Ann. Ist. Super. Sanità, vol. 29, n. 2 (1993), pp. 209-223

Prediction of the environmental fate of chemicals

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Summary. - An overview is presented of the possibilities of applying multimedia compartmental evaluative models, and in particular the fugacity approach, to predict the environmental distribution and fate of organic chemicals. The use of this predictive approach for the evaluation of exposure to pollutants in the aquatic system is described, with reference to different environments or discharge patterns (surface and groundwaters, point and diffuse sources of pollution). The value and limitations of this approach are noted and the need for more research to improve predictive capability and practical usefulness is indicated. Finally some practical applications of evaluative models in the proposal of quantitative indices for ecotoxicological evaluation of risk from chemicals are described.

Key words: organics, predictive models, fugacity approach.

Riassunto *(Previsione del destino ambientale delle sostanze chimiche)*. - Viene presentato un quadro delle possibilità di applicazione dei modelli valutativi di ripartizione multicompartimentale, con particolare riferimento al modello di fugacità, per la previsione della distribuzione e del destino ambientale delle molecole organiche. In particolare viene descritto come questo approccio previsionale possa essere utilizzato per la valutazione dell'esposizione a potenziali contaminanti nell'ambiente acquatico in diverse situazioni (acque superficiali o sotterranee, contaminazione puntiforme o diffusa). Vengono esaminati i limiti attuali di questo approccio, gli aspetti ancora scoperti e le necessità di ricerca per aumentarne l'efficacia e incentivarne le possibilità applicative nella questione dei potenziali contaminanti. Infine, vengono descritti alcuni esempi di applicazione pratica nella formulazione di indici quantitativi per la valutazione del rischio chimico.

Parole chiave: composti organici, modelli previsionali, fugacità.

Introduction

Since World War II, the huge development and production of new chemical substances (xenobiotics) created a growing concern about their environmental effects. More than 2 million compounds have been synthetized by man and about 100,000 are produced in significant quantities. It has also been estimated that about 2% of new products, synthetized at an approximate rate of 25,000 per year, will be taken into serious consideration for production and, among them, several compounds are likely to reach the natural environment in substantial quantities.

This led to some considerations:

- it is practically impossible to produce, in a relatively short time, sound and complete environmental quality criteria for all potentially harmful substances;
- there is the need for predictive approaches able to produce at least a rough ranking of potential hazard, in order to make priority lists of dangerous chemicals.

Moreover it is recognized that potential harm should not be evaluated only on the basis of the effects on living organisms and on the ecosystems but also on the basis of possible exposure. It can be assumed that no exposure means no need for toxicity information and that, on the other hand, more dangerous chemicals, for the global environment, are not the most toxic but those that can produce high exposure, due to their persistence and distribution patterns. DDT is not included among the most toxic pesticides, but, due to its high persistence and bioaccumulation potential, is classified among the most dangerous chemicals.

The need for predictive approaches was emphatically recognized by two important Regulations, the Toxic Substances Control Act [1] in the USA and the Directive on Dangerous Substances [2] in the European Economic Community.

This led to a rapid development of predictive ecotoxicology and one of its principal concepts was that of "hazard assessment".

Basically a hazard assessment is a comparison between a measure of the effects (e.g. a NOEL: No Observed Effect Level) and a measure of the exposure (e.g. a PEC: Predicted Environmental Concentration). The prediction of exposure could be obtained by means of predictive models.

Complex large-scale environmental models, produced in the sixties and in the early seventies, such as those proposed by Randers [3] for DDT, proved ineffective. In fact, large quantities of input data are needed and their predictive capability is very limited.

The concept of environmental chemodynamics was then proposed as a holistic approach for the comprehensive understanding of the behaviour of chemical substances in the environment, and simple evaluative models with high predictive capability have been developed since the late seventies.

Partition analysis and evaluative models

Chemical substances introduced into the environment will move from their point of entry to their final destination i.e. the environmental compartment for which they have more affinity. From here, if it is not a "sink" but a "reservoir", the chemicals can be transferred again to other compartments. In the meantime chemicals can undergo chemical transformations in every environmental compartment including biota.

Fig. 1 shows in a schematic way the major environmental compartments and the modality of transport among them. For each compartment the relevant degradation processes are also listed.

To evaluate the environmental distribution of a pesticide the parameters are: Henry constant (H), water solubility (S), soil sorption coefficient (Koc) and n-octanol/water partition coefficient (Kow). The numerical value of each parameter indicates the degree of affinity for the four basic ecological compartments: air, water, soil and biota.

Recently the n-octanol/air partition coefficient (Koa) has been introduced as an indicator of accumulation in terrestrial plant biomass.

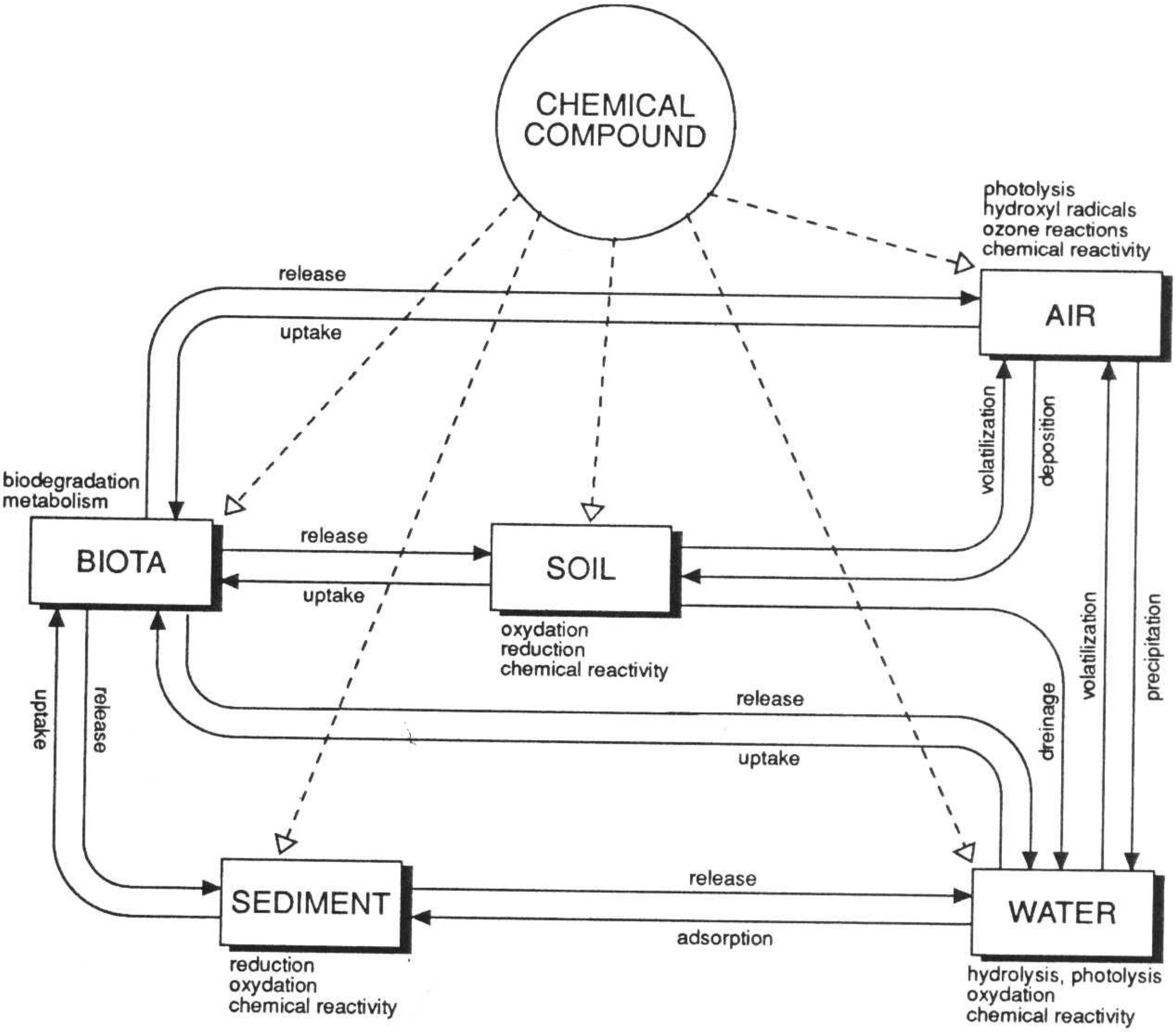

Fig. 1. - Scheme of the main transport and transformation processes for chemical compounds in environmental compartments.

Looking at Table 1, the concept outlined above finds a practical basis for a classification scheme for organic chemicals. In fact if a compound has, for example, a solubility at $g \cdot l^{-1}$ level it has a high affinity for the water compartment, if the Kow is lower than 10^3 the substance does not accumulate in biota etc.

One can improve classification by increasing the degrees of affinity (i.e. very low, very high etc.) considering that, for example, the solubility has a range of about seven orders of magnitude and Koc about eleven. However, this type of classification is valid as a first approach, being particularly useful only for molecules with characteristics at extreme values. Moreover ranking can widely vary if organic industrial chemicals are included and the classes of affinity modified in accordance. Finally this first approach does not give an idea of the behaviour of the compounds when the properties are considered all together in an integrated manner, better simulating what happens in the real world.

To overcome these limitations, models of compartmental analysis were proposed starting from the late seventies.

To predict environmental distribution and fate of chemicals, Baughman and Lassiter [4] introduced the concept of an evaluative model with the aim of developing a quantitative approach for exposure estimation. According to these authors, evaluative models "incorporate the dynamics of no specific environment but are based on the properties of stylized environment of hypothetical pollutants for which we specify (rather than measure) inputs".

In the ensuing years, many publications appeared on the same subjects [5-11]. The Organization of Economic Cooperation and Development, within the framework of its Chemical Group and Management Committee in the Hazard Assessment Project, prepared a report on practical approaches for the assessment of environmental exposure [12].

Table 1. - Classes of affinity of organic chemicals for the different environmental compartments in relation to the physico-chemical characteristics of the substance

Affinity	Air H $Pa \cdot m^3 \cdot mol^{-1}$	Water S $g \cdot l^{-1}$	Soil Koc	Kow
Low	$<10^{-3}$	$<10^{-3}$	<1	$<10^{-3}$
Medium	10^{-3}-1	10^{-3}-1	1-10^3	10^3-10^5
High	>1	>1	$>10^3$	$>10^5$

The fugacity approach

Several authors produced simple evaluative models [13-16]. A "fugacity" model was proposed to calculate the relative amount of a substance that would ultimately partition into each environmental compartment [17].

Among the various models proposed, the fugacity approach appeared as one of the most promising. The basic fugacity concept was then applied to several relatively more complex multimedia models, such as the QWASI (Quantitative Water Air Sediment Interaction) [18] and the SMCM (Spatial Multimedia Compartmental Model) [19].

All these evaluative models need very few input data.

In particular, the fugacity approach at the level 1 in its standard form requires only some basic physico-chemical properties of the molecule: molecular weight, water solubility, vapor pressure and octanol-water partition coefficient.

Fugacity (f) is an old physico-chemical concept that Mackay [14] rediscussed in new terms and defined as the tendency of a chemical substance to escape from one phase to another. This property can be calculated in units of pressure (Pa).

The fugacity model introduces the concept of a standard "unit of world" of 1 km^2 divided into six compartments (air, water, soil, sediments, suspended solids, aquatic biomass) with defined volumes, representing, more or less, $1/50 \cdot 10^6$ of the real world. A further compartment, the terrestrial plant biomass, was then added to the unit of world [20, 21] (Fig. 2).

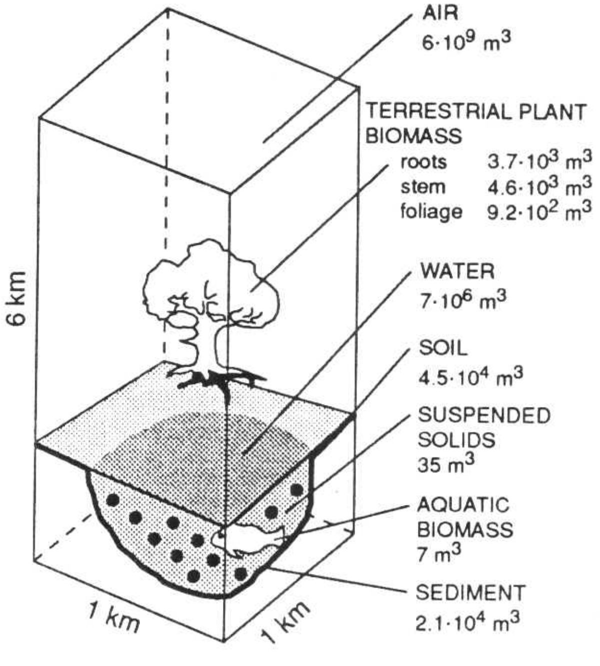

Fig. 2. - Scheme of the "unit of world" proposed by Mackay [14] and modified by the inclusion of the terrestrial plant biomass [21].

Another fundamental concept of the fugacity approach is the environmental capacity of each compartment ($Z = \mathrm{mol} \cdot \mathrm{m}^{-3} \cdot \mathrm{Pa}^{-1}$) from which the theoretical concentrations ($C = \mathrm{mol} \cdot \mathrm{m}^{-3}$) could be calculated after an immission of a given amount of chemical compound

$$C = f Z \qquad (1)$$

Equilibrium is attained when the fugacities are equal in all the compartments

$$f_1 = f_2 \qquad (2)$$

therefore

$$C_1/Z_1 = C_2/Z_2 \qquad (3)$$

and

$$C_1/C_2 = Z_1/Z_2 = K_{12} \qquad (4)$$

K_{12} is the partition coefficient determining the distribution of the substance between two phases.

The capacity of each compartment (Z) can be determined, as function of partition coefficients. If equilibrium, good mixing, no reaction and no advection are assumed, the relative mass distribution and relative concentrations can be calculated.

In practice, after the application of the fugacity model (level 1) one can know in which compartment most of the compound is found and where the highest concentrations in the "unit of world" are.

The model is extremely useful to describe the trends of environmental partitioning of a molecule among environmental media for screening purposes and as a working instrument to understand environmental distribution patterns.

The model at level 1 can be applied not only in the standard form, to the standard unit of world, but in real conditions, to a real environment. In this case further input data would be the characteristics of the environment, such as:

- volumes of various environmental compartments at the moment of the application of the model:
- temperature;
- soil and sediment characteristics (% OC);
- quantity of chemical introduced.

In this form the model is more site specific and can be used for rough predictions of environmental concentrations and as a means for planning more effective research or environmental monitoring.

At level 2, environmental persistence can be evaluated if the transformation rates of various degradation processes in different environmental compartments (photolysis, hydrolysis, biodegradation, etc.) are known. Higher levels of complexity of the fugacity model require more input data, as described in further chapters.

How to predict distribution and fate of chemicals in aquatic environments

Environmental pollution can be studied at different levels and scales in terms of space and time. The scale of distribution of a contaminant in the environment depends, in the short run, on the uses and discharge patterns, and in the long run, on the mobility and persistence of the substance. In Fig. 3 some examples of persistence are shown. In function of the different space and time scales of the effect of pollution, various levels of evaluation of ecotoxicological risk must be taken into account (Fig. 3):

- small scale risk due to direct emission;
- local scale risk for man and the environment;
- global scale risk.

With regard to discharge patterns, point and diffuse sources of pollution should be taken into account.

Different approaches should be applied if surface waters or groundwaters are considered. In any case, two different steps should be undertaken. As a first phase, the distribution and fate and the transport patterns in the whole environment should be studied in order to evaluate the inflow into the body of water. In the second step, distribution and fate in the various phases of the aquatic environment (water, sediment, suspended solids, biota) and transport patterns in the body of water should be examined.

In practice, examples of the approaches and procedures applicable to predict environmental distribution and fate of chemicals in the aquatic environment in different cases and at different scales could be those described in the following sections.

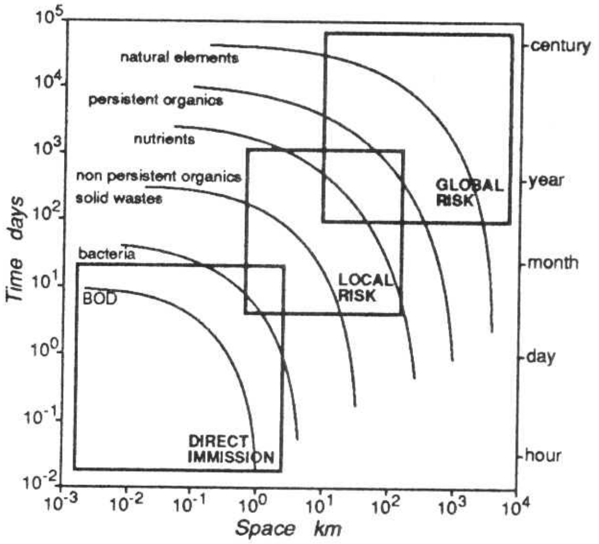

Fig. 3. - Persistence and distribution scales for various environmental contaminants and boundaries of different levels of risk evaluation. Modified from Vighi and Calamari [42].

Surface water pollution by direct emission of a point source

Prediction of water concentration in this case is relatively easy if loads and discharge patterns are known and if information on the characteristics of the receiving water body is available.

If the evaluation is made over a very short scale of time and space, only physic and hydraulic models could be needed in order to describe dilution patterns. Information on partition properties, persistence or other characteristics of the molecule can be assumed as irrelevant. On a larger scale of space, environmental fate in the aquatic environment should be more carefully assessed. A level 1 fugacity approach applied to the aquatic system (water, sediment, aquatic biota), including water-air partition at least for volatile substances, could be utilized.

If the time scale is significant too, transformation patterns should be taken into account and a level 2 fugacity model could be applied in order to predict persistence.

Surface water pollution by diffuse sources

This case deals, for example, with pollution from pesticides. The load and the transport patterns to the aquatic environment should be evaluated by means of the application of predictive approaches to the whole environmental system. In many cases a level 1 or level 2 fugacity approach applied repeatedly in correspondence with particularly significant times (e.g. in function of emission patterns or of the hydrologic or climatic cycle) is able to produce reliable enough data. In this case, input information for the model includes, besides the characteristics of the molecule, data on emission patterns and a characterization of the environmental system under study.

Recently, a modified form of the original fugacity model has been developed, the AGRIFUG model, especially for this kind of repeated application [22].

The second step should be, even in this case, the application of the model to the aquatic system involved.

As a practical example of this kind of application of the fugacity approach the case history of the Lake of Chiusi (Siena, Italy) is useful [23]. In the catchment area of the lake, an area of about 100 ha was treated with a single dose of atrazine applied at 1 kg · ha^{-1} at the beginning of May. A storm immediately following the treatment led to the emission of atrazine into the lake by water runoff.

The application of the fugacity model in its standard form, modified by the inclusion of vegetable biomass, indicates the high affinity of atrazine for the water compartment. More than 90% of the chemical is present in water, at equilibrium distribution in the standard unit of world (Table 2).

The model was then adapted to the specific environmental system, according to the following assumptions:

- an air compartment 100 m high was considered;
- the water compartment was represented only by rainwater (about 4 cm);
- a soil compartment of 4 cm deep was considered;
- treatment was made at pre-emergence and plant biomass was very low (about 3 m^3);
- in the system 464 moles of atrazine were introduced.

Table 2. - Predicted distribution of introduced moles of atrazine in the standard unit of world of the fugacity model and in different field conditions in the Lake Chiusi area

	Standard unit of world	**Field system initial time**	**Field system at 130 days**	**Lake system**
Air	8×10^{-3}	0.016	2×10^{-3}	2×10^{-4}
Water	92.4	62.51	-	57.3
Soil	3.8	401.5	53.8	-
Aquatic biomass	2×10^{-3}	-	-	2×10^{-3}
Terrestrial plant biomass	0.23	7×10^{-3}	3.1	-
Suspended solids	6×10^{-3}	-	-	7×10^{-3}
Sediments	3.6	-	-	5.1
Total introduced moles	100	464	57	62.5

The theoretical distribution, reported in Table 3, shows that about 62 moles were transported by rain water to the lake and about 401 moles remained in the soil.

The following months were characterized by particularly dry weather. Irrigation rates were relatively low and did not cause runoff losses. The model was then applied to a new condition, corresponding to 130 days after the treatments, with the following assumptions:

- the water compartment was considered as negligible;
- losses by air advection were negligible;
- the crop was at the end of its growing period with a total biomass of about 8,000 t;
- laboratory experiments, performed on soils having the same characteristics as the area under study, showed a degradation constant K = 0.015 ($t_{1/2}$ = 47 days).

Therefore, according to the equation:

$$C_t = C_o\, e^{-kt} \qquad (5)$$

total moles present in the system should be about 57.

Table 3. - Concentration of atrazine in the Lake Chiusi area, in various environmental compartments, at different times after the treatment

Time (days)	Concentrations µg/kg Water	Soil	Sediments
90	1.10	-	-
130	0.70	150	-
180	0.55	70	8.25
230	0.45	35	-

In this condition, 54 moles are present in soil and 3 moles are within the crop (Table 3).

A third step was the application of the model to the lake system with the following assumptions:

- an air compartment of $300 \cdot 10^6$ was considered (lake surface: $3 \cdot 10^6$ m^2);
- the lake volume was $10 \cdot 10^6$ m^3;
- sediments, suspended solids and aquatic biomass had a volume of 70,000, 100 and 10 m^3 respectively;
- in the system there was an initial introduction of 62.5 moles through runoff transport.

Equilibrium distribution in the lake system, excluding degradation processes, is shown in Table 2. Analytical measurements of atrazine residues were performed in various environmental media at different times. Reliable data on lake water are only available starting from 90 days after the treatment mainly due to the slow mixing. Soil concentrations were measured at 130, 180 and 230 days. Lake sediments were analysed after 180 days. Some analytical results are shown in Table 3.

On these bases a mass balance can be calculated for atrazine in the system (lake and drainage area) and experimental results can be compared with the theoretical prediction.

A good agreement is shown in Table 4 between the amount of atrazine present in the soil at different times and those predicted by distribution and degradation.

Water analyses indicated a loss rate constant K = 0.0041 in the lake [23]. This rate includes degradation and distribution in phases other than water (principally sediments). From lake concentration levels at 90 days a value of 66.5 moles can be calculated as the total mass present, very close to the theoretical one.

As far as sediments are concerned, the predicted value at equilibrium is 5 moles. Considering the unknown time needed to reach equilibrium between water and

Table 4. - Total amount of atrazine (moles) in various environmental compartments of the Lake Chiusi area, at different times after the treatment. The predicted values (calculated by means of the fugacity model) and the observed one (derived by measured concentrations) are reported

Time (days)	Soil		Vegetable biomass		Lake water		Lake sediments	
	predicted	observed	predicted	observed	predicted	observed	predicted	observed
0	401	-	10^{-3}	-	62 (57*)	(66**)	(5*)	-
90	104	-	-	-	-	46	-	-
130	54	42	3	-	-	32	-	-
180	26	20	-	-	-	25	-	1.8
230	11	9	-	-	-	21	-	-

(*) Equilibrium distribution values between water and sediments.
(**) Calculated from the loss rate constant.

sediment and the degradation rate in this last phase (probably close to those observed in soil or higher), the experimental value of 1.8 moles can be considered a reasonable one.

It can be concluded that advection by runoff is the route of transport of atrazine from the terrestrial to the aquatic environment and degradation in soil and water are in agreement with laboratory and literature data.

By means of a simplified scenario of the field and the fugacity model, it has been possible to predict with enough reliability and precision the distribution and fate of atrazine in an ecosystem and eventually to determine the acceptable load on the area in the presence of average rainfall in order to establish acceptable levels of atrazine in lake water.

Groundwater pollution

In groundwater contamination, diffuse sources are generally involved even if cases of point source pollution cannot be neglected.

Substances of major concern are those directly applied to the soil, like herbicides.

To predict the transport of chemicals to groundwater and their fate in the soil environment, different approaches should be utilized because of the characteristics of different soil layers.

In the surface system belonging to the unsaturated zone, partition among various environmental compartments must be taken into account: air, water, soil (organic and inorganic components) and biota. In this layer transformation patterns, mainly bioaccumulation, are relatively intense.

The thickness of this layer is highly variable because of several factors (geopedological characteristics of the soil, soil coverage, tillage, etc.), ranging from some centimeters up to 1 meter.

In the deepest layers only inorganic components of the soil and water are involved. In this case only some ionic reactions should eventually be evaluated but the prevailing process is mass transport with water. Moreover transformation patterns are low, mainly due to the absence of biodegradation.

To describe the transport patterns of chemicals in the soil environment by means of the fugacity approach, a simple surface soil model was developed [24], applicable at least to the surface layer system.

In the model the soil matrix is treated in four phases: air, water, organic matter and mineral matter. For each compartment a capacity value Z is calculated on the basis of partition coefficients, and the general principles of the model are the same described for fugacity level 1. Partitioning among the different soil components provides an insight into the amounts present in the air and water phases and thus subject to migration or diffusion. It also shows the extent to which organic matter dominates the sorptive capacity of the soil.

Another approach, more aproximate, but in many cases useful for practical purposes, is represented by the so-called "leaching indices". These kinds of indices are based on a few physico-chemical properties of the molecules and, in some cases, on a few soil characteristics easily available. They are not comparable in versatility to evaluative models like those based on the fugacity concept and do not allow the prediction of an environmental concentration. Nevertheless they can be successfully utilized, at least for screening purposes.

Several of these indices have been proposed, such as the LEACH [25], the AF (attenuation factor) and RF (retardation factor) [26], the MR (mass residual) [27], the GUS [28]. As an example the GUS (Groundwater Ubiquity Score) is based on the following algorithm:

$$\mathrm{GUS} = \log t_{1/2} \, (4 - \log \mathrm{Koc}) \qquad (6)$$

where $t_{1/2}$ is the half life in soil and Koc is the partition coefficient between organic carbon in the soil and water.

Threshold values of the GUS index have been empirically determined in order to classify organic chemicals as leachers ($\mathrm{GUS} > 2.8$), transition compounds ($2.8 > \mathrm{GUS} > 1.8$), and non-leachers ($\mathrm{GUS} < 1.8$), as shown in Fig. 4.

Other leaching indices (such as the AF, RF and MR) are more site specific, requiring as inputs some local soil characteristics, such as field capacity, depth of water table or soil porosity.

Value and limitations of the described approach

Prediction of distribution on different spatial scales

The partition approach has been applied successfully on a relatively small scale. A good predictive capability has been proved in small drainage areas or in experimental fields, in surface areas ranging up to some hundreds of hectars.

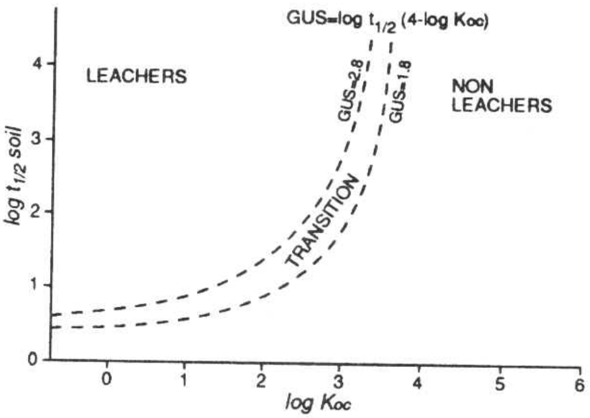

Fig. 4. - Graphic representation of the GUS index. Dotted lines represent the boundaries of leachers (GUS > 2.8), transition (2.8 > GUS > 1.8) and non leachers (GUS < 1.8) compounds.

At this level, environmental variables are in general relatively easy to control and to describe. Mass transport patterns can be described without the need of specific models.

A simple partition approach, such as the fugacity model level 1, can be applied in a sequence of environmental conditions taking into account the changes in environmental variables (water flow, biomass growth, temperature, etc.).

A specific program based on an iterative application of the fugacity model as a function of changed environmental parameters is the previously cited AGRIFUG [22].

On the other hand, a partition approach can work successfully on a global scale.

The global environment can be assumed as a closed system where persistent chemicals, on a long time scale, can reach an equilibrium distribution among various compartments. Mass transport patterns are not easy to describe, nevertheless, approximations are compensated for on the global scale and a rough knowledge of main transport processes (winds, currents) can be of enough help.

An example of the application of the partition approach to global pollution is a recent paper by Calamari *et al.* [29].

More difficult is a reliable prediction on the mean scale, i.e. at the regional level or at the level of a hydrographic basin with a surface area of some hundreds of km^2. In this case environmental variables are less easy to control and describe. The system is open and the flow of air and water into and within the system must be evaluated.

One way of overcoming this problem could be by increasing the complexity of the partition approach by means of a level 3 fugacity model.

An example of the level 3 fugacity approach, in a four compartment system (air = 1; water = 2; soil = 3; sediment = 4), is shown in Fig. 5.

At equilibrium, for each compartment the sum of all inputs is equal to the sum of all outputs. This condition can be expressed by the following equations:

$$E_1+G_{a1}C_{b1}+f_2D_{21}+f_3D_{31}=f_1(D_{12}+D_{13}+D_{a1}+D_{r1}) \tag{7}$$

$$E_2+G_{a2}C_{b2}+f_1D_{12}+f_3D_{12}+f_3D_{32}+f_4D_{42}= f_2(D_{21}+D_{24}+D_{a2}+D_{r2}) \tag{8}$$

$$E_3+f_1D_{13}=f_3(D_{31}+D_{32}+D_{r3}) \tag{9}$$

$$E_4+f_2D_{24}=f_4(D_{41}+D_{r4}) \tag{10}$$

For these equations all the following variables must be assumed as known and utilized as inputs of the model:

E_i = emission rates of the chemical substance under study in the different environmental compartments (moles h^{-1});

G_{ai} = advective inflow rate into the system; it can be applied to all the different media but can be assumed as negligible for soil and sediment (m$^3\cdot$h^{-1});

C_{bi} = background concentration of the chemical substance in the various media in the environment surrounding the system studied and transported into the system by means of advective inflow (moles m^{-3});

D_{ij} = transport coefficient between two compartments; it depends on the advective and diffusive flows among compartments; it is equal to $G_{ij}Z_i$ where G_{ij} is the flow between the two compartments and Z_i is the fugacity capacity of "i" compartment (it is to be remembered the concentration $C_i = Z_i f_i$); thus D_{ij} depends on the characteristics of the compartments and their exchange rates and on the physico-chemical properties of the substance (moles Pa^{-1} h^{-1});

D_{ai} = transport coefficient for advection from the compartment "i" to the surrounding environment; it is equal to $G_{ai}Z_i$ (moles Pa^{-1} h^{-1});

D_{ri} = reaction coefficient, represents the loss due to various transformation processes and is equal to V_iZ_iK (moles Pa^{-1});

K = transformation rate constant; K values should be known for all possible transformation processes (biodegradation, photodegradation, hydrolysis, etc.); it is expressed in adimensional units.

If all these variables are known, then the four equations contain four unknowns (the fugacities f_1 to f_4) and solution is possible.

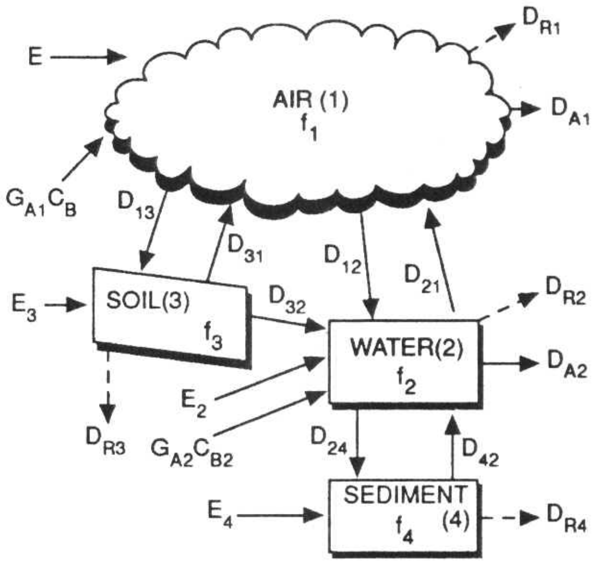

Fig. 5. - Diagram of a level 3 fugacity approach applied to a four compartment system. Modified from Mackay [24].

A level 3 fugacity approach can be easily used and managed if applied in the standard form to the well-defined unit of world, where all compartments and their intermedia transport patterns are fixed and definitely quantified.

Its application to the real environment requires an amount of information about the characteristics of the system not easy to obtain and to manage. If this difficulty could be resolved, a further improvement would be the extension of the level 3 to unsteady state conditions (level 4). This is achieved relatively easily, simply by using differential equations instead of steady state mass balance equations (7 to 10).

Another example of the attempts to extend a partition approach to the regional level is the SMCM (Spatial Multimedia Compartmental Model) proposed by Cohen *et al.* [19]. According to these authors, the existing multimedia models can be classified as "spatial multimedia models" and "uniform compartmental models". Spatial multimedia models are designed to provide the spatial resolution of the pollutant concentration-time profile by using single-medium models linked in series.

This approach produces many difficulties in the simultaneous production of information applied to the separate media and in the connection of various media. However these kinds of models can work successfully in single systems or on a relatively small scale, where the interactions among media can be easily described.

On the other hand compartmental models such as the fugacity model or more complex approaches [18, 30, 31] require many simplifications or approximations acceptable on a small scale but hardly significant on a regional level. For example, in these kinds of models all compartments are assumed as well mixed and uniform.

To overcome those problems, the SMCM was developed as an hybrid approach taking into account the main features of both the previously described types of models. In the model some environmental compartments are assumed as uniform (air, water, biota, suspended solids) others as non uniform (soil, sediments).

Nevertheless, for relatively large scale evaluations, air and water compartments can be divided into subcompartments, in order to account for some degree of nonuniformity. The SMCM provides a lower degree of spatial resolution, compared to spatial multimedia models, but it yields greater resolution than uniform compartmental models and appears much less complex than the existing spatial models.

The model allows for a rapid screening-level prediction of the multimedia partitioning of organic chemicals in the environment on a regional scale.

A further approach, probably more rough but at the same time more easily and practically manageable, could be the simultaneous application of simple partition compartmental approaches (like fugacity level 1) and relatively simple mass transport models for the main compartments.

Transport models for air and water have been around for a long time. In general these kinds of models are quite complex and require a large amount of input data and complicated algorithms for their solution. They have proved highly useful in specific conditions and for particular purposes (e.g. the description of the hydraulic flow in a river) but probably are difficult to manage in connection with partition models in a multimedia system.

Recently some relatively easy mass transport models have been developed [32] that appear to be very promising for this purpose. However more investigation is needed to more precisely define their theoretical basis and for them to be practically applied and validated.

The prediction of mobility

Mobility can be roughly defined as the ability of a molecule to reach environmental compartments or sites far from its immission site.

A more precise definition of mobility and a quantification of this variable is very important in order to answer to two different questions:

- how much time is needed to reach an equilibrium among various phases in a multimedia system?

- how far from its emisssion site may a substance be transported and how long does it take?

The first question could be relevant for the application of models like the fugacity approach, level 1 to 3, describing an equilibrium condition in the system. If the time needed to attain this condition is very long, for example significantly higher than the persistence of the molecule in the compartment where the substance is discharged, the description of an equilibrium state would be meaningless.

This problem is probably relevant only in theory. The more or less rapid attainment of the equilibrium among compartments could be assumed, in general, as depending more on nondiffusive transport processes within the single compartments than on diffusive transport patterns of the molecule among and within compartments. In other words, it depends more on the characteristics of the environmental system than the physico-chemical properties of the molecule.

Taking into account the assumption of a well mixed condition in all environmental compartments, as in the fugacity approach, the differences in the time needed to attain equilibrium should be relatively irrelevant. In practice, experiments in simulation chambers demonstrated that the time needed to attain a condition approaching equilibrium was very similar for molecules with highly different physico-chemical properties and relatively short even for a complex process like the bioaccumulation in terrestrial plant biomass (on the order of days) [21].

The second question could be more relevant in the study of global transport of chemicals or, more generally, for all problems of large scale contamination.

In this case too, the possibility of long range transport depends on mass transport patterns of the more mobile environmental compartments (air and water) and not on diffusive transport patterns of the molecule. Thus an index of the mobility of a chemical substance, assumed as the ability to be transported far from its emission site, could be based on the affinity for the two more mobile environmental compartments.

The assessment of persistence

The availability of reliable data on persistence is, at present, one of the weakest points in the prediction of environmental fate of chemicals.

The fugacity approach levels 2 and 3 require as input data transformation constants for all the main reaction and transformation processes that can occur in the different environmental compartments. This kind of data is very seldom available in the literature and, when found, its usefulness and reliability must be carefully checked. As an example, a lot of data available on residence time for pesticides in soil refers to a comprehensive disappearance of the molecule due to various processes, including advection or other transport patterns, and not only on reaction and transformation processes. Thus, they are completely useless for persistence evaluations in evaluative models.

A lot of work has been performed on biodegradation of chemicals but in general the interest of microbiologists is more in defining metabolic patterns than in producing rough numbers to quantify degradation time, suitable for the utilization in evaluative models. The lack of experimental data is coupled with an unsatisfactory efficiency of predictive instruments.

Some general information, based on qualitative relationships between chemical structure and biodegradability, was produced very early on. Well known examples are the studies related to the problem of detergents between the 1950s and 1960s, indicating the highly different behaviour of linear and branched alkyl chains of surfactants [33].

The problem of qualitative structure-biodegradation relationships has been extensively tackled by Alexander *et al.* [34-36]. Studying mainly aromatic and aliphatic hydrocarbons, they demonstrated that the presence of particular functional groups could increase or decrease the biodegradability of a molecule.

More recently, many attempts have been made to obtain quantitative relationships in order to predict degradability from physico-chemical properties or other molecular descriptors.

A review of the state of the art of the application of the QSAR (Quantitative Structure-Activity Relationships) approach to the prediction of persistence is given by Vasseur *et al.* [37] for biodegradation and by Macalady and Schwarzenbach [38] for chemical transformation.

Advances in the application of QSARs to environmental fate are proposed in a recent book edited by Hermens and Opperhuizen [39]. The interest in this field of research is rapidly increasing and promising results have been obtained, nevertheless, the practical applicability of the QSAR approach to the prediction of persistence is not yet comparable to those now attained for other aspects of chemicals behaviour (e.g. for aquatic toxicology) and further research is needed.

Recently an approach for the evaluation of a generic "stability index" of chemicals on the basis of fragmentation patterns in mass spectrometry has been proposed [40]. Although, the reliability of this approach is in need of thorough confirmation, it appears to be a promising tool for predicting the environmental persistence of chemicals, at least at a screening level.

Practical application in risk assessment procedures

The assessment of hazard and the evaluation of the risk for man and for the environment determined by the emission of a chemical substance can be made by means of an integrated ecotoxicological approach like those shown in Fig. 6. Through experimental or predictive studies environmental exposure and effective levels can be evaluated and, on these bases, a hazard assessment can be made. Finally a risk evaluation can be completed by means of studies on exposed populations.

This kind of approach can be applied with various levels of precision and with different expenditure of time, effort and money. Moreover, it can be based on *ad hoc* experimental research, made *a posteriori*, or it can be produced *a priori* by means of literature data and predictive instruments.

In many cases there is the need for practical indices, easily obtainable and suitable for the quantification of the ecotoxicological risk deriving from the emission of a chemical substance in the environment. These kinds of indices could be used for preliminary screening approaches, for the performing of priority lists, or they can be applied in Environmental Impact Studies.

Such a quantification should be based on the intrinsic properties of the substance, by determining its biological activity and environmental partitioning and reactivity, and on extrinsic factors depending on human activities (loads, use patterns, etc.) or environmental characteristics (properties of environmental compartments, environmental processes, biological populations, etc.).

Practically speaking quantitative indices could be based on the following main variables:

- loads and use patterns;
- effects on living organisms;
- bioaccumulation;
- distribution in the environmental compartments;
- persistence;
- mobility;
- exposed populations.

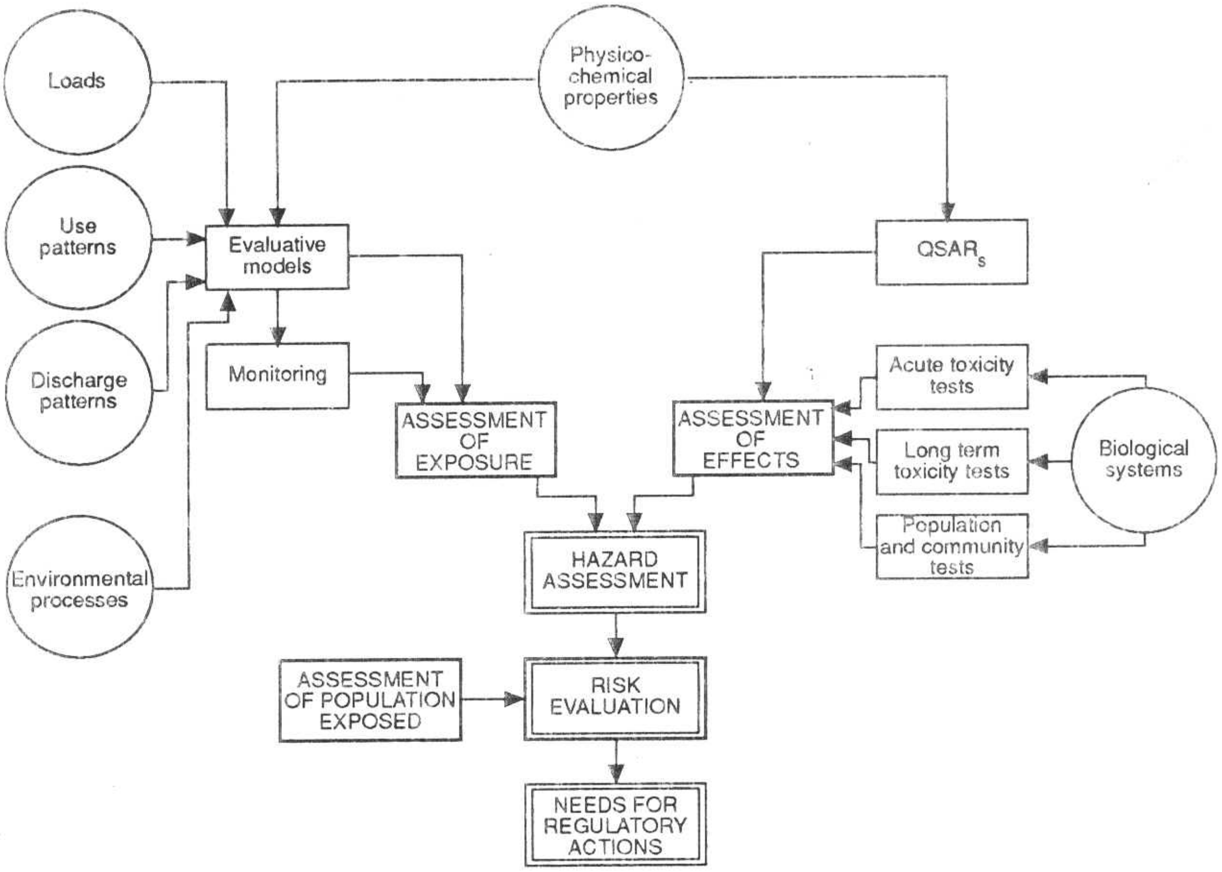

Fig. 6. - Integrated ecotoxicological approach for the management of chemical substances. Modified from Vighi and Bacci [41].

It must be remembered that the risk evaluation can be performed at different time and space levels, as previously shown in Fig. 3, and for each level the specific role and weight of the cited variables can be very different. For example persistence and mobility are the most important variables for a global risk evaluation, while, on a very small scale and in short terms, acute effects on living organism could be pre-eminent.

These concepts have recently been utilized in order to propose numerical indices for the quantification of the ecotoxicological risk in Environmental Impact Studies [42].

Specific parameters have been identified as representative of the previously cited variables and scoring criteria has been produced for each parameter. Risk indices were proposed for different time and space scales and for different targets (man, ecosystems).

In particular, numerical indices have been elaborated for:

- small scale, short term consequences of a direct discharge in air, water and soil;
- long term risk for man and the environment deriving from distribution processes in the various environmental compartments on a local scale;
- long term environmental risk on a global scale.

In these evaluations a predicted environmental concentration (PEC), estimated by means of predictive evaluative models, is needed for all environmental compartments, including plant and animal biomass.

In Tables 5-7 some examples of such indices are shown. The risk index for direct emission is based on the ratio between the PEC in the compartment involved in the discharge (water, air, soil) and a parameter suitable for the quantification of the effects on living organisms (e.g. NOEL: No Observable Effect Level). Moreover an evaluation of the target population has been taken into account.

The risk for man on a local or regional scale was based on the ratio between the Total Daily Intake (TDI) and the Admissible Daily Intake (ADI) proposed by international organizations. The TDI was calculated from multimedia exposure (air, drinking water, food), evaluating a PEC for all media involved. A score for persistence was then added.

For a complete assessment of the environmental impact of chemicals, in particular when highly persistent or mobile molecules are concerned, the evaluation should go beyond local boundaries, and the possibility of unwanted effects on a wide spatial and temporal scale should be taken into account.

Table 5. - Scheme for the calculation of the risk index for direct immission (Id). PEC (predicted environmental concentration), QC (quality criteria), NOEL (no observed effect level) and TL (threshold level) should be evaluated for the environmental compartment where the immission takes place. Modified from [42]

A				B	
PEC/QC or	**PEC/NOEL or**	**PEC/TL**	**Score**	**Target**	**Score**
$>10^2$	>10	>1	5	very important	2
$10 - 10^2$	$1 - 10$	$10^{-1} - 1$	4		
1-10	$10^{-1} - 1$	$10^{-2} - 10^{-2}$	3	important	1
$10^{-1} - 1$	$10^{-2} - 10^{-1}$	$10^{-3} - 10^{-2}$	2		
$<10^{-1}$	$<10^{-2}$	$<10^{-3}$	1	negligible	0.5

Id + A * B

Table 6. - Scheme for the calculation of the risk for man on a local scale (Im). Modified from [42]

A		B	
TDI/ADI	**Score**	**Persistence**	**Score**
> 1	5		
$1 - 10^{-1}$	4	years	2
$10^{-2} - 10^{-1}$	3	months	1.5
$10^{-3} - 10^{-2}$	2	weeks	1
$< 10^{-3}$	1		

Im = A*B

In performing an environmental impact assessment of a single emission source (e.g. an industrial plant) and in evaluating its contribution to the global scale pollution, a PEC is impossible to estimate without complete information on all other emission sources and on the global load of the chemical substance. Nevertheless, environmental fate and exposure parameter are of particular relevance in this case.

Thus the variables used for this index are persistence, mobility, bioconcentration factor (BCF) and an overall evaluation of the toxic potential on living organisms. Finally the contribution of the examined source of emission to the global load is taken into account. The described schemes are only an attempt to propose indices practically applicable in an Environmental Impact Study, by using a predictive ecotoxicological approach. They still have a high level of uncertainty on a quantitative basis and improvement can be achieved by means of

Table 7. - Scheme for the calculation of the risk on a global scale (Ig). Modified from [42]

A		B		C		D		E	
Persistence	**Score**	**Mobility**	**Score**	**Toxicity**	**Score**	**BCF**	**Score**	**Load t/year**	**Score**
years	1.5	very high	1	very high	1	log Kow>3.5	1.5	>100	2
months	0.8	high	0.6	high	0.7	3.5>log Kow>3	0.9	1 - 100	1
weeks	0.4	medium	0.35	medium	0.45	3>log Kow>2.5	0.5	$10^{-2} - 1$	0.5
days	0.2	low	0.2	low	0.3	log Kow<2.5	0.3	$10^{-4} - 10^{-2}$	0.25
								$>10^{-4}$	0.125

Ig = (A + B) · (C + D) · E

Table 8. - Information needed for the evaluation of environmental hazard for chemical substances

Data	Source of information	Availability of data and research needs
Loads	Data on uses, disposal and discarge patterns	In certain occasions data are difficult to obtain
Environmental partitioning	Monitoring	Scattered data
	Evaluative models	Uncertainty on basic physico-chemical data on the kinetics of the phenomenon The predictive capability of evaluative models on the medium scale should be improved and validated
Toxicity	Experimental data	Scattered data
	QSARs	
Bioaccumulation	Experimental data	Scarce data on metabolic transformations
	Predictive equations	
Persistence	Experimental data	Reliable data on transformation rates are very scarce
	QSARs	More research is needed on QSARs for degradation
Mobiliy	?	A precise definition of what mobility is and how it can be measured is needed

applications to scenarios and case histories. Nevertheless, the conceptual framework that led to the proposed indices is certainly acceptable, at least on a qualitative basis.

Conclusions

The described approach has proved to be a useful tool for the prediction of environmental distribution and fate and, more generally, for the ecotoxicological risk evaluation of organic chemicals. Evaluative models, applied with standard procedures, for preliminary screening purposes, can describe the environmental behaviour of chemicals, producing information about the partition in and affinity for the main environmental media, identification of compartments at risk, and matrices where transformation processes are more likely to be relevant.

At this level, a large number of chemicals can be examined in a relatively short time and with relatively small effort, which is extremely important, for example for preliminary hazard assessment and for priority listing.

Although these models do not attempt to simulate the real environment and despite their simplicity, their site specific application has been validated with experimental field data and a good predictive capability has been demonstrated, at least on a small scale.

Moreover, the partition approach was successfully used to understand some distribution patterns of persistent chemicals on the global scale.

In conclusion, with regard to the ecotoxicological risk evaluation of chemicals, Table 8 shows an overview of the information needed, as well as the methods and approaches necessary to obtain it and of the research needed to improve the practical applicability and the predictive capability of an integrated ecotoxicological approach.

Submitted on invitation.
Accepted on 5 February 1993.

REFERENCES

1. UNITED STATES. ENVIRONMENTAL PROJECT. 1978. Toxic Substances Control Act, Washington, DC. *Fed. Reg.* **43**: 4108.

2. EUROPEAN ECONOMIC COMMUNITY. 1979. Council Directive 79/831. Regard to Council Directive 67/548/EEC as emended for the sixth time by Directive 79/831/EEC concerning the classification, packaging and labelling of dangerous substances and preparations. *Off. J. Eur. Comm.* No. L 10 Vol. 22, p .259 of 15 October 1979 (79/831/EEC).

3. RANDERS, J. 1973. DDT movement in the global environment. In: *Towards global equilibrium*. D.L. Meadows & D.H. Meadows (Eds). Wright-Allen Press, Cambridge, MA. pp. 9-83.

4. BAUGHMAN, G.L. & LASSITER, R.R. 1978. Prediction of environmental pollutant concentration. In: *Estimating the hazard of chemical substances to aquatic life*. J.Jr. Cairns, K.L. Dickson & A.W. Maki (Eds). *Am. Soc. Test. Mater. Spec. Tech. Publ.* **657**: 35-54.

5. GESELLSCHAFT FÜR STRAHLEN FORSCHUNG. 1985. *Environmental modelling for priority setting among existing chemicals*. Workshop, 11-13 November 1985, München-Neuherberg Gesellschaft für Strahlen und Umweltforschung mbH, München.

6. GUNTHER, F.A. 1983. Residues of pesticides and other contaminants in the total environment. *Residue Rev.* **85**: 1-307.

7. *Dynamics, exposure and hazard assessment of toxic chemicals*. 1980. R. Haque (Ed.). Ann Arbor Science, Ann Arbor, MI.

8. *The handbook of environmental chemistry. Reaction and processes*. 1980. O. Hutzinger (Ed.). Vol. 2, Part B. Springer-Verlag, Berlin.

9. NEELY, W.B. 1980. *Chemicals in the environment. Distribution, transport, fate analysis*. Marcel Dekker, New York, Basel.

10. *Environmental exposure from chemicals*. 1985. W.B. Neely & G.E. Blau (Eds). Vol. 1. CRC Press, Boca Raton, FL.

11. *Appraisal of test to predict the environmental behaviour of chemicals*. 1985. P. Sheehan, F. Korte, W. Klein & P. Bourdeau (Eds). SCOPE 25, John Wiley & Sons, Chichester, New York, Brisbane, Toronto, Singapore.

12. ORGANIZATION OF ECONOMIC COOPERATION AND DEVELOPMENT. 1986. *Hazard assessment project, report of Workshop on practical approaches for the assessment of environmental exposure*. (ENV/CHEM/CM/86.8).

13. FRISCHE, R., ESSER, G., SCHOENBORN, W. & KLOEPFFER, W. 1982. Criteria for assessing the environmental behaviour of chemicals: selection and preliminary quantification. *Ecotoxicol. Environ. Saf.* **6**: 283-293.

14. MACKAY, D. 1979. Finding fugacity feasible. *Environ. Sci. Technol.* **13**: 1218-1223.

15. NEELY, W.B. 1979. A preliminary assessment of the environmental exposure to be expected from the addition of a chemical to a simulated aquatic ecosystem. *Int. J. Environ. Stud.* **13**: 101-108.

16. ROBERTS, J.R. & MARSHALL, W.K. 1980. Retentive capacity: an index of chemical persistence expressed in terms of chemical-specific and ecosystem-specific parameters. *Ecotoxicol. Environ. Saf.* **4**: 158-171.

17. MACKAY, D. & PATERSON, S. 1982. Fugacity revisited. *Environ. Sci. Technol.* **16**: 654-660.

18. MACKAY, D., JOY, M. & PATERSON, S. 1983. A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in lakes. *Chemosphere* **12**: 981-997.

19. COHEN, Y., TSAI, W., CHETTY, S.L. & MAYER, G.J. 1990. Dynamic partitioning of organic chemicals in regional environments: a multimedia screening-level modelling approach. *Environ. Sci. Technol.* **24**: 1549-1558.

20. CALAMARI, D., VIGHI, M. & BACCI, E. 1987. The role of terrestrial plant biomass as a parameter in the fugacity model. *Chemosphere* **16**: 2359-2364.

21. BACCI, E., CALAMARI, D., GAGGI, C. & VIGHI, M. 1989. Bioconcentration of organic chemical vapors in plant leaves: experimental measurements and correlation. *Environ. Sci. Technol.* **24**: 885-889.

22. DI GUARDO, A. & CALAMARI, D. 1992. AGRIFUG: Prediction of surface water pollution from pesticides with a Fugacity Model (in Italian). *Ing. Ambientale.* (in press).

23. BACCI, E., RENZONI, A., GAGGI, C., CALAMARI, D., FRANCHI, A. & VIGHI, M. 1989. Models, field studies, laboratory experiments: an integrated approach to evaluate the environmental fate of atrazine (S-triazine herbicide). *Agric. Ecosyst. Environ.* **27**: 513-522.

24. MACKAY, D. 1991. *Multimedia environmental models*. Lewis Publisher, Chelsea.

25. LASKOWSKI, D.A., GORING, C.A.I., McCALL, P.J. & SWANN R.L. 1982. Terrestrial environmental. In: *Environmental risk analysis for chemicals*. R.A. Conway (Ed.). Van Nostrand Reinhold Co., N.Y. pp. 198-240.

26. RAO, P.S.C., HORNSBY, A.G. & JESSUP, R.E. 1985. Indices for ranking the potential for pesticide contamination of groundwater. *Proc. Soil Crop Sci. Soc. Fla.* **44**: 1-8.

27. JURY, W.A., FOCHT D.D. & FARMER, W.J. 1987. Evaluation of pesticide groundwater pollution potential from standard indices of soil-chemical adsorption and biodegradation. *J. Environ. Qual.* **16**: 422-428.

28. GUSTAFSON, D.I. 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* **8**: 339-357.

29. CALAMARI, D., BACCI, E., FOCARDI, S., GAGGI, C., MOROSINI, M. & VIGHI, M. 1991. Role of plant biomass in the global environmental partitioning of chlorinated hydrocarbons. *Environ. Sci. Technol.* **25**: 1489-1495.

30. LYMAN, W.J. 1981. *Prediction of chemical partitioning in the environment: An assessment of two screening models*. Prepared under Contract 68-01-5949. EPA, Washington, DC.

31. McKONE, T.E. 1985. *The use of environmental health-risk analysis for managing toxic substances*. UCRL-92329; Lawrence Livermore National Laboratory, Livermore, CA.

32. PRETI, F. 1992. Agricoltural nonpoint pollution analysis by distributed modeling: assessment of basin-scale potential contamination (in Italian). *Ing. Ambientale* **21**: 93-104.

33. SWISHER, R.D. 1970. *Surfactant biodegradation*. Marcel Dekker Inc., New York, N.Y.

34. ALEXANDER, M. & LUSTIGMAN, B.K. 1966. Effect of chemical structure on microbial degradation of substituted benzenes. *J. Agric. Food Chem.* **14**: 410-418.

35. DIAS, F.F. & ALEXANDER, M. 1971. Effect of chemical structure on the biodegradability of aliphatic acids and alcohols. *Appl. Microbiol.* **22**: 1114-1124.

36. HAMMOND, M.W. & ALEXANDER, M. 1972. Effect of chemical structure on microbial degradation of methyl substituted aliphatic acids. *Environ. Sci. Technol.* **6**: 732-740.

37. VASSEUR, P., KUENEMANN, P. & DEVILLERS, J. 1993. Quantitative structure biodegradability relationships for predicting purpose. In: *Chemical exposure prediction*. D. Calamari (Ed.). Lewis Publishers, Chelsea.

38. MACALADY, D.L. & SCHWARZENBACH, R. 1993. Predictions of chemical transformation rates of organic pollutants in aquatic systems. In: *Chemical exposure prediction*. D. Calamari (Ed.). Lewis Publishers, Chelsea.

39. *QSAR in environmental toxicology. IV.* 1991. J.L.M. Hermens & A. Opperhuizen (Eds). Elsevier, Amsterdam.

40. TREMOLADA, P., DI GUARDO, A., CALAMARI, D., DAVOLI, E. & FANELLI, R. 1992. Mass spectrometry-derived data as possible predictive method for environmental persistence of organic molecules. *Chemosphere* **24**: 1479-1491.

41. VIGHI, M. & BACCI, E. 1989. The Mediterranean Sea: environmental impact of chemicals. *Proceeding of the 1. European Conference on Ecotoxicology*. The Technical University of Denmark, Copenhagen.

42. VIGHI, M. & CALAMARI, D. 1992. Ecotoxicological risk indicators for environmental chemicals. In: *EUROCOURSE Environmental Impact Assessment*. A.G. Colombo (Ed.). Kluwer Academic Publishers, Dordrecht, The Netherlands.