Approaches for the Prediction of Environmental Fate of Pesticides

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Abstract

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The need for predictive approaches for the evaluation of environmental exposure to pesticides is envisaged not only by the scientific community but also by administrative authorities. Several internationals regulations require the use of predictive approaches for preventive risk assessment. Multimedia compartmental models are, at present, the most effective tool to predict the environmental distribution and fate of organic chemicals. An overview is given of the practical possibilities of applying these kinds of models, at different space scale, from micro ecosystems to global pollution. Examples of application and experimental validation are described. Value and limitations of the approach and research needs will also be discussed.

Introduction

There are several reasons for supporting the unreplaceable role of predictive approaches for the evaluation of environmental exposure to potentially dangerous chemicals. From a practical point of view, environmental monitoring can be performed only *a posteriori*, after the emission of contaminants and, in extreme cases, after the occurrence of an environmental damage. Therefore monitoring could allow to plan recovery rather than preventive measures.

From a scientific point of view, the measurement of a given environmental concentration gives a picture of a punctual situation, in time and space, but does not give information about the environmental processes producing it.

The knowledge of the main features of the biogeochemical cycle allows the development of conceptual instruments capable to describe and predict distribution and fate patterns. On this basis, the occurrence of a chemical in the ecosystems and its trend in time can be reconstructed. Moreover, it is evident that predictive approaches represent the only possibility to plan suitable preventive measures against the risk.

For these reasons, the need for predictive approaches for the evaluation of environmental exposure to pesticides is envisaged not only by the scientific community but also by administrative authorities. Several international regulations require the use of predictive approaches for preventive risk assessment. For example, in the Directive of the European Union 91/414, concerning the placing of plant protection products on the market (8), predictive models are proposed as a tool for the quantitative assessment of predicted environmental concentrations (PEC).

In the last few years, several predictive approaches have been developed at different levels of complexity and descriptive/predictive precision.

The Role of Molecular Properties

A first, very simple approach, rough but practically useful at least for preliminary screening evaluations, can derive from the quantification of the main molecular properties regulating environmental partitioning of a chemical. The properties needed and their environmental meanings are the following:

- Water solubility (S). It quantifies the affinity of a substance for the water compartment.
- Vapour pressure (VP). It indicates volatility and, therefore, the affinity for the air compartment, even if the latter is better quantified by the Henry's law constant.
- Henry's Law Constant (H). It could be generally expressed as the ratio between vapor pressure and water solubility (H = VP/S). In practice, H represents, but for a constant, a partition coefficient between air and water. Therefore H can be assumed as an index of the affinity for the air compartment.
- Octanol/water partition coefficient (Kow). It quantifies the lipophilicity of a substance and is therefore assumed

as an index of the ability to pass through biological membranes and to bioaccumulate in living organisms. Thus it is utilized as a measure of the affinity for the biota.

- Octanol/air partition coefficient (Koa). Koa has been recently defined as the key parameter for the evaluation of bioaccumulation in plants (13). Octanol/air partition coefficient can be obtained as follows:

  Koa = (Kow/H) RT

  where R is the gas constant (R = 8.314 Pa m^3 mol^{-1} $°K^{-1}$) and T is the absolute temperature (T°K =273 .15 + t°C).
- Organic carbon sorption coefficient (Koc). This parameter, usually assumed as an index of soil affinity, represents in practice the sorption coefficient for the organic carbon of the soil. The use of Koc as an index of affinity for soil is suitable for relatively hydrophobic and non-ionic substances. For these compounds interactions with the inorganic matrix of soil are negligible and soil sorption can be assumed as determined only by partition with the organic matrix.

A proposal of a qualitative scheme for the classification of the affinity of chemicals for the different environmental compartments is shown in table 1. As indicated in the table, the classification is more reliable for the extreme values of parameters. A solubility higher than 1 g/l clearly indicates that this property is the main driving force and the affinity for water is always very high. On the other side, log Kow and log Koc values around 6 unequivocally indicate very high bioaccumulation and soil sorption potential. At intermediate levels the simultaneous effect of various properties is more complex and classification must be taken as purely indicative.

Leaching Indexes and Ranking Systems

A further step, quite more advanced than the simple evaluation of single molecular parameters, is represented by comparative indexes and ranking systems. This approach requires a few input data, either molecular properties or environmental parameters, and is based on simple algorithms that cannot be assumed as true models. These indexes produce non quantitative values that allow the comparison of several compounds and the hazard ranking for one or more environmental compartments.

In particular, most of these systems were produced specifically for groundwater and therefore allow a classification of the leaching capability of chemical substances. A critical review of the most common and currently utilized leaching indexes is reported by Vighi and Di Guardo (15).

An example of this kind of indexes is the GUS (Groundwater Ubiquity Score) index, based on Koc and half life in soil ($t_{1/2}$) (10):

$$GUS = \text{Log } t_{1/2} (4 - \text{Log Koc})$$

On the basis of the previous algorithm, pesticides can be classified as follows:

non leachers:	GUS < 1.8
transition compounds:	1.8 ≤ GUS ≤ 2.8
leachers:	GUS > 2.8

The reliability of the extremely simple algorithm of the GUS index was successfully validated by a procedure of application of a complex model like GLEAMS (9).

The GUS index, as well as most leaching indexes, does not take into account pesticide application rate. Therefore these kinds of indexes measure an intrinsic leaching capability of the chemicals instead of a realistic pollution potential of the applied compound. This is a severe limitation to the practical meaning of these indexes, particularly in relation to the big differences of application rates of many new generation active ingredients (such as sulfonylureas herbicides), applied at the level of grams per ha, in comparison with traditional compounds applied at the levels of kilograms per ha (e.g. triazine herbicides).

A possible improvement of the practical reliability of the index could be the introduction in the algorithm of the application rate, as in the modified GUS index (16):

$$GUSm = \text{Log } t_{1/2} (4 - \text{Log Koc}) Ar$$

where Ar is the application rate, expressed in kg/ha of active ingredient.

Partition Analysis and Multicompartmental Models

The concept of evaluative models for the prediction of partition among environmental compartments was introduced by Baughman and Lassiter (3). This kind of models utilizes the main molecular properties in an integrated way in order to give a comprehensive picture of environmental distribution of a chemical substance.

These models were originally developed as "instruments for thinking" and for the indication of general trends in environmental partitioning and not as quantitative tools for the prediction of environmental concentrations. Nevertheless, they were proved as highly versatile instruments and in the last few years several "site specific" models were developed.

Table 1. Affinity of an organic chemical for the different environmental compartments according to the main molecular parameters, from (15).

Affinity for The Compartments	Water (WS) g / L	Air (H Pa m^3 / mol	Soil log Koc	Animal Biomass log Kow	Vegetal Biomass log Koa
Very high	> 1	> 10	> 5	> 5	> 8
High[a]	$1 - 10^{-2}$	$10 - 10^{-1}$	5 - 4	5 - 3.5	8 - 7
Average[a]	$10^{-2} - 10^{-3}$	$10^{-1} - 10^{-2}$	4 - 2	3.5 - 3	7 - 5
Low[a]	$10^{-3} - 10^{-5}$	$10^{-2} - 10^{-4}$	2 - 1	3 - 1	5 - 4
Very low	$< 10^{-5}$	$< 10^{-4}$	< 1	< 1	< 4

[a] influenced by other parameter values.

At the time being, multicompartmental partition analysis models have been proved as the most effective tool for the quantitative prediction of environmental distribution and fate of chemical substances. Several kinds of models have been developed at different levels of complexity and validated at different spatial scales (15).

Relatively complex models, as the PRZM (4) requiring a detailed description of environmental features as input data, can give very good predictions at the field scale (not more than a few hectares) (5) but they fail on a larger scale. There are no theoretical objections to the application of such models on a wider area, but the variability of environmental parameters makes it practically impossible to obtain a description as detailed and accurate as the model requires.

On the contrary, more simple models, requiring only an approximate description of the main driving forces as input data, produce less precise results but their versatility allows their application on relatively non homogeneous areas and, therefore, on a larger scale. Simple runoff models derived from the fugacity approach (11) have been successfully validated, indicating an acceptable predictive capability (within one order of magnitude) in several experimental areas of hundreds of hectares (7), up to the drainage area of a small river, with a surface of more than 100 km^2 (2) (Figure 1).

An outline of the paramount role of multimedia models in predicting environmental fate of chemicals is given by Cowan *et al.* (6).

Fugacity-based models have been applied successfully on a wide scale range, from microecosystems up to regional or global environment. An example of application on the microscale is the "hive fugacity model" (14), developed to predict the fate of pesticides used against parasites of bees in the hive compartments (wax, honey, bees, etc.). On the large scale, the ChemCAN model (12) developed to predict chemical fate in Canada, is an example of a regional fugacity model. Finally, the meridian multi-media model (17) is a global model developed through the modular application of fugacity models to the various climatic zones of the world.

Major difficulties may be encountered at the intermediate scale (large hydrographic basins, agricultural comprensories, large administrative regions of a country, etc.) which is the most interesting for management purposes. On this scale, environmental variables are not easy to control or relatively homogeneous as on the small scale. On the other hand, to obtain enough reliable results, large approximations and generalizations, as for regional or global models, are not allowed.

Thus, the major problems for the application of multi media models at the mesoscale, are related to the difficulties in the description of the environmental scenario, due to the spatial inhomogeneicity of the territory.

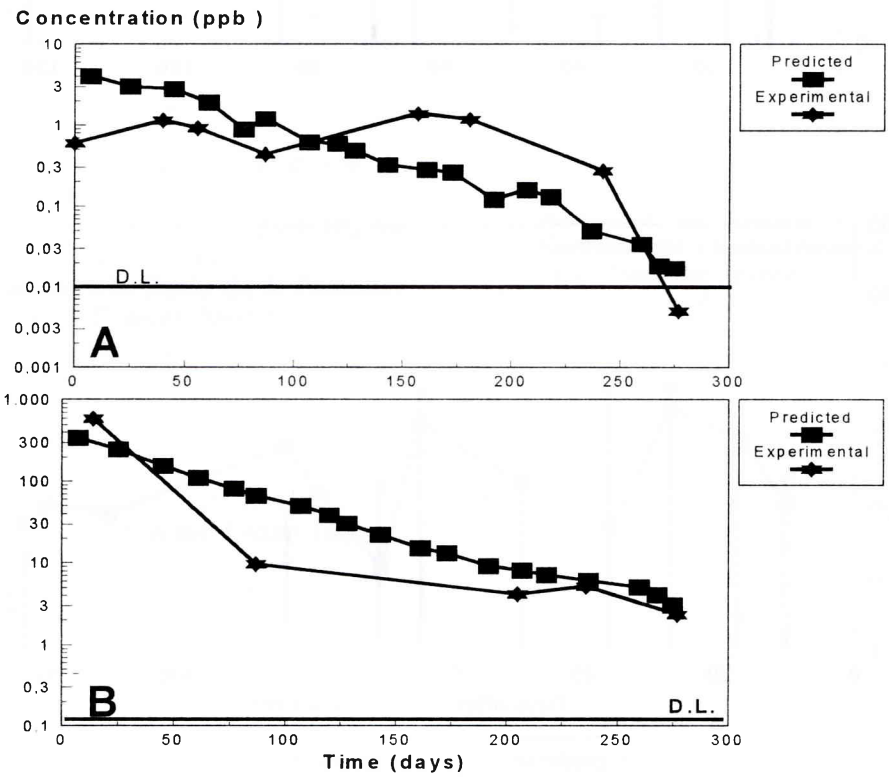

Figure 1. Tijeral watershed (Central Chile). Concentrations of the herbicide chloridazon in surface water (A) and in soil (B) measured and predicted with the SoilFug model. D.L.= Detection limit, modified from (2).

One of the more effective tools available, at the time being, to manage spatial information is represented by the Geographical Information System (GIS). The suitability of the combination of multimedia models and GIS has been recently investigated by Wania (18). Experimentally, the approach has been applied and validated in a pilot research carried on in a small hydrographic basin (about 400 km^2) in Norhern Italy (1). The preliminary results obtained are very promising (Fig. 2).

Conclusions

Multi-media fate models are, at present, the most effective tool to predict the environmental distribution and fate of organic contaminants and, in particular, of pesticides.

Even if some questions are still open, mainly referring to their possibility of application and reliability on the mean and large scale, this approach can be proposed for use in regulatory decision making for assessing the environmental fate of pesticides.

Some of the areas identified for a possible application of these models are:

- preventive risk assessment of new and existing pesticides
- chemical ranking and scoring
- optimizing testing and monitoring strategies
- assessment of indirect exposure
- determining dispersion and recovery time.

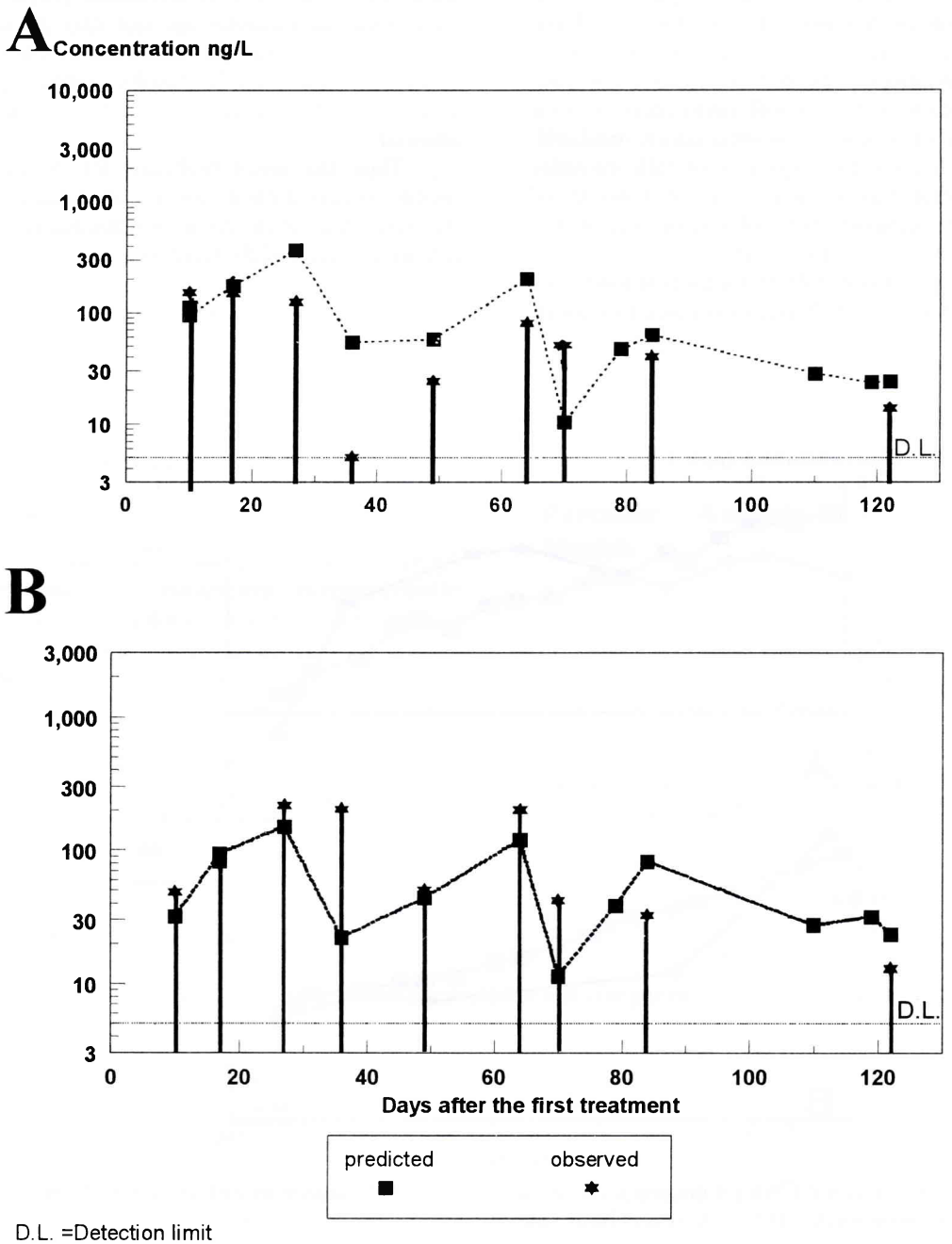

Figure 2. River Lambro watershed (Northern Italy). Concentrations in surface water of the herbicides metholachlor (A) and tebuthylazine (B) experimentally measured and predicted with the SoilFug model.

الملخص

فيجي، ماركو. 1997. الطرق المستخدمة في التنبؤ عن مصير المبيدات في البيئة. مجلة وقاية النبات العربية. 15(2): 150-154.

إن الحاجة لوجود طرق للتنبؤ عن مدى تعرض البيئة للآفات الزراعية ليست أمراً مقصوراً على الهيئات العلمية بل يتعداها إلى الادارات العامة. ان الكثير من القوانين الدولية تتطلب استخدام طرق التنبؤ لتقييم مخاطر التعرض لهذه المبيدات وكيفية التقليل منها أو منعها. إن الطرق التي تعتمد على النماذج المتعددة الوسائل الاعلامية المجزأة هي حالياً أفضل الوسائل للتنبؤ عن التوزع البيئي ومصير المواد الكيماوية العضوية. سيقوم الباحث بعرض شامل للاستخدامات العلمية في تطبيق هذه النماذج في مناطق صغيرة ومحددة أو بشكل واسع وشامل. وسيتم عرض بعض الأمثلة وكيفية اختبار مدى فعاليتها. كما سيتم مناقشة مدى أهمية هذه الطرق وكذلك البحوث الواجب اجراؤها في هذا المجال.

References

1. **Barra R., P. Ferrario, G. Senes and M. Vighi**. 1996. Prediction of herbicide inputs to surface waters at mesoscale by using fugacity models and GIS. Proceedings of the X Symposium on Pesticide Chemistry, A.A.M. Del Re, E. Capri, S.P. Evans, M. Trevisan (Eds.), pp 329-336, Piacenza, Italy.
2. **Barra R., M. Vighi and A. Di Guardo.** 1995. Prediction of Surface Water Input of Chloridazon and Chlorpyrifos in an Agricultural Watershed in Chile, Chemosphere, 30: 485-500.
3. **Baughman G.L. and R.R. Lassiter.** 1978. Prediction of Environmental Pollutant Concentration. In Cairns J. Jr., Dickson K.L. and Maki A.W. (Eds.) Estimating the Hazard of Chemical Substances to Aquatic Life. ASTM STP 657, Philadelphia.
4. **Carsel R.F., L.A. Mulkey, M.N. Lorber and L.B. Baskin.** 1985. The Pesticide Root Zone Model (PRZM): A Procedure for Evaluating Pesticide Leaching Threats to Ground Water, Ecological Modeling, 30: 46-69.
5. **Carsel R.F., W.B. Nixon and L.B. Ballantine.** 1986. Comparison of Pesticide Root Zone Model Predictions with Observed Concentrations for the Tobacco Pesticide Metalaxyl in Unsatured Zone Soils, Environ. Toxicol. Chem, 5:345-353.
6. **Cowan C.E., D. Mackay, T.C.J. Feijtel, D. van de Ment, A. Di Guardo, J. Davies and N. Mackay.** 1994. The Multimedia Fate Model: a vital tool for predicting the fate of chemicals. SETAC, Pensacola, FL.
7. **Di Guardo A., D. Calamari, G. Zanin G., A. Consalter and D. Mackay.** 1994. A Fugacity Model of Pesticide Runoff to Surface Water: Development and Validation, Chemosphere, 28:511-532.
8. **EEC.** 1991. Council Directive 91/414/EEC concerning the placing of plant protection products on the market. EEC O. J. n. L230, 19.08.1991.
9. **Goss D.W.** 1992. Screening Procedure for sSoils and Pesticides Relative to Potential Water Quality Impacts, Weed Technology, 6:701-708.
10. **Gustafson D.I.** 1989. Ground Water Ubiquity Score: A Simple Method for Assessing Pesticide Leachability, Environ. Toxicol. Chem., 8:339-357.
11. **Mackay D.** 1991. Multimedia Environmental Models, The Fugacity Approach. Lewis Publishers, Inc., Chelsea, Mi.
12. **Mackay D., S. Paterson, D.D. Tam, A. Di Guardo and D. Kane.** 1996. ChemCan: a regional level III fugacity model for assessing chemical fate in Canada. Environmental Toxicology and Chemistry, 15:1638-1648.
13. **Paterson S., D. Mackay, E. Bacci and D. Calamari.** 1991. Correlation of the Equilibrium and Kinetics of Leaf-Air Exchange of Hydrophobic Organic Chemicals, Environ. Sci. Technol., 25:866-871.
14. **Tremolada, P., M. Vighi, M. Colombo, M. Spreafico.** 1996. Distribution and fate of coumaphos in the hive: preliminary data for a "Hive Model". Proceedings of the X Symposium on pesticide chemistry, A.A.M. Del Re, E. Capri, S.P. Evans, M. Trevisan (Eds.), pp 441-448, Piacenza, Italy.
15. **Vighi M. and A. Di Guardo.** 1995. Environmental Distribution and Fate and Exposure Prediction. In Vighi M., and E. Funari (Eds.) Pesticide Risk in Groundwater. Lewis Publishers, Inc., Boca Raton FL.
16. **Vighi M., R. Lloyd and C. Sbriscia Fioretti.** 1997. Environmental Toxicology: the Background for Risk Assessment. In: Swanson T., Vighi M. (Eds.) Regulating Environmental Chemical Accumulation" Cambridge University Press, Cambridge (in press).
17. **Wania F. and D. Mackay.** 1995. A global distribution model for persistent organic chemicals. Sci. Total Environ., 160/161:211-232.
18. **Wania F.** 1996. Spatial variability in compartmental fate modelling. Linking fugacity models and GIS. Environ: Sci. & Pollut. Res., 3:39-46.