of fatalities.

Experience/Validation: SAFETI is a system for risk analysis in relation to planning activities. A simulation of a tank rupture incident (Lonsdale, 1975) has been done by the authors of the system.

Limitations: Complex terrain, building wake effects, chemical reactions in plume are not handled.

COMPENDIUM H. PDM3

PDM3 (Probabilistic Dilution Model) is a US EPA river dilution model frequently applied for initial exposure assessments of chemical notifications (US EPA, 1987). The calculations are based on a comprehensive database on the simulated, usually large, area. The model is used to calculate the surface water concentrations of chemicals released by point source discharges and takes into account the variability of stream flow. It calculates a probability distribution of a released chemical, e.g. to assess how frequently a specified concentration can be exceeded. Selecting only part of the input data for a certain site allows a site specific assessment. The calculation is based on mass balance.

Data Requirements: The data needed on chemical release and on the simulated rivers and discharging sewage treatment plants are listed in the OECD Compendium (1989). For the US a large database is available from the EPA.

Output: The results of the simulations are given in the form of a table containing the specified concentration, the percentage of time or release events that this concentration is exceeded, and the number of release days per year during which the specified concentration is exceeded.

Experience/Validation: The PDM3 model is being used for an initial exposure assessment for several hundred chemical notifications per year.

Limitations: Discharge events are not correlated with stream flow, i.e. seasonal changes in release are not simulated appropriately. An extensive database on stream flows and discharge points is only available for the US and would need to be developed for other countries. Removal processes of the chemical from the water body (e.g. by biodegradation or adsorption) are not considered.

COMPENDIUM I. PG ROUT

PG ROUT can be considered as another level of river dilution modelling (Rapaport and Caprara, 1988; Caprara and Rapaport, 1991). It allows the calculation of chemical concentrations further downstream from sewage outfalls by taking into account advection/dispersion along the stream flow and degradation/adsorption processes between the sewage discharge locations.

PG ROUT is a large scale exposure model which was developed to predict the distribution of consumer product chemicals in rivers but can also be applied to the assessment of any chemical which is discharged through municipal sewage treatment plants. The algorithm of the model is a one-dimensional advective/dispersive equation. The in-stream removal of the chemical as a result of degradation and adsorption is calculated by a first-order lump term.

> **Data Requirement:**
>
> ■   **for the rivers:** in the simulated area: river flow and velocity at average and critically low river flow conditions, discharge flow of tributary rivers, water quality data (O_2, NH_3, BOD etc.), and location of drinking water intakes.
>
> ■   **for the sewage treatment plants:** along these rivers: location, type -(mechanical, biological, physico-chemical; municipal or industrial operational parameters), effluent discharge volume, and population connected to the plant.
>
> ■   **for the chemical:** yearly usage per capita, fraction disposed of to drain (e.g. for most household chemicals = 1.0), removal in the different steps of sewage treatment (mechanical, biological, physico-chemical), in-stream elimination (mainly biodegradation, but also photolysis, sorption/settling, volatilisation, hydrolysis) which are summarised in a lumped first-order term.

The first two sets of data are provided by US EPA databases which are accessed by PG ROUT (limited databases are available in Europe, e.g. the Netherlands, and France). The third set of data is inserted in the model for simulating a particular chemical.

Output: PG ROUT calculates the frequency distribution of concentrations versus the number of river kilometres in the considered region, i.e. the fraction of river lengths that fall into a given concentration range. This takes into account the chemical loads at the points of discharge along the routed rivers and in-stream elimination further downstream. The simulation can define areas of relatively elevated concentrations where further monitoring or a more detailed modelling would be advisable. PG ROUT provides also the possibility to

model a selected river. Concentrations can be predicted above and below each sewage treatment plant, at each drinking water intake or at any chosen river location.

Experience/Validation: The model algorithms were applied to the river Rhine (Hennes and Rapaport, 1989). The database covers 850 river kms and 34 municipal sewage treatment plants. A validation exercise was conducted for LAS by comparing predicted concentrations with monitoring data. Although the Rhine input data needs to be updated and the analysed LAS concentrations are only derived from MBAS measurements (50% of MBAS), the model predicts the trend and the concentration values with reasonable accuracy (within a factor of 2).

The PG ROUT model which was developed for the US by using EPA data bases includes river locations for > 800,000 km and 11,500 municipal sewage treatment plants (Caprara and Rapaport, 1991). It was applied to predict LAS concentrations throughout all routed US streams. Validation was carried out for LAS concentrations in the Rapid Creek below a particular sewage outfall which achieved also an accuracy within a factor of 2. Other validation exercises were carried out in the US for NTA and LAS (Caprara and Rapaport, 1991).

Limitations: Predictions using PG ROUT are more accurate than those obtained by simple or advanced river dilution modelling without in-stream degradation of the chemical. However, the necessary databases need either to be developed or updated in Europe. Promising starts exist in the Netherlands; their database can principally be used for PG ROUT modelling. Starting data are available for the river Rhine and for France.

PG ROUT is applicable for predictions over large regions while taking maximum advantage of site specific data that are available on rivers and sewage treatment plants. Although the model can be operated in a river specific mode its strength is in its large scale predictions. A detailed fate assessment of a specific location, such as the distribution within the water column, will require more descriptive parameters of the site concerned (as in the EXAMS model).

COMPENDIUM J. EXAMS

EXAMS (Exposure Analysis Modelling System) was developed by the US EPA as a first attempt to combine all relevant transport and transformation processes concerning the fate of a chemical in surface waters in one model (Burns *et al*, 1982; Burns and Cline, 1985). It is probably the most widely used surface water exposure model. EXAMS is part of the program package MEXAMS (Felmy *et al*, 1984a) which includes the exposure model part and a speciation model named MINTEQ (Felmy *et al*, 1984b). MINTEQ calculates the species distribution of inorganic or organic chemicals in the aqueous phase, i.e. the formation of their various complexes.

EXAMS is a box model which divides the simulated space into physically homogeneous elements. The different boxes are connected through advective and dispersive flows. Each box is a distinctive volume element of the system and contains water, sediments, biomass, dissolved and sorbed chemicals. Within the box an ideal mixing is assumed.

The model combines chemical loadings, transport processes from the system and transformation processes within the system into a set of differential equations and uses the law of conservation of mass as an accounting principle. The calculations can be conducted in different modes: (a) steady-state conditions regarding chemical input and environmental parameters, (b) pulse chemical loadings but steady-state environmental parameters, or (c) changing chemical loadings in determined intervals or pulse loadings and environmental parameters changing at regular intervals.

> **Data Requirements**: Due to the complexity of the model a considerable amount of data is needed (cf. OECD compendium; 1989). The chosen dataset differs with the purpose of the calculations. EXAMS is written in modular form and consequently certain modules may be excluded and replaced by rate constants experimentally determined.
>
> **Output**: The EXAMS models provides the following information:
>
> ■ the environmental concentration of the chemical according to the chosen loading pattern (exposure),
>
> ■ the distribution of the chemical and the relative dominance of the different transport and transformation processes (fate),
>
> ■ the time required for an effective purification of the system after termination of the chemical loadings (persistence).
>
> **Experience/Validation**: The EXAMS model has been extensively reviewed and validated by independent experts (Games, 1982; Hern *et al*, 1983; Reinhert and Rogers, 1986; Kolset and

Heiberg, 1988). For example, Schwarzenbach *et al* (1979) applied the model to the fate of 1,4-dichlorobenzene in Lake Zurich (epilimnion, hypolimnion, and benthic sediment) and verified the calculations with measured data.

Limitations: Certain limitations to the applicability of EXAMS derive from its design for rivers, lake and ponds. The program is less suitable for estuaries and coastal areas where water flow patterns are much more complex. It is also not designed for the simulation of chemical spills because chemical loadings are assumed to be longer term and time averaged. Its is not valid for concentrations above trace levels since the linear isotherms are only valid for low concentrations. Other limitations concerning the behaviour of particular chemicals are well summarised by OECD (1989).

COMPENDIUM K. WASP4

WASP4 (Water Analysis Simulation Programmes) is a refined surface water model designed to predict concentrations of chemicals arising from various source types such as point sources, diffuse sources, continuous or time-varying. The model will cater for most conventional organic chemicals and can be applied to all types of aquatic systems, including estuaries and coastal waters. It contains the same chemical transformation reactions and mass balance principles as for the EXAMS model, together with a hydrodynamic module which will compute one dimensional time-varying flows for tidal environments. Like EXAMS, this model will provide information about the fate of chemical breakdown products. Details of the model are given in Ambrose *et al* (1987) and a useful overview is given by OECD (1989).

> **Data Requirements:** The chemical data requirements are the same as for EXAMS. The data used for any simulation can be as little or as extensive as data is available. The environmental data required depends on which of the transformation processes are important. At its simplest level, WASP4 can be used as a first-order model for simple dispersion or degradation investigations. At a more detailed level, the model can utilise large quantities of data in simulating second-order processes and time-varying functions.
>
> **Output:** WASP4 provides information about:
>
> - chemical concentrations in every segment for which the model is set up, which may include the water column and the sediment;
>
> - erosion, deposition and transport of sediment;
>
> - the relative importance of transport and transformation processes.
>
> **Experience/Validation:** The model has been used for a wide range of applications. Some of these are referenced by OECD (1989). The model has been used under various names (WASTOX, TOXIWASP, WASP & WASP4) which seem to have changed as the model has become more developed over the years. **COMMENT ON VALIDATION - CHRISTA ?**
>
> **Limitations:** WASP4 is not strictly valid for concentrations higher than trace levels since the linear isotherms in the model are only valid for low concentrations (as for EXAMS). The model cannot take into account any feedback mechanisms, such as environmental properties (e.g. bacterial populations) which may be affected by the chemical degradation process.
>
> WASP4 generally requires considerable effort to set up and use. For a given problem the estimated time will depend heavily on the experience and ability of the user.

COMPENDIUM L. SPILL

SPILL was developed by the ICI Group Environmental Laboratory to predict chemical concentrations in water, and the extent of toxic zones in an estuary resulting from a spill. It is publicly available. It has been designed for use on a chemical site where the normal liquid effluent is discharged into an estuary. It was developed as an operational tool for assessing the effects of a chemical spill in the effluent and for developing management strategies for storing and handling bulk chemicals.

The model provides a rapid evaluation over a short time scale (up to one tidal cycle) of the contaminated patch movement and dilution. It is designed for use "hands on" when a spill occurs, and gives a good assessment as to the magnitude of any problem and whether or not any action is required such as turning off the pumps, or diverting the spilled material into an emergency containment area. The predicted concentrations are automatically compared to a data base which contains LC50 values of chemicals used on the site.

> **Data requirements**: The model requires base data sets in the form of a regular grid of data. These are:

- **Depths:** these are normally obtained from Admiralty charts and/or from echo sounding work.

- **Tidal currents:** current speeds and directions are required for peak flood tide over the model area. These may be obtained from a hydrodynamic model or interpolated from observed current measurements.

- **Residual currents:** as with tidal currents, may be generated hydrodynamically or interpolated from field observations. Both speeds and directions are required.

- **Harmonics:** at least one harmonic component is required (depending on the complexity of the tidal regime) to stimulate the variation of current velocity and water surface height throughout the tide.

- **Mixing data:** normally obtained from dye experiments, K_z and K_h values are required.

- **Flow rate:** the model assumes a constant flow which is taken to be the normal effluent flow from the factory (m^3/s).

Generating the above data sets is the time consuming part but once this is done the model is ready to use for spill simulations. The additional data required for any simulation are: mass of chemical spilt, time of low water, time of day of spill, spill duration, tidal range.

Output: The model will quickly give an indication of the seriousness of a spill, and then proceed to calculate the movement and dilution of the contaminated patch which can then be displayed graphically on a screen. The graphics show the size of the patch where concentrations exceed the "safe" level (usually the LC_{50} divided by 10) at half hourly intervals as it moves up and down the estuary.

Experience / Validation: The model uses a Gaussian approach which is widely applied in the context (see Csanady, 1973; Lewis, 1982; Bowden, 1983; Neely & Lutz, 1984; Keating, 1986). It has been installed in the Grangemouth works of ICI and undergone extensive calibration and validation tests (Riddle, 1991).

Limitations: The model allows for degradation of a chemical if the decay rate is known, but does not cater for chemical changes within the estuary, nor is it suitable for representing the movement of oils or heavy particulate material.

The model is limited to short time scales (of the order of one tidal cycle), because as the patch becomes larger the edges of the patch are influenced by different tidal streams and reflection by the coastline. However, for the operational mode this limitation is not important.

For more detailed and longer term assessments, the so-called random walk approach could be used (Chu and Gardner, 1986). This method overcomes the limitations of the Gaussian approach but takes too long to run on most computers to be useful in an emergency. It is more appropriate for use as a planning tool for assessing the hazard posed by chemicals on the site, and for planning how and in what quantities the material should be stored.

COMPENDIUM M. CHEMSPIL

CHEMSPIL was developed by Shell to calculate the fate of poorly water soluble, volatile organic liquids following a tanker accident. This model can be used to calculate the expansion of a floating layer and the chemical concentration in water as a function of time. Model calculations have demonstrated that the physico-chemical properties of a substance essentially determine the extent of transfer of chemicals into water. This model was developed for the classification of chemicals transported in bulk across the open sea. Other models which consider local flow conditions and other site specific parameters are essential for quantitative calculations of concentrations in coastal regions.

Data requirements:

- **Environmental data:** sea water temperature, depth and density of sea water, wind speed.

- **Spill data:** volume and density of the spill, spreading coefficient.

- **Physico-chemical data:** molecular weight, melting point, boiling point, solubility in water, vapour pressure, lateral and vertical dispersion factors (which will be replaced by estimated fixed values if not known), acute toxicity (expressed as LC_{50}).

Output: CHEMSPIL provides a graphical representation or grid plot of the concentration-distance profile of the dissolved compound for different time periods. This grid plot represents half of the vertical cross section of the circular plume of the contaminated water where the top of the left corner of the grid plot represents the point of the spill and thus the centre of the plume. The extent of a floating layer is given and the shades of the grid blocks give an indication of either the concentration greater than the LC_{50} value, between LC_{50} and $0.1\ LC_{50}$, between $0.1\ LC_{50}$ and $0.01\ LC_{50}$, and below the $0.01\ LC_{50}$ value. The plot also provides information on the maximum concentration, the time lapse since the spill occurred, the fraction of the spill that is dissolved and the fraction that has evaporated.

Experience/validation: CHEMSPIL was developed for comparison and categorisation of liquid chemicals with a density lower than or equal to that of sea water. It can also be used for rough estimates of the sea water concentrations after an accidental spill in the open sea under mild weather conditions. The report by ECETOC (1990c) provides a detailed discussion of the model and the mechanisms involved.

Limitations: Advection and droplet formation is not included in the model. For mixtures the model has only limited applicability. The model is not applicable for solid chemicals and those compounds which have a density higher than sea water.

COMPENDIUM N. PRZM

PRZM (Pesticide Root Zone Model) is a soil leaching model which was developed by the US EPA especially for the assessment of pesticide leaching. The hydrology component of PRZM includes runoff, erosion and evapo-transpiration. Soil-water movement is simulated by an empirical model based on soil water capacity terms including field capacity, wilting point and saturation. The chemical transport component calculates a pesticides vertical movement (leaching), foliar loss, dispersion, retardation (sorption), uptake by plants, degradation and surface runoff. The time step in the PRZM model is one day. The soil is divided into a number of soil layers. For each layer the model performs separate solutions of the transport equation. For the surface layer additional terms are included for chemical losses associated with surface runoff.

> **Data Requirements:** These are listed earlier (cf. Section 4.4.3.); for further detailed information consult the OECD Compendium (1989).

> **Output:** The output of the assessment by PRZM is the amount of pesticide leaving the root zone and entering the water table. Dynamic simulations allow the consideration of pulse loads and the estimation of time varying mass emission or concentration profiles.

> **Experience/Validation:** PRZM is widely used by authorities, universities and industry for the assessment of pesticide leaching behaviour. It is validated by comparison with field data (Jones and Estes, 1987; Hegg *et al*, 1988; Smith *et al*, 1990).

> **Limitations:** The model is limited to the vertical movement of the chemical. The Freundlich Adsorption Exponent is adjusted to 1 and cannot be modified to a non-linear relationship. Chemical transport by soil and air is not included in the model.

COMPENDIUM O. SESOIL

SESOIL is a soil leaching model. It is a one-dimensional model for predicting the migration of organic chemicals and metals through the unsaturated zone. The model predicts chemical partitioning into the dissolved, gaseous, and adsorbed phases. The model accepts time-varying chemical loading and generates time profile results. Loadings to the soil surface and to various soil layers are possible.

The hydrologic portion of SESOIL simulates both soil moisture content and moisture flux, using a statistical treatment of the climate and soil input data. The chemical transport modules estimate concentrations within four distinct soil layers, each layer having up to ten distinct sub layers. The processes represented include vertical advection, volatilisation, adsorption, cation exchange, complexation of metals, hydrolysis and general first order decay. Depth dependant variations in adsorption coefficients are also allowed.

> **Data requirements:** These are listed earlier (cf. Section 4.4.3.); for further detailed information consult an OECD Compendium (1989).

> **Output:** SESOIL generates concentration profiles monthly giving the mass distribution of the chemical in each phase and for each soil sublayer. It also calculates the water content of each soil sublayer and the amount of chemical entering the ground water.

> **Experience/Validation:** SESOIL has been used by the US EPA for assessments of polychlorinated biphenyls and petroleum constituents such as benzene and naphthalene. Earlier versions of the model have been used in environmental fate studies of chlorinated solvents and an assessment of detergent additive releases from septic tanks. **R.W/ 1 or 2 sent on validation and refs**

> **Limitations:** All hydrology parameters are on a monthly basis. This limits the output data to average monthly values. SESOIL cannot be applied to sites exhibiting large vertical variations in soil properties because a single homogenous soil column is used in the hydrologic cycle. Chemical transport by soil and air is not included in the model.

COMPENDIUM P. ILLINOIS STATE MODEL

The ILLINOIS STATE Random Walk Model is an example for a groundwater model; it is available under an alternative name PLASM.

The Illinois State model is designed to simulate one- or two-dimensional solute transport, including the effects of convection and dispersion for chemical problems such as hazardous waste leachate and injection of chemical wastes into disposal wells. It allows for variations in the soil properties across the area of interest. Essentially the model consists of two parts:

- the flow model; the solution to the governing flow equation is obtained by the use of a finite difference technique,

- the solute transport model; based on a particle in a cell for convection and random walk for dispersion.

The flow model is capable of dealing with a wide range of groundwater conditions including steady/non steady flow, time varying pumping or injection by wells and groundwater evapo-transpiration. Although the model is designed to deal with two-dimensional problems the flow model can be made quasi three-dimensional by the use of layers.

The transport model will allow the specification of the water quality of any segment of the model including injection of waste water in wells, leachate from landfills, leakage from overlying source beds of different water quality and water sources such as contaminated streams and lakes. It is in the solute transport that the model differs from many others by using a random walk technique. This avoids the necessity to solve both the flow and the solute transport equations.

Data Requirements: These have been defined previously (cf. Section 4.3.3.).

Output: The water heads and concentration of chemicals are given for each grid node in the model and these are suitable for contouring as maps.

Experience / Validation: The model output has been compared with theoretical solutions and applied to a field problem in the USA by the Illinois State Department of Energy and Water Resources in order to recommend remedial cleanup methods.

Limitations: The model can only simulate solute transport. It cannot simulate the effects of fractures, nor explicitly model adsorption or chemical reactions. These processes are not modelled explicitly but are generally inferred by use of a retardation factor. The random walk model is very computer intensive, especially if a large number of particles are required to produce an acceptable solution. Similarly, a large memory and disk storage is needed for

simulation with large numbers of particles. The method also requires considerable judgment in terms of deciding the number of particles needed to produce sufficient output resolution.

COMPENDIUM Q. RUSTIC

RUSTIC (Risk of Unsaturated / Saturated Transport and Transformations of Chemical Concentrations) is a model which covers both soil and groundwater. RUSTIC is the latest major US EPA model for predicting chemical movement in soil. It is designed primarily for simulating the behaviour of pesticides entering the soil surface, but can be applied to other organic chemicals. The model simulates movement in the root zone, unsaturated zone and in the saturated groundwater zone. It will predict only the movement of dissolved constituents and cannot be applied to free phase components (light or dense hydrocarbon layers). The model comprises three distinct sub models as follows:

PRZM   Pesticide Root Zone Model
VADOFT   Vadose Zone Flow and Transport Model
SAFTMOD   Saturated Zone Flow and Transport Model

These models can be linked in various ways depending on the modelling scenario, or can be used as stand alone models if, say, the problem at hand only requires knowledge of transport in the groundwater zone. PRZM has already been described in detail (cf. Compendium N).

> **Output:** RUSTIC is a new model and thus has not been extensively reviewed or validated. The model is available from the US EPA Environmental Research Laboratory, Athens. Of the individual models, PRZM is by far the most used, reviewed and validated of the three. It is worth noting that this version of PRZM takes into account vapour pressure phase transport. SAFTMOD was developed from an existing code used for saturated zone modelling, being modified to allow for two-dimensional horizontal, vertical and axisymmetric simulations. VADOFT was written specifically for RUSTIC in order to link PRZM and SAFTMOD.

ASK R W TO PUT N STANDARD FORMAT

COMPEDNIUM R. MOFAT-2D

MOFAT-2d (Multi-phase Flow And Transport Simulator) [also called MOTRANS] is a two-dimensional model (vertical slice) for simulating the flow and transport of water and oil phases in both soil and groundwater. The model thus has the capability to simulate situations such as an oil layer floating on the surface of the water table, or a dense layer at the bottom of an aquifer. This is a feature not included in any of the other models. The model can simulate transport of up to five partitionable organic components. A gas phase is also considered but is assumed to remain constant at atmospheric pressure. Equilibrium partitioning between the oil, water, solid and gas phases is assumed and the effects of hysteresis are ignored. Convection and dispersion are modelled for components in the water and oil phases and diffusive transport only is considered in the gas phase. Pressure gradients in the gas phase are neglected.

Data Requirements: Additional requirements over and above those defined earlier for the flow model (cf. Section 4.4.3.) are bulk liquid properties, that is density and viscosity, various scaling parameters and the initial conditions which are the prescribed pressure head values for both water and oil phases with the option of 'no-oil' condition in flow analysis. For the transport model the following additional data on the partitionable component are needed; the diffusion coefficient, dispersivity, the equilibrium partition coefficients and the first-order rate constant for reaction.

Output: MOFAT gives chemical concentrations in the water, oil, gas and solid phases for each organic component. It also provides the total mass of each component in each phase, the total volumes of oil and water together with net changes and the saturations and velocities at each node at user specified intervals.

Experience/Validation: MOFAT-2D is one of the first of its kind in terms of multi-phase flow. It is being used for various courses in multi-phase flow modelling, in Europe (the International Groundwater Modelling Centre) and in the USA. Consultants in the UK are also starting to use this model for land contamination problems.

Limitations: The equations of flow are non-linear and thus considerable care must be taken in choosing the appropriate grid size. It is often necessary to set up an enormous model to get sufficient detail at a smaller scale.

The model requires several coefficients to describe the saturation of the different fluid phases in the soil, many of which may not be readily available. Also, the complexity of the model makes it difficult to asses the accuracy of the model output. The model requires a 386/486 personal computer with a 4Mb RAM and math co-processor.

GLOSSARY

Advection: the process of transport of a chemical by the movement of the containing medium.

Box model: a model based on a coordinate system where properties and concentrations are given as average values for each box defined by the coordinates.

Buoyancy: a kinetic force within an air or water plume due to density or temperature differences.

Dry deposition: the adsorption or absorption of air borne chemicals on soil, vegetation or water.

Diffusion: (see also dispersion) the movement of a chemical from regions of high concentration to regions of low concentration by molecular motion.

Dispersion: (see also diffusion) the movement of a chemical from regions of high concentration to regions of low concentration by turbulence.

Dispersion parameters: parameters associated with stability classes in air; (see also stability classes).

Downwash: the downward mixing of an air-borne plume in the lee of the stack by vortex motions which are generated by the wind flow around the stack.

Dynamic models: the load or discharge (and often other parameters that affect the fate and behaviour of the chemical) can be varied in time and space, resulting in estimated concentrations of the chemical that may vary spatially and temporally.

Ecokinetic models: models to estimate the rate of transport or reaction of chemicals in different parts of the environment, for example dispersion or phototransformation.

Effective source height: the sum of the physical source height (which is the height of the source above ground level) and the plume rise.

Eulerian Model: a co-ordinate system in which the properties of a flow are described as a function of time for each grid co-ordinate.

Fate and exposure models: models to estimate the concentration of chemicals in (parts of) the environment and therewith the potential exposure of environmental species to that chemical. QSARs and ecokinetic models are often used as building blocks for these models.

Fugacity: an 'escaping tendency' for a chemical substance within a phase; it has units of pressure and is a function of the environmental concentration.

Gaussian plume model: an approximation of the dispersion of a plume from a continuous point source for which the concentration distribution perpendicular to the plume axis is assumed to be Gaussian.

Grid model: a model based on a coordinate system where properties and concentrations are defined for each coordinate point.

Half-life: (see also life-time) the time necessary for the concentration to be reduced by 50%. For first-order rate processes half-life is independent of the initial concentration and is equal to the inverse of the rate constant multiplied by ln2 (i.e. 0.693).

Heavy gas: a mixture of a gaseous chemical and air, where the density of the mixture is greater than that of air. Its dispersion is determined by gravity.

Inversion layer: generally used in meteorology indicating a stable layer created by differences in temperature or density which limits the transfer of chemicals.

Lagrangian Model: a co-ordinate system in which the properties of a flow are described as a function of time for each fluid particle.

Life-time: for first-order rate processes life-time is independent of the initial concentration and is equal to the inverse of the rate-constant. The expression half-life is more appropriate for environmental concentrations.

Plume rise: (see effective source height) the upward motion of a gaseous plume from the source due to its buoyancy caused by the temperature and/or density differences or exit velocity.

Puff model: a model simulating a constant release of a chemical by subdividing it into a number of puffs; the model calculates transport and dispersion of the chemical within each puff.

Random walk: the step-wise path along which a particle moves, where each step is determined by chance with regard to direction and/or with regard to magnitude.

Receptor point: the coordinate for which a chemical concentration is measured or calculated.

Residence-time: (see life-time).

Roughness length: a parameter to express the roughness of a surface which has units of length.

Scavenging: removal process; often used to indicate the capture of gaseous chemicals or particles in the atmosphere by water droplets.

Sedimentation: the settling out of particles due to gravitational forces.

Slab models: heavy gas models assuming that mass transfer occurs by entrainment of air across the cloud boundaries and that internal mixing is fast enough for the concentration within the cloud to be uniform.

Source height: (see effective source height) the physical height of a source above ground level.

Stability classes: (see dispersion parameters) a system to classify the turbulence structure of the air layer above the earth's surface. Turbulence is expressed as dispersion parameters and is calculated from stability classes and wind speed.

Turbulent diffusion: (see dispersion).

Washout: (see wet deposition and scavenging) the scavenging of gaseous or air borne chemicals and particles by rain droplets.

Wet deposition: (see washout and scavenging) deposition of a chemical scavenged in precipitation on the earth's surface.

Wind field: combined data for wind speed and direction for a specific region and time.

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