

# Rating Systems for Pesticide Risk Classification on Different Ecosystems

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Received July 20, 2000

A novel approach is proposed to quantitatively assess the environmental risks associated with the use of plant protection products. Different ranking indexes for the classification of pesticide risk in various environmental systems at different time and space scales have been developed: PRIHS-1 and PRIHS-2 (Pesticide Risk Index for Hypogean Soil Systems), PRIES-1 and PRIES-2 (Pesticide Risk Index for Epygean Soil Systems), and PRISW-1 and PRISW-2 (Pesticide Risk Index for Surface Water Systems). Such indexes identify the risk for each environmental system immediately after a pesticide spraying (PRIHS-1, PRIES-1, and PRISW-1) or in a wider time-space scale scenario (PRIHS-2, PRIES-2, and PRISW-2). Moreover, a general index (ERIP: Environmental Risk Index of Pesticides) was developed for quantifying the comprehensive risk for the environment. The indexes were calibrated by applying to a large number of pesticides for which data were available. The results of the different indexes are compared and the value and limitations of the approach are discussed. © 2001 Academic Press

**Key Words:** pesticides; hazard assessment; risk indexes; risk classification; rating systems.

## INTRODUCTION

Modern management of plant protection products tends to use the risk assessment approach as a useful tool in evaluating the potential environmental side effects of these chemicals on nontarget organisms. Today, registration procedures in many countries (i.e., EU) require the evaluation of all potential risks of environmental damage that might be caused by the use of plant protection products. Different strategies in risk management have been proposed in the last few years with different purposes; however, at present, the criteria used to decide the acceptability of environmental risks are generally based on the concept of toxicity-exposure ratio (TER). A TER is the ratio between a toxicological end point (i.e., LD<sub>50</sub>, NOEL) and a predicted

environmental concentration (PEC). This ratio should be calculated for each of the environmental compartments at risk (ground water, surface water, soil) to establish critical thresholds as a trigger for the need of further information. On the other hand, TERs can be used for making comparisons with appropriate “safety factors” representing the acceptable limit of risk for the different components of the environment.

A different approach that has often been utilized is the ranking of pesticides in terms of their environmental hazard by prespecified criteria. In general, the proposed systems (Sampaolo and Binetti, 1986; Kovach *et al.*, 1992) are based on a development of a score for a set of physico-chemical, toxicological, and ecotoxicological properties of the substances considered. The scores are then combined through an algorithm to obtain a numerical index useful for comparative purposes. In this framework, the Italian Environment Protection Agency (ANPA: Agenzia Nazionale Protezione Ambiente) in 1997, 1998 sponsored a project for setting up different rating indexes for pesticides for different environmental scenarios (Finizio, 1992a,b). The present work aims at highlighting the results of such a project and to discuss the methodological approach followed for setting up the different indexes.

## DEVELOPMENT OF INDEXES

### *The General Approach*

The indexes presented here are totally based on the information required by Annex VI of Directive 414/91/EEC for placing plant protection products on the market (Uniform Principles). An outline of the framework whereby the different risk indexes have been set up is briefly discussed in this section. Three different environments (surface waters, terrestrial hypogean, and epygean systems) are considered in the context of a worst-case scenario. For each of these systems two different time-space scales are considered. The short term at local scale indexes refers to a risk posed by a pesticide, immediately after application, to the three different systems. On the contrary, other indexes are finalized to evaluate pesticide risk in a medium period and in a wider

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area. Finally, a comprehensive index, with the aim of evaluating the overall risk posed by pesticides, is developed.

The indexes are based on exposure indicators (rate of application, environmental distribution, bioaccumulation, and soil persistence) and on the effects (i.e.,  $EC_{50}$ , NOEL) that these substances can exert on nontarget organisms considered representative of the three environmental systems, according to Directive 414/91/EEC (e.g., algae, *Daphnia*, fish for surface water).

An extensive literature search on both physical-chemical and toxicological properties of most pesticides registered in Europe was performed. On the basis of the quantity and quality (i.e., determination methods) of the available data, selected values were chosen. Further information on the database obtained and on the criteria utilized for the selection of the values is reported in Finizio (1999a). When literature data were not available (e.g., microorganisms), default or estimated values have been applied.

As a general procedure for the development of the indexes, a PEC is calculated using simple dilution models or more complex models based on the fugacity approach such as Fugacity Level I (Mackay, 1991) or SoilFug (Di Guardo *et al.*, 1994), specific for surface water inputs. An exhaustive explanation of the environmental scenarios in which the PECs are calculated is reported by Finizio (1999a,b). However, in order to calculate a PEC for surface water, a comparable approach could be used.

Once a PEC is obtained, TERs are calculated using toxicity data for the selected bioindicators. To each TER value a subscore is assigned, which is weighted in function of its role in the overall risk evaluation and then combined in suitable algorithms for a final synthetic score. For the long-term and general indexes, the procedure is sometimes different, in particular due to the difficulty in quantitatively calculating a PEC. Thus, exposure parameters, including persistence and bioaccumulation, are qualitatively evaluated.

#### Short-Term Pesticide Risk Index for the Hypogean Soil System (PRIHS-1)

This index calculates the risk for nontarget hypogean organisms immediately after a pesticide application. PEC is calculated assuming that the product spreads uniformly on a surface of 1 ha and on a layer of 5 cm. Assuming the density of soil to be equal to 1.5 g/cm<sup>3</sup>, the PEC can be calculated as

$$PEC = MRA/750, \quad (1)$$

where MRA = maximum rate of application (g/ha), and  $750 = 10,000 \text{ m}^2 \times 5 \text{ cm} \times 1.5 \text{ g/cm}^3 = 750,000 \text{ kg}$ . As the PEC is expressed as milligrams per kilogram of soil, this value is corrected by a factor of 1000.

**TABLE 1**  
**PRIHS-1: TER Categories with Relative Scores and Weight for Nontarget Organisms Representative of the Hypogean Soil System**

Earthworms (A)		Beneficial arthropods (B)		Mammals (C)	
( $EC_{50}$ /PEC)	Score	% Effect (MRA)	Score	( $LD_{50}$ cut./PEC)	Score
> 1000	0	( $2 \times MRA$ ) = 0%	0	> 1000	0
1000–100	1	$0\% < MRA < 30\%$	2	1000–100	1
100–10	2	$MRA > 30\%$	4	10–100	2
10–1	4	( $0.5 \times MRA$ ) > 30%	8	10–1	4
< 1	8			< 1	8
$W = 5.5$		$W = 5$		$W = 2$	

Earthworms, beneficial arthropods, and mammals have been selected as nontarget organisms representative of the soil system according to the Uniform Principles. A low weight was assigned to mammals (for cutaneous exposure), assuming that their ecological role is relatively low in the hypogean system.

Table 1 shows the scores and weights assigned to the different intervals of categories in which the possible TER values have been subdivided. According to the test method proposed by EPPO (1994a), a real TER cannot be calculated for beneficial arthropods. Indeed, the endpoint of the method is the assessment of certain levels of inhibition of activity (above or below 30%) at fixed exposure levels ( $MRA \times 0.5$ , 1, 2). Therefore, the score is assigned in function of the effect observed at the three exposure levels. The final score of the chemical, ranging from 0 to 100, can be calculated by means of the following algorithm:

$$PRIHS-1 = (A \times 5.5) + (B \times 5) + (C \times 2). \quad (2)$$

#### Long-Term Pesticide Risk Index for the Hypogean Soil System (PRIHS-2)

In this case the period of time application and the persistence of the substance must also be considered. Consequently a time-weighted average PEC is calculated as

$$PEC_{LT} = PEC_{ST}(1 - e^{-kt})/kt, \quad (3)$$

where  $PEC_{LT}$  = predicted environmental concentration in soil after a given time;  $PEC_{ST}$  = predicted environmental concentration immediately after the application (cf. previous index);  $t$  = period of time considered in function of the toxicological test (i.e., 14 days for earthworms, 730 days for mammals); and  $k = \ln 2/DT_{50}$ .

Microorganisms, not considered in the short-term index, have been included, assuming that their role is higher in the

**TABLE 2**  
**PRIHS-2: TER Categories with Relative Scores and Weight for Nontarget Organisms Representative of the Hypogean Soil System**

Earthworms (A)		Microorganisms (B)		Beneficial arthropods (C)		Mammals (D)	
(NOEC/PEC) (14 d)	Score	% Effect	Score	% Effect	Score	(NOEL/CD) (2 years)	Score
> 1000	0	(2 × MRA) = 0%	0	(2 × MRA) = 0%	0	> 1000	0
1000–100	1	0% < MRA < 25%	2	0% < MRA < 30%	2	1000–100	1
100–10	2	MRA > 25%	4	MRA > 30%	4	10–100	2
10–1	4	(0.5 × MRA) > 25%	8	(0.5 × MRA) > 30%	8	10–1	4
< 1	8					< 1	8
	W = 4		W = 4		W = 3		W = 1.5

long run. As for arthropods, the expression of test results does not allow the calculation of a real TER. For mammals, exposure via contaminated food has been considered. In this case a diet concentration (DC: mg/kg), expressed as the product of the bioconcentration factor (BCF) and the  $PEC_{LT}$ , has been calculated. Table 2 reports the scores and weights assigned to the different intervals of categories in which the possible TER values (or effect levels) have been subdivided. The final score of the chemical can be obtained by means of the following algorithm:

$$PRIHS-2 = (A \times 4) + (B \times 4) + (C \times 3)(D \times 1.5). \quad (4)$$

*Short-Term Pesticide Risk Index for the Epygean Soil System (PRIES-1)*

This index evaluates the risk for epygean nontarget organisms immediately after a pesticide application. For bees, the score is applied to the hazard quotient (HQ) (EPPO, 1993), i.e., the ratio between the MRA (g/ha) and the  $LD_{50}$  (µg/bee). For birds and mammals the scores refer to the ratio between the  $LD_{50}$  and the total daily intake (TDI) (mg/kg) (EPPO, 1994b). The TDI is calculated on the basis

of the concentrations typically reached on crops after a pesticide treatment, evaluated according to Hoerger and Kenaga (1972). Table 3 reports the risk classification interval for the selected non target organisms together with their relative scores and weights for calculating the PRIES-1 index. Weight values may be justified as follows: birds are assumed to be more endangered than mammals, due to their higher mobility; bees and other beneficial arthropods are set at the same level, with a lower weight, because scores for arthropods are taken twice in the index calculation. The final score is obtained as follows:

$$PRIES-1 = (A \times 3) + (B \times 4) + (C \times 3) + (D \times 2.5). \quad (5)$$

*Long-Term Pesticide Risk Index for the Epygean Soil System (PRIES-2)*

The index evaluates the risk for the epygean soil system when a wider time-space scale is considered. In relation to the variability of possible environmental scenarios, a PEC cannot be calculated, consequently this index is qualitative due to the impossibility of obtaining a quantitative TER. Scores are assigned to a selected number of exposure and

**TABLE 3**  
**PRIES-1: Risk Classification Intervals, Scores, and Weight for Epygean Nontarget Organisms**

Bees (A)		Birds (B)		Beneficial arthropods (C)		Mammals (D)	
HQ	Score	( $LD_{50}/TDI$ )	Score	% Effect	Score	( $LD_{50}/TDI$ )	Score
> 1	0	> 1000	0	(2 × MRA) = 0%	0	> 1000	0
1–10	1	1000–100	1	0% < MRA < 30%	2	1000–100	1
10–100	2	100–10	2	MRA > 30%	4	10–100	2
100–1000	4	10–1	4	(0.5 × MRA) > 30%	8	10–1	4
> 1000	8	< 1	8			< 1	8
	W = 3		W = 4		W = 3		W = 2.5

**TABLE 4**  
**PRIES-2: Scores Assigned to the Exposure Parameters**

Persistence (P)		Bioaccumulation (B)		Air affinity (A) Fugacity Level I		Soil affinity (S) Fugacity Level I		Application rate (MRA)	
DT <sub>50</sub> (d)	Score	(log K <sub>ow</sub> )	Score	%	Score	%	Score	g/ha	Score
<10	1	<2.5	1	<0.01	1	<1	1	<50	1
10–30	2	2.5–3.5	1.1	0.01–5	1.25	1–20	1.25	50–200	2
30–90	3	>3.5	1.25	>5	1.5	>20	1.5	200–1000	3
90–300	4							1000–10,000	4
>300	5							>1000	5

effect parameters (Tables 4 and 5). Besides application rate, exposure parameters include persistence expressed as DT<sub>50</sub> in soil; bioconcentration potential expressed as log K<sub>ow</sub>; and affinity for the soil and air compartment expressed as percent and distribution calculated by means of the standard Fugacity Level I model (Mackay, 1991).

It must be emphasized that in the standard unit of world of the Fugacity Level I model, a very large water compartment is included; therefore, the amount of chemicals reaching the air or soil compartments is relatively low. An amount as high as 5% in air and 20% in soil indicates a very high affinity for the air and soil compartment, respectively.

Among the relevant organisms, plants, not included in PRIES-1, have been added. It has been assumed that, in the treated area, the crop is not affected (by definition of a plant protection product), while, outside the treated area, an effect on other plant species is likely to occur. A NOEL range is not indicated for plants; only a rough indication of the presence or absence of phytotoxicity is reported. The lowest score for toxicity has been set at 0.1, instead of 0, to avoid a final score of 0 from toxicity alone, despite with extremely high exposure factors. Toxicity and exposure scores are then combined through an algorithm for the final calculation of the index:

$$\text{PRIES-2} = \frac{\sum_{i=1}^5 Ti}{5} \times \frac{(A + S)}{2} \times B \times P \times \text{MRA}. \quad (6)$$

Theoretically, the final value of PRIES-2 ranges between 0.1 and 187. Nevertheless, due to the complexity of the index, values higher than 100 are very rare. Indeed, it is unlikely for a chemical to be classified as highly toxic for all organisms (from plants to mammals) and to show high affinity for both air and soil.

#### *Short-Term Pesticide Risk Index for the Surface Water System (PRISW-1)*

This index evaluates the risk occurring immediately after pesticide application in a surface water system (1-m depth) adjacent (20 m) to the treated area. The PEC is obtained by the sum of drift and runoff. Drift is calculated by

$$Q_D = \text{MRA} \times D_F, \quad (7)$$

where  $Q_D$  = rate of pesticide reaching the water body by drift; MRA, maximum rate of application; and  $D_F$  = drift fraction (assumed to be 4% according to Ganzelmeyer *et al.*, 1995).

The quantity of pesticide reaching the water body by runoff ( $R_0$ ) has been calculated by using SoilFug model (Di Guardo *et al.*, 1994) applied to a worst-case scenario (e.g., rain one day after treatment, high runoff rate). As mentioned above, further information on regarding this scenario can be obtained in Finizio (1999a). Pesticide concentration in the

**TABLE 5**  
**PRIES-2: Scores Assigned to the Effect Parameters**

Plants (T1)		Bees (T2)		Beneficial Arthropods (T3)		Birds (T4)		Mammals (T5)	
FITOT.	Score	NOEL (µg/bee)	Score	NOEL (g/ha)	Score	NOEL (mg/kg diet)	Score	NOEL (mg/kg diet)	Score
+	4	<0.1	4	<10	4	<0.1	4	<0.1	4
–	0.1	0.1–1	3	10–100	3	0.1–1	3	0.1–1	3
		1–10	2	100–500	2	1–10	2	1–10	2
		10–100	1	500–1000	1	10–100	1	10–100	1
		>100	0.1	>1000	0.1	>100	0.1	>100	0.1

**TABLE 6**  
Risk Classification Intervals, Scores, and Weight for  
Nontarget Organisms in Surface Water System

Algae (A)		<i>Daphnia</i> (B)		Fish (C)	
(EC <sub>50</sub> /PEC)	Score	(EC <sub>50</sub> /PEC)	Score	(LC <sub>50</sub> /PEC)	Score
> 10,000	0	> 10,000	0	> 10,000	0
10,000–1000	1	10,000–1000	1	10,000–1000	1
1000–100	2	1000–100	2	1000–100	2
100–10	4	100–10	4	100–10	4
10–2	6	10–2	6	10–2	6
< 2	8	< 2	8	< 2	8
<i>W</i> = 3		<i>W</i> = 4		<i>W</i> = 5.5	

water body in the short term (PEC<sub>ST</sub>) can be calculated as the sum of drift and runoff processes (PEC<sub>ST</sub> =  $Q_D + R_0$ ).

Table 6 reports the score and weight assigned to each TER, obtained as ratio between the acute toxicity (EC<sub>50</sub> or LC<sub>50</sub>) and the PEC<sub>ST</sub>, for the selected organisms representative of the surface water system. The final score is obtained as follows:

$$\text{PRISW-1} = (A \times 3) + (B \times 4) + (C \times 5.5). \quad (8)$$

*Long-Term Pesticide Risk Index for the Surface Water System (PRISW-2)*

As for PRIES-2, a quantitative PEC can hardly be calculated; therefore a qualitative approach is used, based on Fugacity Level I percentage distribution. Nevertheless, a correlation (log-probit scale) was verified between PEC<sub>ST</sub> calculated with SoilFug model (assuming a constant application rate of 1 kg/ha) and the percentage of distribution in water calculated with Fugacity Level I. The relationships allowed a series of classes of concentrations (Table 7) to be identified. In this way it was possible to define six different classes of water concentration (**CCW**: bold in Table 7) corresponding to the upper limits of the intervals of PEC<sub>ST</sub> (worst-case scenario). A theoretical concentration in water (TCW) is calculated by multiplying CCW times maximum rate of application (MRA) and dividing by a factor of 10, assumed as a dilution factor in the receiving water body at the mean scale:

$$\text{TCW (mg/L)} = (\text{MRA} \times \text{CCW})/10. \quad (9)$$

Finally, a theoretical exposure in water (TEW: mg/L) is obtained by multiplying TCW times a score for persistence. The score for DT<sub>50</sub> may be justified by taking into account that, after a long time (e.g., 90 days), a chemical showing a DT<sub>50</sub> lower than 5 days will practically disappear (<0.01%); with a DT<sub>50</sub> of 90 days the remaining amount is

**TABLE 7**  
Classes of Concentrations in Function of the Relationship  
between the Percentage of Water Distribution (Fugacity Level I)  
and the PEC<sub>ST</sub> Obtained Using SoilFug Model

% H <sub>2</sub> O (Fugacity level I)	PEC <sub>ST</sub> (SoilFug) (mg/L)	DT <sub>50</sub> soil (d)	Score
> 95	1.0E-02– <b>1.0E-01</b>	< 5	0.01
60–95	1.0E-0.3– <b>1.0E-02</b>	5–10	0.1
20–60	1.0E-4– <b>1.0E-03</b>	10–30	1
2–20	1.0E-05– <b>1.0E-04</b>	30–90	10
0.1–2	1.0E-06– <b>1.0E-05</b>	90–300	50
		> 300	100

*Note.* Also reported is the classification of DT<sub>50</sub> in soil together with relative score.

50% of the applied dose; and if DT<sub>50</sub> is higher than 300 days the chemical is almost completely present.

The procedure for calculating TEW is complicated and largely arbitrary and the TEW figure is not a realistic exposure estimate but only a numerical value, expressed as a concentration and valid in comparative terms. The advantage of using it instead of the percentage of distribution in water is the possibility of calculating semiquantitative TERs as the ratio between the NOEL for aquatic organisms and the TEW expressed in milligrams per liter. Table 8 reports the TER classification with their relative scores and weights.

The final score, ranging from 0 to 100, can be calculated by

$$\text{PRISW-2} = \Sigma(\text{TER} \times W) \times B \times S, \quad (10)$$

where *B* and *S* refer to the scores of the bioaccumulation potential (log *K<sub>ow</sub>*) of the substance and its percentage distribution in sediments (Fugacity Level I) (Table 8). The role of sediments may be included in the index only as an exposure factor due to the nonavailability of toxicity data on sediment-dwelling organisms.

*Environmental Risk Index for Pesticides (ERIP)*

This index is an attempt to give general information about the overall risk for the environment posed by the use of pesticides. Obviously, due to the high number of parameters involved in the characterizing environmental risk and the impossibility of producing quantitative values for either exposure or effects, such a system yields only qualitative information.

Exposure parameters include percentage distribution in the main environmental compartment (air, soil, water, and sediment) calculated by Fugacity Level I, persistence, bioaccumulation potential, and MRA (Tables 9 and 10). Different

**TABLE 8**  
**TER Classification, Score, and Weight for Nontarget Organisms Representative of Surface Water System**

Algae		<i>Daphnia</i>		Fish		Bioaccumulation		Sediment affinity Fugacity Level I	
TER	Score	TER	Score	TER	Score	log $K_{ow}$	Score (B)	%	Score (S)
> 1000	0	> 1000	0	> 1000	0	$\leq 2.5$	1	< 1	1
100–1000	1	100–1000	1	100–1000	1	2.5–3.5	1.1	1–30	1.1
10–100	2	10–100	2	10–100	2	> 3.5	1.25	> 30	1.25
1–10	4	1–10	4	1–10	4				
< 1	8	< 1	8	< 1	8				
$W = 2$		$W = 3$		$W = 3$					

Note. Also reported are scores assigned to bioaccumulation and percentage of distribution in sediments.

weights are attributed to the four environmental compartments assuming a higher relevance for water and a lower role for sediments in a comprehensive environment assessment.

For the evaluation of effects, toxicity data on organisms representative of major levels of taxonomic and ecological organization for the three environmental typologies (aquatic, terrestrial epygean, terrestrial hypogean) have been taken into account. Toxicological values typical for each environment ( $T_{WAT}$ ,  $T_{EPY}$ ,  $T_{HYPO}$ ) have been defined as the mean of the scores assigned to the toxicity of pesticides on selected organisms belonging to the same environment (Tables 11, 12, 13). In many cases, both acute and chronic toxicity data can be used in function of the availability of data. The score for the effects can be calculated as

$$T_x = \left( \sum_1^n scores \right) / n, \quad (11)$$

where  $T_x$  = average score for the toxic effects of the substance in a particular environmental system; and  $n$  = numbers of individual toxicity scores utilized.

For each environmental system the scores obtained from the average of effect parameters ( $T$ ) are then multiplied with those obtained from the corresponding exposure parameters ( $D$ ). Assuming that it is very unlikely that a chemical will produce high risk in all environments, it is important to stress the role of the more impacted environment in the final assessment. Therefore, different weights ( $W_i$ ) have been assigned in function of the  $D \times T$  value (1.5 for the system most at risk and 0.5 for the other two systems). Thus, the index can be calculated by means of the equation

$$ICRA = [(D_{[(W+SED)/2]} \times T_{WAT}) \times W_1 + (D_{[(A+S)/2]} \times T_{EPY}) \times W_2 + (D_S \times T_{HYPO}) \times W_3] \times P \times B \times MRA, \quad (12)$$

where  $D_{[(W+SED)/2]}$  = mean of the scores assigned to the percentage of chemical distribution in water and sediments (Fugacity Level I);  $D_{[(A+S)/2]}$  = mean of the scores assigned to the percentage of chemical distribution in air and soil (Fugacity Level I);  $D_S$  = mean of the scores assigned to the percentage of chemical distribution in soil (Fugacity Level I);  $T_{WAT}$ ,  $T_{EPY}$ ,  $T_{HYPO}$  = average scores for effects in water,

**TABLE 9**  
**Air, Water, Soil, and Sediment Classes of Affinity for Pesticides and Relative Scores and Weights**

Air affinity Fugacity Level I (DA)		Water affinity Fugacity Level I (DW)		Soil affinity Fugacity Level I (DS)		Sediment affinity Fugacity Level I (DS <sub>ED</sub> )	
%	Score	%	Score	%	Score	%	Score
< 0.1	0.5	< 1	0.5	< 0.1	0.5	< 0.1	0.5
0.1–1	1	1–10	1	0.1–5	1	0.1–5	1
1–5	1.25	10–50	1.25	5–10	1.25	5–10	1.25
5–20	1.5	50–90	1.5	10–30	1.5	10–30	1.5
> 20	2	> 90	2	> 30	2	> 30	2
$W = 1$		$W = 1.5$		$W = 1$		$W = 0.5$	

Note. Affinity is obtained by the application of Mackay's model (Fugacity Level I).

**TABLE 10**  
**Risk Classification Intervals, Scores, and Weight for Persistence, Bioaccumulation, and Rate of Application of Pesticides**

Persistence (P)		Bioaccumulation (B)		Max. rate of application (MRA)	
DT <sub>50</sub> (d)	Score	(log <i>K</i> <sub>ow</sub> )	Score	(g/ha)	Score
<10	0.5	<2.5	1	<50	0.5
10–30	1	2.5–3.5	1.1	50–200	1
30–90	2	>3.5	1.25	200–1000	2
90–300	3			1000–10,000	3
>300	4			>10,000	4

epigeal and hypogeal soil systems; *W* = weights (see explanation in the text); *P* = score for persistence; *B* = score for the potential bioaccumulation; and MRA = score at the maximum rate of application. Theoretically, the final value of ERIP is in the range 0.05 to 200; nevertheless, as for PRIES-2, values higher than 100 are very rare.

#### APPLICATION OF THE INDEXES

The procedure described for the development of the indexes is based on a simple and sound conceptual approach, i.e., the use of exposure and effect parameters to quantify the hazard. Nevertheless, it is largely arbitrary, in particular for the quantitative attribution of scores and weights to the different exposure and effect indicators. Consequently, the reliability of the indexes must be checked by applying a suitable number of chemicals and by evaluating the coherence of the results.

The major problem encountered is the lack of data on the side effects of these substances (i.e., microorganisms, beneficial arthropods) or the big difference (in some cases more than one order of magnitude) among literature values for the same toxicological end point or for physical–chemical properties. This, at present, represents a limitation in the possibility of applying the indexes and the results obtained

should be considered a partial example, useful in verifying the methodological approach proposed.

Only for the two surface water indexes (PRISW-1 and PRISW-2) was information completely available for a relevant number of chemicals. For all other indexes, some data were completely or almost completely lacking; therefore default figures were used.

(a) PRIHS-1: no or very few data are available on beneficial arthropods; as a default, the same score given to bees in PRIES-1 was used.

(b) PRIHS-1: no or very few data are available on beneficial arthropods and microorganisms; for arthropods, default figures were assigned as in PRIHS-1; for microorganisms the lowest score (0.1) was assigned to herbicides and insecticides, the highest (8) to fungicides. Consequently, many herbicides and insecticides were probably underestimated, and fungicides overestimated.

(c) PRIES-1: no data are available for beneficial arthropods and plants: for beneficial arthropods, default figures were assigned as in PRIHS-1; for plants the lowest score (0.1) was assigned to insecticides and fungicides, the highest (4) to herbicides. Consequently, many insecticides and fungicides were probably underestimated, and herbicides overestimated.

(d) ERIP: no data are available for beneficial arthropods microorganisms and plants: in this case default values were attributed using the same approach used in the other indexes.

Therefore, with some default data it was possible to apply all the indexes to a large enough number of chemicals to allow a suitable calibration of the scores and weights (Table 14). The complete database, as well as an electronic page for the calculation of the seven indexes are available upon request to the authors.

On the basis of this application, taking into account the distribution of chemicals within the range of variability of each index, the risk classes in Table 15 can be proposed. An example of application of the indexes is shown in Figs. 1, 2, 3 where a series of chemicals are shown, for which information was available for calculating the indexes. In the figure

**TABLE 11**  
**Long- and Short-Term Toxicity Classification and Their Relative Scores for Algae, *Daphnia*, and Fish**

Algae			<i>Daphnia</i>			Fish		
(NOEC) (96 h)	EC <sub>50</sub> (96 h) (mg/L)	Score	(NOEC) (21–28 d)	EC <sub>50</sub> (48 h) (mg/L)	Score	(NOEC) (14–28 d)	EC <sub>50</sub> (96 h) (mg/L)	Score
<0.01	<1	2	<10E-3	<0.1	2	<10E-3	<0.1	2
0.01–0.1	1–10	1.5	10E-3–10E-2	0.1–1	1.5	10E-3–10E-2	0.1–1	1.5
0.1–1	10–100	1	10E-2–10E-1	1–10	1	10E-2–10E-1	1–10	1
1–10	100–1000	0.5	10E-1–1	10–100	0.5	10E-1–1	10–100	0.5
>10	>1000	0.1	>1	>100	0.1	>1	>100	0.1

only the six indexes referring to specific compartments are reported, as ERIP is more incomplete and difficult to compare with more specific indexes. The database for the calculation is reported in the Appendix. From the figures, the following comments can be made:

(1) As a general rule, insecticides tend to be more dangerous than other compounds. This tendency is more evident in

short-term terrestrial indexes due to their high acute toxicity on animals. With the exception of PRIHS-2, the highest score are always reached by insecticides. It must be noted that fungicides in PRIHS-2 are reasonably overestimated due to the high score given by default to microorganisms. Herbicides are also possibly overestimated in PRIHS-2 due to the high score given by default to phytotoxicity. Herbi-

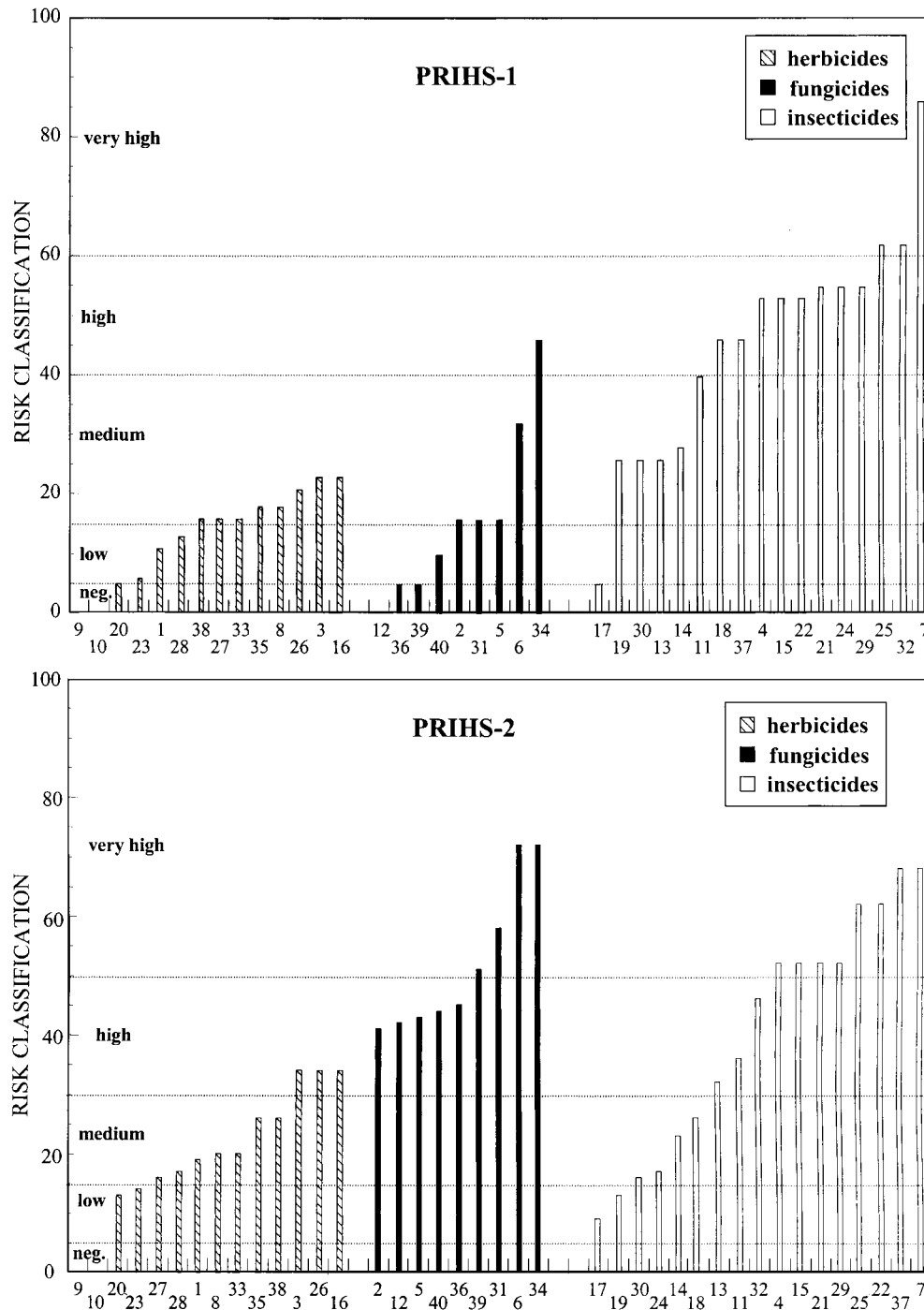


FIG. 1. Risk classification of pesticides for the hypogean soil system according to PRIHS-1 and PRIHS-2 indexes (for numbers, refer to the Appendix).



**TABLE 12**  
**Classification of Pesticide Toxicity and Relative Scores on Terrestrial Epygean Nontarget Organisms**

Plants		Bees			Ben. arthropods		Birds			Mammals		
Phyt	Score (A)	NOEL (μg/bee)	LD <sub>50</sub> (μg/bee)	Score (B)	(%)	Score (C)	NOEL (mg/kg d)	LD <sub>50</sub> (mg/kg d)	Score (D)	NOEL (mg/kg d)	LD <sub>50</sub> (mg/kg d)	Score (E)
+	2	<0.01	<0.1	2	> 80	2	<1	< 10	2	<1	< 10	2
–	0.1	0.01–0.1	0.1–1	1.5	80–50	1.5	1–10	10–10E2	1.5	1–10	10–10E2	1.5
		0.1–1	1–10	1	50–30	1	10–10E2	10E2–10E3	1	10–10E2	10E2–10E3	1
		1–10	10–100	0.5	30–10	0.5	10E2–10E3	10E3–10E4	0.5	10E2–10E3	10E3–10E4	0.5
		> 10	> 100	0.1	< 10	0.1	> 10E4	> 10E3	0.1	> 10E4	> 10E3	0.1

cides are more likely to reach “high” or “very high” scores for the aquatic environment. This is generally due to their lower hydrophobicity and to high algal toxicity.

(2) Sulfonylureas herbicides always show low or negligible risk for all compartments, due to their low application rate and low persistency. This same trend is also evident for other compounds not shown in the figure, even if some slightly higher figures (always within the “low class”) are possible in PRISW-1 due to their affinity for the water compartment and toxicity for algae. Another low-risk herbicide is imazametabenz-CH<sub>3</sub> due to its low application rate and low toxicity on all nontarget organisms.

(3) Triazine and triazinone herbicides generally show medium to high risk. The high score of metribuzin in the aquatic environment is mainly due to its high toxicity for fish. Most other herbicides fall into the “low” to “medium” risk range with some differences among indexes. For example, propyzamide and metholachlor show higher risk for the terrestrial compartments due to their relatively high hydrophobicity.

(4) Among fungicides, if the overestimated PRIHS-2 is excluded, some compounds are always classified within “low” or “negligible” classes (triforine, cyproconazole). Captan, due to its high toxicity for aquatic animals, shows very high risk for PRISW-1, but its low persistence highly reduces the risk in PRISW-2. On the contrary, the highly persist-

ent tebuconazole shows medium risk for all indexes, in spite of its relatively low toxicity on all nontarget organisms. Pyrazophos, prochloraz, and carbendazim are toxic for aquatic, as well as for terrestrial, organisms and show medium to high risk for all indexes, with higher scores in the long term for the latter two, due to their relatively high persistence.

(5) Pyrethroid insecticides show high to very high risk for the aquatic environment in the short term due to their extremely high toxicity for aquatic animals. The risk is greatly reduced in the long-term index, due to their low persistence and hydrophobicity.

(6) Organophosphorus insecticides are a complex group with variable environmental and toxicological characteristics. Some chemicals generally show medium to low risk, such as demeton-s-methyl and heptenophos due to their low application rate and low persistency (heptenophos shows high risk only for aquatic environments in the short term). Others always show high to very high risk, due to high application and high toxicity for nontarget organisms, such as diazinon and isophenphos. As a general rule, for most organophosphates, the risk seems to be higher in the short term, due to high toxicity and relatively low persistence.

(7) High variability also applies to carbamates, where pirimicrab (low application rate, low persistence) generally shows medium risk, even if the toxicity for nontarget

**TABLE 13**  
**Classification of Pesticide Toxicity and Relative Scores on Terrestrial Hypogeal Nontarget Organisms**

Earthworms			Microorganisms	
NOEL (mg/kg d.)	LD <sub>50</sub>	Score (A)	% Effect	Score (B)
<0.1	<1	2	(0.5 × MRA) > 25%	2
0.1–1	1–10	1.5	MRA > 25%	1.5
1–10	10–10E2	1	0% < MRA < 25%	1
10–100	10E2–10E3	0.5	(2 × MRA) = 0%	0.1
> 100	> 10E3	0.1		

**TABLE 14**  
**Number of Pesticides for Which the Seven Indexes were Calculated**

Indexes	Herbicides	Insecticides	Fungicides	Total
PRIHS-1	34	45	26	105
PRIHS-2	29	31	17	77
PRIES-1	49	55	31	135
PRIES-2	16	24	5	45
PRISW-1	52	32	32	116
PRISW-2	49	49	33	131
ERIP	42	41	29	102

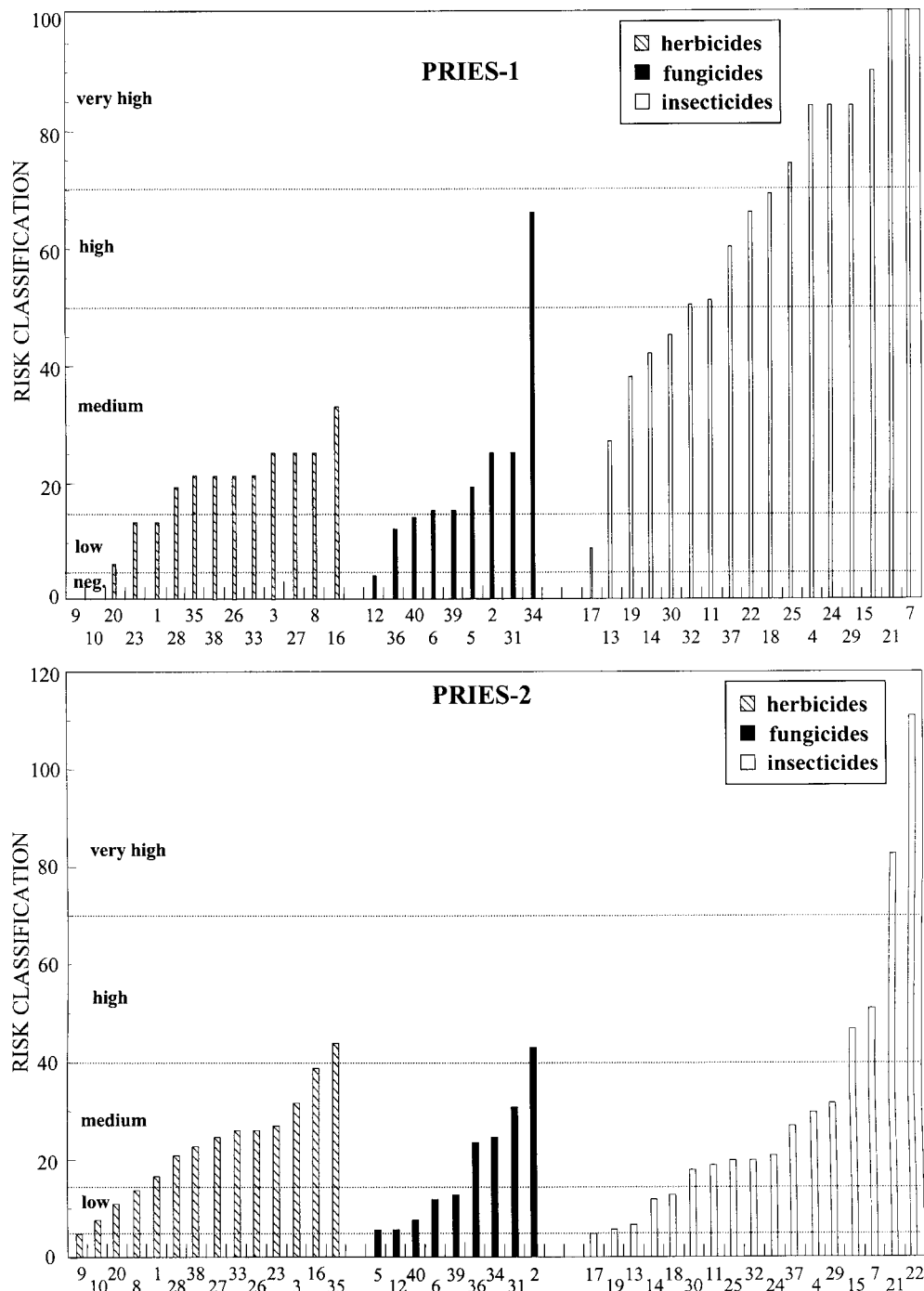


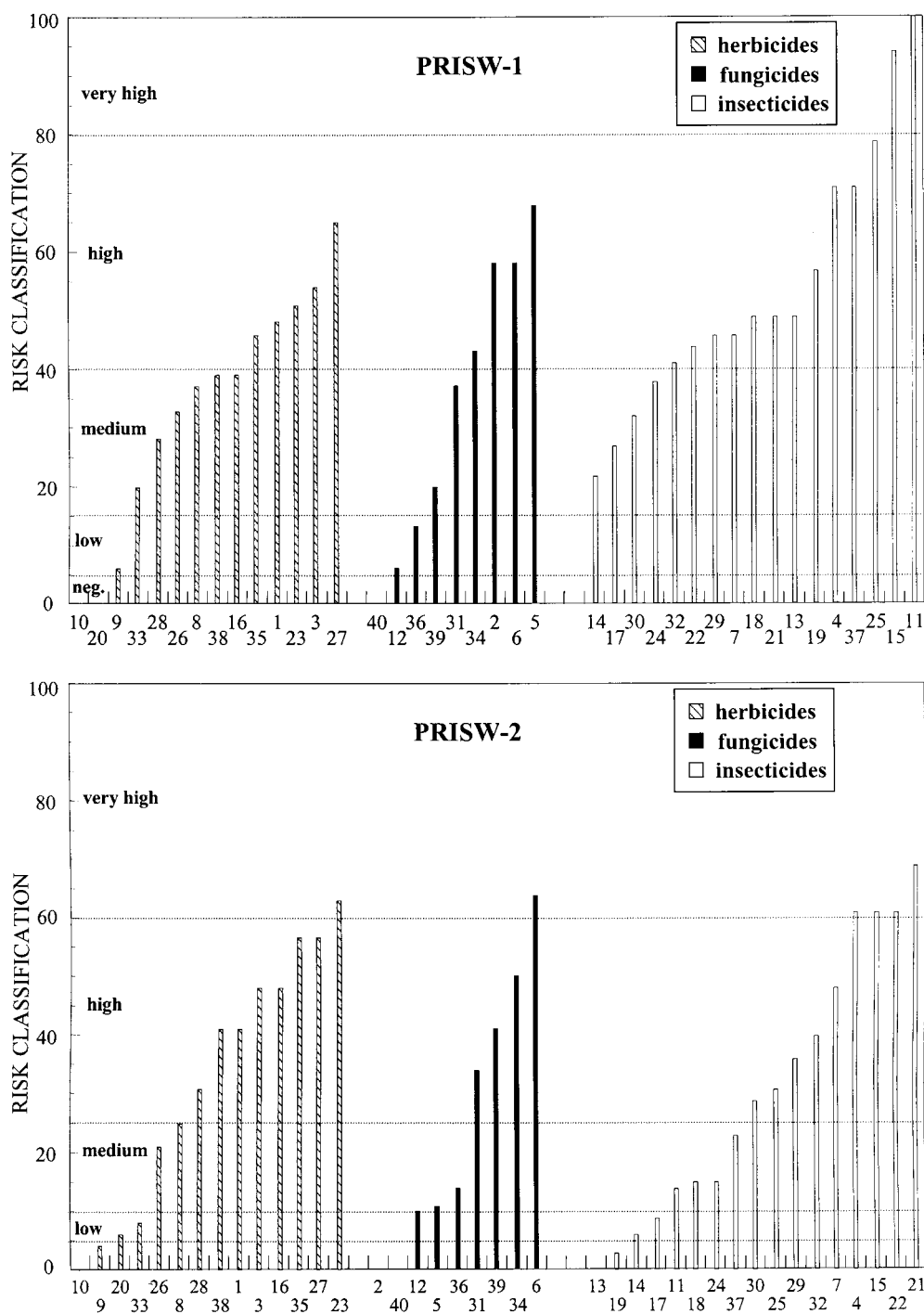
FIG. 2. Risk classification of pesticides for the epyean soil system according to PRIES-1 and PRIES-2 indexes (for numbers, refer to the Appendix).

organisms is high, while carbofuran (high application rate, high persistence) always shows high to very high risk.

(8) Finally, the case of lindane is very interesting, showing high risk in all short-term indexes and very high scores in all long-term indexes, according to its toxicity and persistence.

## CONCLUSIONS

As mentioned above, the main problem encountered in applying the risk indexes is the lack of basic data, in particular on the effects of pesticides on some groups of nontarget organisms. In order to be realistically applicable, indexes



**FIG. 3.** Risk classification of pesticides for the surface water system according to PRISW-1 and PRISW-2 indexes (for numbers, refer to the Appendix).

have been developed considering only data required, for registration procedures, by European Directive 414/91 EEC. Thus, in the near future, probably this will be largely remedied.

Due to the difficulty in obtaining reliable data to apply and compare all the indexes, the results obtained in many

cases should not be considered real risk classification of pesticides, but an example of application, whose validity is related to the data utilized. The main objective of such application was to verify the methodological approach proposed.

From the examples of application showed in this article, as well as from the application to a larger number of

**TABLE 15**  
**Risk Classification of Pesticides**

Level of risk	PRIHS-1	PRIHS-2	PRIES-1	PRIES-2	PRISW-1	PRISW-2	ERIP
Negligible	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5	≤ 5	≤ 10
Low	> 5– ≤ 15	> 5– ≤ 15	> 5– ≤ 15	> 5– ≤ 15	> 5– ≤ 15	> 5– ≤ 10	> 10– ≤ 20
Medium	> 15– ≤ 40	> 15– ≤ 30	> 15– ≤ 50	> 15– ≤ 40	> 15– ≤ 40	> 10– ≤ 30	> 20– ≤ 40
High	> 40– ≤ 60	> 30– ≤ 50	> 50– ≤ 70	> 40– ≤ 70	> 40– ≤ 80	> 30– ≤ 60	> 40– ≤ 60
Very high	> 60	> 50	> 70	> 70	> 80	> 60	> 60

chemicals, not reported here, some general conclusions can be drawn.

1. The higher risk classification for insecticides, in comparison with the other two categories of pesticides, derives from the structure of the indexes, where, generally, more weight for the protection of ecosystems was assigned to animals, in comparison with microorganisms and plants. This could be a critical aspect of the formulation of the indexes; nevertheless, the animal component of an ecosystem seems to be more sensitive (subject) to stress (long resilience time) than microorganisms and plants. Therefore, it seems reasonable to make this component of the biological community a priority.

2. The different levels of risk for the different environments is well described by the specific indexes in function of exposure patterns and effects on the various groups of nontarget organisms.

3. The role of persistence is well described by short-term and long-term indexes. Persistent chemicals generally show higher risk in long-term indexes. For very persistent chemicals (e.g., DT<sub>50</sub> above 3 months), a nonnegligible risk was always calculated, even for chemicals with very low effects on nontarget organisms.

4. The indexes seem to follow the principle of congenericity. Similar substances tend to reach a comparable degree of

risk. It is evident that structurally congeneric substances exert a comparable toxicity on nontarget organisms. The differences are generally due to exposure parameters, such as different rates of application. This is particularly evident for relatively homogeneous classes of chemicals, with comparable toxic effects as well as environmental properties (for example, sulfonylureas and triazines). For more complex groups of chemicals, such as organophosphate insecticides with extremely different environmental behaviors (for example, water solubility ranging from hundreds of grams up to a few micrograms per liter), variability in risk classification is much higher.

In conclusion, one must be aware that some assumptions adopted for the development of the indexes are highly arbitrary, in particular those related to the attribution of scores and weights for the various effect and exposure factors. Nevertheless, the examples of application and comparison among indexes, as well as the application of larger amounts of chemicals, not shown in this article (results are available upon request to the authors), indicate a good level of coherence in the classification of pesticides in relation to the risk to different environments. Therefore, the proposed indexes may be considered a useful tool for the management of plant protection products.

## APPENDIX

### Physical–Chemical Properties and Ecotoxicological Values Utilized for Calculating the Risk Indexes of Pesticides (Data were Taken from FITOX Database Available on Request from the Authors)

No.	Chemical	Use	MRA	S (mg/L)	VP (Pa)	Log K <sub>ow</sub>	DT <sub>50</sub> (d)	EC <sub>50</sub> algae (mg/L)	Daphnia (mg/L)	LC <sub>50</sub> fish (mg/L)	LD <sub>50</sub> bees (µg/bee)	LD <sub>50</sub> birds (mg/kg b.w.)	LD <sub>50</sub> earth.w mamm. (mg/kg)	EC <sub>50</sub> earth.w (mg/kg soil)
1	Alachlor	Herb.	3768	240	2.9E–03	3.087	30	6.0E–02	10	1.8	32000	1536	5620	387
2	Anilazina	Fung.	2760	8	8.2E–07	3.79	1	1.02	0.07	0.15	100	2000	4000	1000
3	Atrazine	Herb.	4000	30	4.0E–05	2.63	180	3.8E–02	5.7	4.5	160	940	1869	78
4	Azinphos-methyl	Ins.	750	29	3.0E–05	2.69	64	3.6	1.1E–03	0.02	1.5E–01	32.2	4.4	59
5	Captan	Fung.	1743	5.1	1.1E–05	2.54	3	44.5	0.007	0.034	91	2000	8400	237
6	Carbendazim	Fung.	600	8	6.5E–08	1.4	120	1.3	0.13	0.83	50	5826	15000	2
7	Carbofuran	Ins.	2880	351	8.0E–05	2.32	100	204.48	3.86E–02	22	1.6E–01	5.04	8.8	3.09
8	Chloridazon	Herb.	4851	400	1.0E–05	1.12	21	1.1	132	32	200	2000	2140	1050
9	Chlorsulfuron	Herb.	15	7000	6.1E–04	–1	42	1.35E–01	370	250	> 25	> 5000	5545	2000
10	Cinosulfuron	Herb.	80	4000	1.0E–05	3.78	20	4.8	2500	100	100	2000	5000	1000

## APPENDIX—Continued

No.	Chemical	Use	MRA	S (mg/L)	VP (Pa)	Log $K_{ow}$	DT <sub>50</sub> (d)	EC <sub>50</sub> algae (mg/L)	Daphnia (mg/L)	LC <sub>50</sub> fish (mg/L)	LD <sub>50</sub> bees (μg/bee)	LD <sub>50</sub> birds (mg/kg b.w.)	LD <sub>50</sub> mammals (mg/kg)	EC <sub>50</sub> earth.w (mg/kg soil)
11	Cyfluthrin	Ins.	51	2.0E-03	1.0E-08	6	63	1	1.4E-04	0.0006	5.1E-02	2000	869	1000
12	Cyproconazole	Fung.	30	140	3.0E-05	2.91	110	7.7E-02	26	19	1000	150	1020	335
13	Deltamethryn	Ins.	31	2.0E-04	4.0E-08	6.5	23	9.1	3.5E-03	0.00091	8.0E-02	1000	300	28.57
14	Demeton-S-methylsulfon	Ins.	150	60	3.5E-02	1.2	15	22.1	2.3E-02	6.4	1.9E-01	44	35	60
15	Diazinon	Ins.	4000	60	8.0E-03	3.42	65	17.3	9.6E-04	0.09	5.0E-02	5.2	300	130
16	Dichlobenil	Herb.	8100	18	7.0E-02	2.74	180	2	6.2	22	160	683	4460	1000
17	Diflufenzuron	Ins.	140	2.0E-01	1.2E-07	3.88	10	10	7.1E-03	250	100	2000	4000	780
18	Fenitrothion	Ins.	1030	30	1.3E-04	3.397	4	3.9	15E-04	1.7	5.8E-02	23.6	504	231
19	Heptenophos	Ins.	640	2.8	6.5E-02	2.32	1.4	35	2.2E-03	0.056		17	96	98
20	Imazametabenz-CH <sub>3</sub>	Herb.	126	1370	1.5E-06	1.82	45	127	100	100	100	2150	5000	1000
21	Isofenphos	Ins.	5000	23.8	4.0E-04	4.04	300	5.7	3.9E-03	3.3	6.1E-01	8.7	20	404
22	Lindane	Ins.	1050	7.3	4.1E-03	3.7	400	1	4.6E-01	0.06	2.0E-01	120	88	59
23	Linuron	Herb.	1190	75	2.0E-03	2.76	100	2.2E-02	1.2E-01	3.15	1600	940	1500	1000
24	Methamidofos	Ins.	990	2,000,000	4.0E-02	-0.8	15	86	2.7E-01	40	2.2E-01	10	20	17
25	Methidathion	Ins.	668	220	4.5E-04	2.57	28	11	7.2E-03	0.01	1.3E-01	23	25	4.8
26	Metolachlor	Herb.	1918	530	4.2E-03	3.28	46	7.7E-02	25	3.9	110	2150	1200	140
27	Metribuzin	Herb.	1050	1200	1.3E-05	1.99	60	4.3E-02	4.5	0.076	35	168	1090	331.8
28	Monolinuron	Herb.	1500	735	2.0E-02	2.3	60	2.1E-01	32.5	56	296.3	1260	1430	1000
29	Parathion-methyl	Ins.	576	50	1.3E-03	3	44	15	4.0E-03	2.7	2.8E-02	7.56	14	40
30	Pirimicarb	Ins.	350	2700	4.0E-03	3.43	10	140	8.0E-05	29	2.2	8	147	60
31	Prochloraz	Fung.	1082	34	1.5E-04	4.38	120	2.4E-02	4.3	1.5	60	662	1600	230
32	Propoxur	Ins.	600	1800	4.0E-04	1.5	79	5.3	1.5E-01	3.7		28	50	5.2
33	Propyzamide	Herb.	2000	15	5.4E-02	3.26	60	5.5	5.6	72	100	8770	5620	350
34	Pyrazophos	Fung.	804	4.2	1.0E-04	3.8	20	65.5	3.6E-04	0.48	2.5E-01	118	151	1000
35	Simazina	Herb.	2000	5	8.5E-06	2.2	180	5.6E-02	1	100	160	2000	5000	1000
36	Tebuconazole	Fung.	375	32	9.6E-07	3.7	652	4.01	11.5	6.4	50	2000	4000	1381
37	Terbufos	Ins.	675	5	4.3E-02	4.477	27	1.4	3.1E-04	0.01	4.1	28.6	1.3	4.6
38	Terbuthylazine	Herb.	1100	8.5	1.5E-04	2.88	60	1.6E-02	21	3.8	100	1000	1590	200
39	Tridemorph	Fung.	563	12	6.4E-03	4.2	50	2.8E-01	1.3	3.4	200	1388	480	880
40	Triforine	Fung.	570	30	2.7E-05	2.2	21	380	117	1000	10	5000	16,000	1000

## ACKNOWLEDGMENT

The authors acknowledge the financial support of the Agenzia Nazionale per la Protezione dell'Ambiente (ANPA), Italy.

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