

Ecological relative risk (EcoRR): another approach for risk assessment of pesticides in agriculture

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Abstract

A site-specific methodology was developed to assess and compare the ecotoxicological risk that agricultural pesticides pose to ecosystems. The ecological relative risk (EcoRR) is a composite scoring index for comparing relative risks between different plant protection products, and is used to assess the potential ecological impact their residues have after being applied to agricultural systems. The EcoRR model is based on standard frameworks for risk assessment (e.g. PEC/toxicity), but takes account of factors such as persistence of residues and biodiversity of ecosystems. The exposure module considers the environmental concentrations of a substance, its persistence, bioaccumulation and probability of exposure in several environmental compartments (water, sediment, soil, vegetation, air). The toxicity module takes into account the biodiversity of the ecosystems affected, whereby the endpoints used are weighted by the proportional contribution of each taxon in a given environmental compartment. EcoRR scores are calculated independently for each compartment and affected areas, thus enabling pinpointing of where risks will occur. The procedure to calculate EcoRR scores is explained using an example, and a sensitivity analysis of the model is included. A simulated risk assessment of 37 pesticides intended for use in a cotton development is also given as a case study. Exposure data were obtained using fugacity model II in areas previously defined by spray drift models. Toxicity data to vertebrate taxa and crustaceans were obtained from several databases, and biodiversity data from local sources. EcoRR scores were calculated for each compartment both on- and off-farm, during a normal growing season and during a flood, and a comparative relative assessment for all pesticides is discussed. EcoRR scores were also compared to traditional assessments using quotients for some taxa in the aquatic and terrestrial environments, revealing a good correlation between both models in some cases. It is apparent that EcoRR scores reflect adequately the potential risk of those chemicals to ecosystems, though they are less dependent on toxicity to sensitive species than the simple quotient. This methodology can be used either with field measured data or model predicted data, so management options for new chemicals can be tested prior to their application on crops. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Standard methodologies for assessing the risk of chemicals in the environment are based on the framework of hazard identification, exposure and toxicity assessments, concluding with a risk characterisation

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(Norton et al., 1992; US EPA, 1996). While exposure and toxicity assessments require a great deal of quantification, risks can be formulated in many ways and do not conform necessarily with quantitative approaches (Suter II, 1990). Most of the current assessments refer to acute effects of chemicals on aquatic environments, while little attention has been paid to terrestrial and long-term hazards from pesticides (Van Straalen and Van Gestel, 1999), despite the importance of agricultural systems on terrestrial ecotoxicology (Kendall and Akerman, 1992).

Recently, new approaches have emerged to deal with the difficult issue of assessing the environmental impact of contaminants in its broadest sense, i.e. at the ecosystem level (Levitán et al., 1995). The latest kind of assessment implies that a judgement has to be made regarding the threats to the environment and several taxa through different routes of exposure. Most approaches opt for 'environmental impact scores' or relative risk indices which compare the potential environmental and economic risks of different pesticides using single or aggregated indicators (Higley and Wintersteen, 1992; Kovach et al., 1992; Penrose et al., 1994; Linders and Luttkik, 1995), and though semi-quantitative in nature their simplicity makes them ideal for farmers to use (Van der Werf, 1996). After all, the ultimate end of relative risk scores is to encourage a more responsible agriculture, one where the ecological cost is taken into account together with other production costs, and that is a task for the farmers themselves.

However, it is becoming a necessity to assess quantitatively the potential ecological risks among different chemicals, so as to compare pesticides used in the same agricultural ecosystem in respect to their environmental impact. In this context, environmental impact points (EIP) provide a simple and practical way of estimating the impact that different compounds applied to a site-specific farm would have in surrounding surface and ground waters (Reus and Pak, 1993). Other approaches consider a larger set of factors (soil type, climate, distance to waterways, dosage, etc.) to produce an indicator that may help farmers decide on chemicals with the lowest risk potential in their particular environments (Gyldenkaerne, 1996). The model SYNOPSIS (Gutsche and Rossberg, 1997) compares the risk potential of different chemicals using an aggregated index, calculated in a four-step process which

considers the environmental exposure to several compartments, the biological exposure to various taxa, and the application patterns and doses applied. The SYNOPSIS model includes application patterns and a comprehensive range of factors to produce a detailed assessment of chemicals in production systems as a whole. More recently (Roussel et al., 2000), a fuzzy expert system structured in modules (Ipest) was used to assess the environmental risks in air, groundwater and runoff water, of pesticides applied to specific crops, after considering several application techniques and site-specific conditions. This paper introduces another composite model for calculating a relative risk score to assess site-specific impacts of pesticides used in any crop production system.

The ecological relative risk (EcoRR) approach is site-specific, taking into account the dose of chemical applied, its partitioning into air, soil, vegetation, surface water and groundwater, its rate of degradation and hence its persistence in each compartment, its bio-concentration in animal tissues and its toxicity to all species present in those compartments.

The work presented in this paper is based on simulation data, though a partial validation of the predicted environmental concentrations used is currently under way on a cotton farm development in south eastern Australia. This methodology is intended for any agricultural farm, and indeed for any specific site where pesticides or other hazardous chemicals are applied. Under the current plans for expansion of the cotton industry in Australia many relatively pristine areas will be cultivated in the incoming years, raising questions from land-holders, graziers and urban dwellers concerning the safety of the new cotton developments, since the use of chemicals is regarded as affecting their environment, their cattle/sheep business, wildlife and human health. The community at large is likely to demand an objective assessment of the risks associated with new cotton developments, specially when they are located near sensitive areas such as urban centres, livestock farms, national parks or heritage reserves. Although extensive studies have been conducted on the environmental fate and behaviour of pesticides in cotton production systems in Australia (Kimber et al., 1995; Kennedy et al., 2001), their ecotoxicological impact has not been addressed in detail, and Australian regulatory authorities usually base their assessment of new products on data obtained in trials overseas.

2. Materials and methods

With the aim of developing an objective approach to assess and compare the ecotoxicological risk of chemicals used in plant crop protection, the EcoRR model considers application patterns, exposure factors and toxicity to multiple species in a single numerical expression (score) that is used to compare risk among different pesticides at a site-specific level. The scores are first calculated separately for each environmental compartment, and are then aggregated to obtain a total risk score for specific areas, which represents a relative risk to the affected ecosystem rather than an absolute risk.

The procedure to calculate EcoRR scores is described first, using the example of the insecticide chlorpyrifos to guide the reader through the various steps required. A simulation case study is then presented to illustrate the possibilities of applying this methodology to site-specific risk assessments under several scenarios.

2.1. Step 1: exposure assessment

The module of exposure assessment in EcoRR is done separately for each environmental compartment, namely air (A), soil (S), vegetation (V), groundwater (GW), surface water (W) and sediment (SD). In each compartment, the dose of residues per affected area, their probability of exposure and persistence in a certain environmental compartment, indicated by both the half-life of a chemical and bioaccumulation in organisms, are combined in a single number as follows:

$$\text{Exposure (X)} = D \times P \times t_{1/2} \times \text{BCF} \quad (1)$$

where D is the dose, P the probability of exposure to a compartment, $t_{1/2}$ the half-life of a chemical in such compartment and BCF a bioconcentration factor in animal tissues.

Prior to calculating these exposure components, the areas affected by residues of agricultural chemicals must be defined first. The target crop on-farm will be the major recipient of all chemicals applied, whether as granules laid or buried in the field or liquid formulations sprayed from booms on ground-rigs or aircraft. As considerable amounts of sprayed pesticides drift onto nearby land (Pimentel, 1995), it is important to define the extent of the surrounding off-farm areas af-

ected using any of the drift models available (i.e. Bird et al., 1996). The size of these potential drift zones depend mainly on the type of chemical application, since aerially sprayed pesticides spread further than those sprayed from ground-rig booms (Fig. 1). In any case, under recommended agricultural practices drift falls downwind, so drift residues occur only on certain parts of the entire potential drift zone surrounding the field. Furthermore, since the downwind distribution of residues usually follows a Gaussian pattern (Bache and Sayer, 1975), is preferable to subdivide the drift zone into two parts: a narrow band adjacent to the sprayed field that contains the majority of the drift residues (i.e. $\geq 50\%$) and the remainder of the drift zone which extends much further from the field, up to 1200–1500 m or even more distant. Following the accepted terminology in Australian agriculture, the narrow band will be called here ‘buffer’ (de Snoo and de Wit, 1998) to distinguish it from the more extensive drift zone usually extending beyond the farm boundaries, to be referred here as the off-farm affected area (Fig. 1). The buffer zone is normally located entirely or for the most part within the farm.

The area, size and volume of matrices in each compartment are then estimated for the specific layout of the site. An example is given in Table 1(1) for an irrigated cotton farm. In cases like this, the surface water compartment can be divided into irrigation waters and runoff waters if they are expected to have different concentration of chemical residues.

Having defined the affected areas on a map, the predicted environmental concentrations (PEC) of all chemicals in a risk assessment should be either modelled or measured on field, buffer and off-farm areas. Modelling the data is preferable for assessments of large number of chemicals, and it is the only way possible for new chemicals that have not yet been used. Models that describe the fate and partitioning of residues in all environmental compartments have an obvious advantage over those that can only predict concentrations of residues in soil or in water, and in this regard the multimedia models (e.g. CHEMCAN, SIMPLEBOX, etc.) based on the fugacity approach (Mackay, 1991) seem the most appropriate for estimating PECs (Guinée and Heijungs, 1993). For instance, transport of residues by runoff surface waters and groundwater takes place in both crop and off-farm areas, and can be estimated using models designed

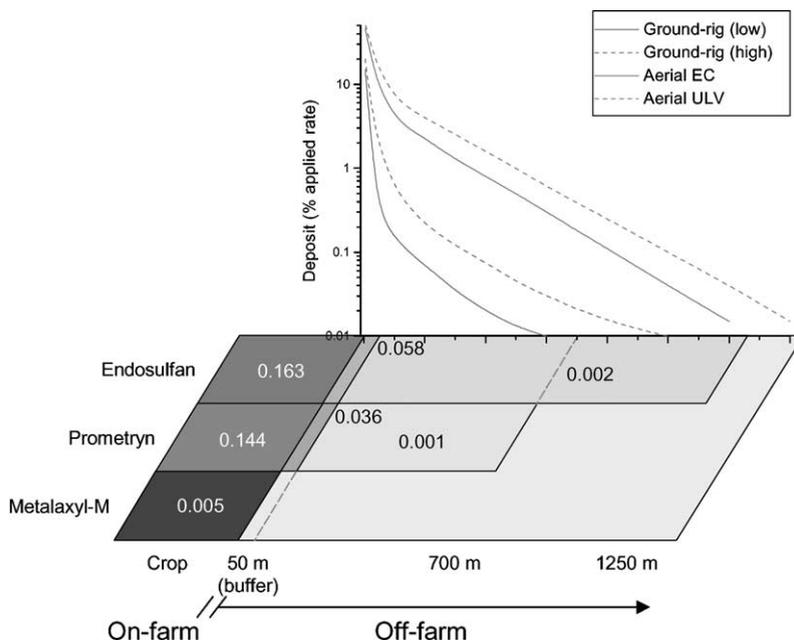


Fig. 1. Areas affected by downwind drift can be estimated using Gaussian diffusion models for different application types and formulations (EC: emulsifiable concentrate; ULV: ultra-low volume). The buffer area (50 m wide around the crop field) was estimated to capture 50% of aerial drift and 75% of ground-rig drift deposits. PECs in soil (mg kg^{-1}) for endosulfan applied by aircraft, prometryn applied by ground-rig booms and metalaxyl-M applied as seed coating are indicated for each area as examples.

for these situations (e.g. GLEAMS, SLOOTBOX, etc.), whereas sufficient accuracy for risk assessment purposes has been obtained using the fugacity based SOILFUG model (Di Guardo et al., 1994). If anything, fugacity models may overestimate the predicted concentrations in runoff (Brooke and Matthiessen, 1991), but this is not an undesirable feature because data modelled this way can represent a worst case scenario, or can be corrected by validation if required by the assessment. PECs should be calculated for a single application only, as repeated additions of a substance do not translate into residue build-up by the same amount in any compartment (Dushoff et al., 1994). An example of estimated PECs for a single application of chlorpyrifos (rate 31 ha^{-1} or $1.51 \text{ a.i. ha}^{-1}$) in the above irrigated cotton farm is shown in Table 1(4). Groundwater residues are also indicated in Table 1, but they will not be included in the final EcoRR assessment for the simple reason that these residues do not have an effect on the site, but rather represent a net loss from the system which moves off elsewhere.

The PECs are converted to doses (D) for each affected area using the simple equation

$$D = \text{PEC} \times \frac{\text{Vol}}{\text{Ar}}$$

where Vol is the volume of matrix (air, soil, etc.) in m^3 for each compartment and Ar the area in hectares of the corresponding affected zone. For PEC expressed in mg kg^{-1} or mg l^{-1} , the calculated dose has units of g ha^{-1} . At this point it is necessary to take into account the mode of application of each chemical, as ground applications will require a smaller drift area and volumes than aerial applications; in the present example, chlorpyrifos is applied by aircraft and therefore only the large off-farm drift area is considered (Table 1(2)).

The assessment of exposure is by no means concluded after having measured or modelled the PECs of a chemical in all compartments. Exposure as such is determined by the probability of those residues reaching the non-target organisms under consideration. The term P in Eq. (1) refers to such probabilities of exposure, which must be estimated for

Table 1

Stepwise procedure to calculate the exposure component (X_C) of EcoRR scores, using the insecticide chlorpyrifos^a as an example

	Area (ha)	Air (A) (m ³)	Soil (S) (m ³)	Vegetation (V) (m ³)	Groundwater (GW) (m ³)	Water ^b (W) (m ³)	Sediment (SD) (m ³)
(1) Areas and volumes							
Field	300	3.00×10^{10}	3.00×10^5	6.72×10^4	4.5×10^4	–	–
Buffer	36	3.58×10^9	3.58×10^4	4.92×10^3	5.37×10^3	1.7175×10^5 (IW)	3875
Off-farm GS ^c	608	6.08×10^{10}	6.08×10^5	8.85×10^4	9.12×10^4	2.57×10^3 (RW)	58
Off-farm AS ^c	1330	1.33×10^{11}	1.33×10^6	1.88×10^5	1.995×10^5	5.99×10^3 (RW)	136
(2) Dose D (=PEC \times Vol/Ar, g ha⁻¹)							
Field		789	367	80.8	0.4	–	–
Buffer		9.0	4.2	5.7	0.2	82.1	40.3
Off-farm AS		13.6	6.3	8.8	<0.1	158.7	40.3
(3) Probabilities (P)							
On-farm ^d		0.008	0.202	0.202	–	0.411	0.023
Off-farm		0.003	0.582	0.582	?	0.027	0.023
Flood		NA	NA	NA	?	0.010	0.001
		A ($\mu\text{g l}^{-1}$)	S (mg kg^{-1})	V (mg kg^{-1})	GW ($\mu\text{g l}^{-1}$)	W ($\mu\text{g l}^{-1}$)	SD (mg kg^{-1})
(4) PEC							
Field		0.008	0.367	3.605	2.89	–	–
Buffer		0.003	0.156	1.532	1.23	3.71	80.67
Off-farm AS		<0.001	0.006	0.062	0.05	7.18	80.67
		X_A	X_S	X_V	X_{GW}	X_W	X_{SD}
(5) Exposure^e = $D \times P \times t_{1/2} \times \text{BCF}$							
Buffer		5	122	274	–	4171	526
Off-farm		2	531	1227	?	538	526

^a Chemical data of chlorpyrifos: rate 1.5 (1 ha⁻¹ a.i.); solubility 1.4 (mg l⁻¹); vapor pressure 2.7 (mPa); K_{ow} 50000; BCF = $0.607 + 0.893 \log K_{ow}$ (Chiou et al., 1977) = 4.80; $t_{1/2V}$ (half-life in vegetation) 50 (days); $t_{1/2S}$ (half-life in soil) 30–120 (days), and $t_{1/2W}$ (half-life in water) 26 (days).

^b In the present example, IW: irrigation water, presumed to be within the farm boundaries, and RW: runoff water, discharged outside the farm.

^c GS: ground-rig boom spray; AS: aerial spray.

^d On-farm = field + buffer.

^e Half-lives in air ($t_{1/2A}$) estimated as $t_{1/2W}/2$; in soil $t_{1/2S} = 30$ days and in sediment $t_{1/2SD} = 120$ days.

each compartment in the assumption that all species affected by a given exposure route/compartment will have the same probability of exposure. In agricultural situations, where pesticides are applied once or several times throughout a growing season, P can be multiplied by the number of applications (frequency) taking place on a specific site. The examples shown in Table 1(3) refer to probabilities on-farm (i.e. field plus buffer zone), off-farm areas and flooding scenarios, and were estimated as follows.

2.1.1. Inhalation of airborne residues

The probability of inhalation of airborne residues over the field and downwind areas is 1.0 immediately after pesticide application. However, it can be assumed that residues in air of most chemicals will not last longer than 3 days as dissipation processes such as sunlight degradation and wind will remove them very quickly; this translates into a exposure probability of $3/365 = 0.008$ on-farm. In off-farm areas, this figure should be multiplied by the probability of wind blowing towards the prevalent downwind direction, which can be obtained through weather records for a specific site; for instance, if the wind blows over a certain area 0.35 of the time, the exposure probability off-farm would be $0.35 \times 3/365 = 0.003$.

2.1.2. Contact with contaminated soil

The probability of animal species that will reach the contaminated soil is calculated as the ratio of any specified area over the total potential affected area. In the example above, on-farm exposure probability is calculated as $336/1666 = 0.202$, for a field of 300 ha, buffer of 36 ha and total potential affected area of 1666 ha. Off-farm probabilities vary for ground-rig ($608/1666 = 0.365$) and aerial drift zones ($1330/1666 = 0.798$), and their average exposure probability would be 0.582.

2.1.3. Ingestion of contaminated vegetation

The same exposure probabilities as in soil would apply to species feeding on the crop (on-farm) or vegetation contaminated by drift residues in the surroundings of the farm.

2.1.4. Water compartments

The probability of any species, aquatic or terrestrial, being exposed to pesticide residues in water is

estimated as the proportion of the number of days in a year that water is available in a specified area. In irrigated farms, as in the present example, water on the farm irrigation system will be present as long as the growing season requires, e.g. 150 days (5 months) per year, so the probability of exposure to animals living in it or feeding/drinking from it will be $150/365 = 0.411$. Similarly applies to surface waters, which would be running off field whenever an irrigation or a storm event producing runoff takes place; in the above example, it was estimated as $10/365 = 0.027$.

2.1.5. Ingestion of contaminated sediment

Sediments can be found only at the bottom of channels, water storages and drains, whether forming part of a farm irrigation system or located in the surrounding areas of agricultural land. One way of expressing the probability of aquatic and terrestrial animals ingesting sediments is by the proportion of the total volume of sediment with respect to the volume of water in such water system. In this example, the sought probability is $3875/171250 = 0.023$.

2.1.6. Flood scenarios

When the farm is covered by flood waters, exposure to soil and vegetation residues is nil, while residues in air are presumably inexistent as chemicals cannot be applied in those conditions. The probability of exposure to residues in flood waters can be determined by the frequency of flood occurrence expressed in days per year; in this example 0.12 (annual occurrence) $\times 1/12$ (each flood lasting a month) $= 0.010$. Exposure to soil residues underwater can be expressed as given above, i.e. proportion of topsoil volume with respect to flooding water volume over it.

Probabilities of exposure of non-target organisms to groundwater residues are unlikely if not impossible on a site-specific assessment restricted to a small territory, as is the case of most farms. In the example and case study considered in this paper this compartment was excluded from the calculations.

Persistence of residues must be accounted for in EcoRR because exposure to contaminants has inevitably a temporal dimension, usually due to: (i) the residence time of contaminants in the environment, expressed by half-lives in each compartment, and (ii) the possibility of residue bioaccumulation in animal tissues. As indicated above, both factors are consid-

ered in the exposure assessment. For most agricultural chemicals there is a known range of half-lives in soil and water; in some cases there are data on degradation in plants, while information on the fate of airborne residues is found very rarely. The latter data gap poses a problem for assessment of the majority of pesticides in the air compartment, with no other alternative but to estimate half-lives in air based on behavioural properties in other matrices. When a range of variable half-lives exists, an average value can be used, and the longest half-life can be applied to residues in sediment, where chemical and biochemical degradative processes are slower than in topsoil. The bioconcentration factor (BCF) is determined using empirically derived quantitative structure–activity relationships (QSARs) for large sets of organisms (Cowan et al., 1995). The most commonly used QSARs are based on the octanol–water partition coefficient (K_{ow}), which correlates well with residue build-up in fatty tissues:

$$BCF = 0.607 + 0.893 \log K_{ow} \text{ (Chiou et al., 1977);}$$

$$BCF = 0.048 K_{ow} \text{ (Mackay, 1982), and}$$

$$BCF = 0.79 \log K_{ow} - 0.4 \text{ (Veith and Kosian, 1983).}$$

The latter was derived from PCB data and is ignored in this paper; Mackay’s QSAR is used for estimating PECs in fugacity models, whereas Chiou’s QSAR will be used as part of the persistence factor in the exposure Eq. (1) of EcoRR, but this does not mean other QSAR may be used as well. Half-lives in soil, water and plants, and bioconcentration factor for chlorpyrifos are shown in Table 1 together with other chemical data. In air, the rate of degradation was estimated as double than in the water phase, as indicated in Table 1.

Finally, the exposure component in each compartment (X_C) is calculated using Eq. (1). An example for chlorpyrifos in both buffer and off-farm areas appears at the bottom of Table 1(5) (only these two areas will be considered in the example from here onwards). X_C has units of g day ha^{-1} , but this should not be interpreted as an absolute value, i.e. it cannot be validated by field measurements but rather it is a relative value for use in the calculation of EcoRR scores. All exposure factors have equal weight in the exposure module, but the magnitude of each factor determines the final X_C value (Fig. 2A). Thus, increasing values in one factor can be offset by decreasing values in another.

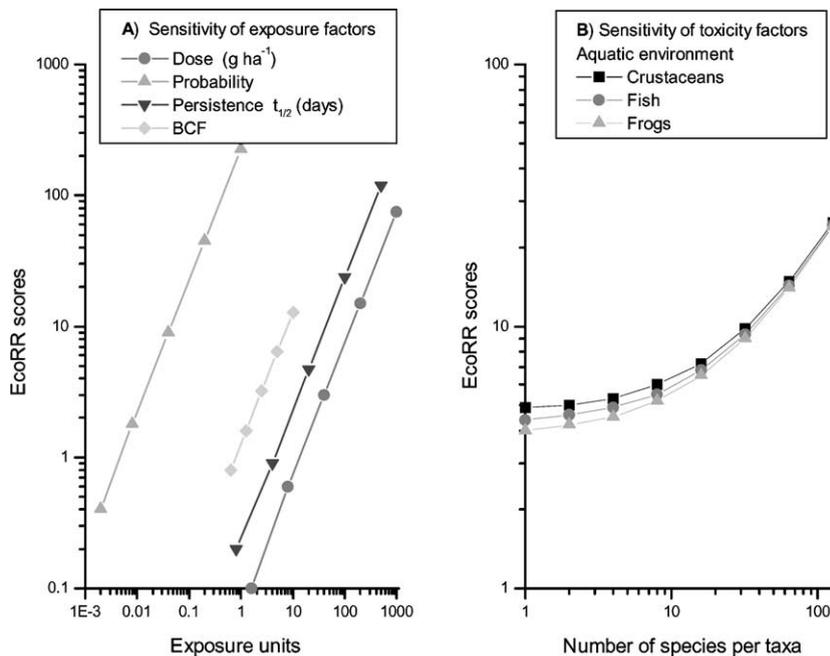


Fig. 2. Sensitivity analysis of EcoRR model. (A) Exposure factors have equal weight and produce linear increases in EcoRR scores, proportional to the magnitude of the variation. (B) Biodiversity increases in individual taxa produce, however, non-linear increases in the final EcoRR score, as illustrated here for three aquatic taxa.

For instance, a double EcoRR score can be obtained by doubling either the PEC, or the probability of exposure, or the half-life or the BCF. Similarly, the same EcoRR score will result if the PEC, and hence D is halved and the probability of exposure or any other factor is doubled. Using the example for chlorpyrifos,

$$\text{on-buffer : } X_S = 122 = 4.2 \times 0.202 \times 30 \times 4.8$$

could also be

$$X_S = 122 = 2.1 \times 0.404 \times 30 \times 4.8$$

2.2. Step 2: toxicity assessment

The toxicity module in EcoRR assessments is focussed on ecosystems rather than individual species, and this approach requires a number of assumptions at several levels. To start with, ecosystem toxicology is assessed as a composite of the toxicology of individual species that are present in such ecosystem, and because the complexities of the ecological relationships among species warrant their accurate expression in mathematical terms, a simplified model based on biodiversity and toxicology to different taxa (which in turn is based on toxicology to single species) is proposed here as follows:

$$\text{ecotoxicity (Ecotox)} = \sum_{i=1}^m \frac{\text{Tgm taxa}_i / (S_i / N)}{N} \quad (2)$$

where Tgm taxa_i is the LC_{50} or LD_{50} geometric mean of each taxon, S_i is the number of species of a taxon, and N the total number of species of all taxa considered. As with the exposure assessment, the ecotoxicity module in EcoRR is considered separately for each environmental compartment. Biomagnification factors through the food chain (Kenaga, 1972) are not considered in EcoRR because the model would become extremely cumbersome, thus defeating the purpose of this methodology. For the same reason, it is impractical to include population densities (Barnhouse, 1998), or interactions among species in communities, or any other factor related to the structural and functional ecology of those species in assessments of this kind.

The choice of acute oral LD_{50} or LC_{50} endpoints is simply due to their greater availability for a wide range of taxa, though data on reptiles and amphibians are scarce for most pesticides and inexistent for old compounds. Dermal LD_{50} and inhalation LC_{50} endpoints

can be used for calculating the ecotoxicity through contact or inhalation exposure routes, but for most substances these data refer only to mammals. Similarly, data on chronic toxicity endpoints such as NOEL are also available for mammals and humans but rarely for other taxonomic groups, rendering it inadequate for use in the EcoRR model at the present moment. So far the EcoRR model has considered only animal taxa, but there is no reason why algae and other plants may not be included other than the lack of available toxicity data at the current moment. Databases such as ECO-TOX, which comprise AQUIRE (US EPA, 1994) and TERRETOX, provide a wealth of toxicological information about toxicity to aquatic organisms and some terrestrial taxa, respectively.

From the available data, a representative toxicity level to each taxon must be obtained in order to estimate ecotoxicity. The EcoRR model uses single-species data to extrapolate the sensitivity of the ecosystem to hazardous substances, as recent studies suggest (Versteeg et al., 1999). A great deal of debate is found in the literature about this issue (Forbes and Forbes, 1993), but it is agreed by many authors that the geometric mean LD_{50} or LC_{50} (Tgm) provides the best value, though it is considered too conservative by others (Van Straalen and Denneman, 1989). There are two methods of calculating the taxa geometric mean, and either of them can be used in EcoRR: (i) obtain the most complete dataset for a taxon, a tedious task indeed; and (ii) extrapolate from one or several surrogate species to all other species in the taxon using toxicity equivalents (TE), which usually are expressed as dose per body weight (mg g^{-1}) of the surrogate species. When using TE extrapolations, sensitivity distributions (Aldenberg and Slob, 1993), allometric relationships based on body weight (Sample and Arenal, 1999) and scaling factors such as proposed by Mineau et al. (1996) must be taken into account to avoid biases (Okkerman et al., 1993). An example of acute LC_{50} and LD_{50} data for chlorpyrifos in several surrogate species, and their corresponding TE and Tgm are shown in Table 2(1). A serious problem arises when pesticide toxicity data are missing for a taxon, as often occurs with amphibians and reptiles. In such cases, either the comparative assessment must exclude those taxa, or some rough estimates can be produced based on TE to other closely related taxonomic groups, i.e. toxicity data for fish can be used

Table 2

Stepwise procedure to calculate the ecotoxicity component (Ecotox C) of EcoRR scores, using the insecticide chlorpyrifos as an example^a

Taxa	Surrogate species	Endpoint	Surrogate (mg kg ⁻¹ or l ⁻¹)	TE (mg g ⁻¹)	Tgm (mg kg ⁻¹ or l ⁻¹)		
(1) Toxicity data ^b							
Crustaceans	Daphnia	Acute LC ₅₀	0.00065	0.117	0.0025		
Fish	Carp	Acute LC ₅₀	0.123	0.063	0.014		
Amphibians	Bog frog	Acute LC ₅₀	2.4	48.0	1.24		
Reptiles ^c	Nil ^c	Acute LD ₅₀	–	0.74	183		
Birds	Duck	Acute oral LD ₅₀	67	0.062	7.2		
Mammals	Rat	Acute oral LD ₅₀	150	0.74	159		
	Rat	Dermal LD ₅₀	2000	4.20	905		
	Rat	Inhalation LC ₅₀	0.2	0.0007	0.15		
		A, inhalation	S, contact	V, ingestion	W, aquatic (Wa)	W, terrestrial (Wt)	SD, ingestion & contact
(2) Exposure routes ^d							
Crustaceans	Buffer	NA ^e	NA	NA	9	NA	1
	Off-farm	NA	NA	NA	9	NA	2
Fish	Buffer	NA	NA	NA	2	NA	2
	Off-farm	NA	NA	NA	12	NA	12
Frogs	Buffer	5	4	NA	4	NA	4
	Off-farm	15	13	NA	14	NA	14
Reptiles	Buffer	6	6	NA	2	NA	1
	Off-farm	48	46	NA	4	NA	3
Birds	Buffer	78	35	25	NA	30	30
	Off-farm	199	35	50	NA	195	67
Mammals	Buffer	9	9	6	NA	9	1
	Off-farm	21	13	10	NA	13	2
N (∑ S)	Buffer	98	54	31	17	39	39
	Off-farm	283	107	60	39	208	100
		A, Tgm/(S/N)	S, Tgm/(S/N)	V, Tgm/(S/N)	Wa, Tgm/(S/N)	Wt, Tgm/(S/N)	SD, Tgm/(S/N)
(3) Fractional components							
Crustaceans	Buffer	NA	NA	NA	0.005	NA	0.098
	Off-farm	NA	NA	NA	0.011	NA	0.125
Fish	Buffer	NA	NA	NA	0.119	NA	0.274
	Off-farm	NA	NA	NA	0.046	NA	0.117
Amphibians	Buffer	24.2	16.7	NA	5.3	NA	12.1
	Off-farm	23.3	10.2	NA	3.4	NA	8.8
Reptiles	Buffer	2.5 ^f	9369 ^g	NA	1553	NA	7126
	Off-farm	0.9 ^f	2421 ^g	NA	1781	NA	6091
Birds	Buffer	9.1	11.1	8.9	NA	9.4	9.4
	Off-farm	10.3	22.1	8.7	NA	7.7	10.8
Mammals	Buffer	1.7 ^f	5432 ^g	821	NA	689	6197
	Off-farm	2.1 ^f	7451 ^g	953	NA	2542	7945
		Ecotox A	Ecotox S	Ecotox V	Ecotox Wa	Ecotox Wt	Ecotox SD
(4) Ecotoxicity = ∑ C/N							
Buffer	0.4	275	27	92	18	342	
Off-farm	0.1	93	16	46	12	141	

^a Groundwater (GW) is excluded, as no taxa were exposed to residues in such compartment. Numbers in step 2 indicate number of species (S) per taxa.

^b TE: toxicity equivalent; Tgm: taxon geometric mean.

^c Extrapolated from acute oral mammalian TE.

^d Letters indicate different compartments as in Table 1(4) (areas and volumes).

^e NA: not applicable.

^f Based on inhalation LC₅₀ (rat).

^g Based on dermal LD₅₀ (rat).

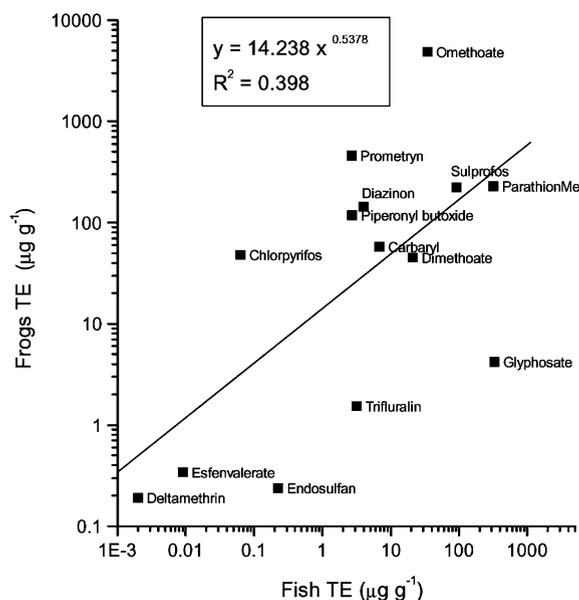


Fig. 3. Regression between toxicity equivalents (TE) of several pesticides in fish and frogs, indicated by an exponential fitting curve.

to extrapolate levels in amphibians, or data on mammals could be used for extrapolation in reptiles. An example is illustrated in Fig. 3, showing a reasonable correlation ($r^2 = 0.39$) between TE in frogs and fish (no other correlation was found between frogs and any other taxa).

The other parameter in the denominator of the ecotoxicity equation is biodiversity. Biodiversity data, i.e. identity and number of species present in a given ecosystem, for selected taxa in agricultural environments can be easily obtained from governmental or local group sources. Moreover, biodiversity alone is a good indicator of the health of an ecosystem (Altieri, 1999), and the decision to include it in EcoRR with preference to other ecological parameters is thus justified (Karr, 1993). Exposure routes for each species must be clearly established before calculating the ecotoxicity in each compartment, and at this point aquatic and terrestrial species are better separated into two distinctive groups, because many terrestrial species share the aquatic environment by feeding and drinking on contaminated waters and sediment. Table 2(2) shows an example of how species are distributed into compartments according to their exposure routes, based on

their ecological characteristics. The same species can share several exposure routes, so the numbers across the columns (compartments) do not necessarily add up. However, for each compartment the total number of species (N) is the sum of species (S) of all taxa present there. Notice that the on-farm buffer zone has fewer species than off-farm areas, since crop fields are usually not available to all animals in the neighbouring land.

The calculated Tgm taxa are weighted by the proportion of their belonging species in each compartment (S/N), so each taxon produces a fractional component (Table 2(3)), and the sum of these fractions divided by the total number of species in a compartment (N) constitutes the ecotoxicity of the compartment (Ecotox C):

$$\text{Ecotox C} = \frac{((\text{Tgm } t_1 / (S_{t_1} / N)) + (\text{Tgm } t_2 / (S_{t_2} / N)) + \dots + (\text{Tgm } t_m / (S_{t_m} / N)))}{N}$$

where t_1, t_2, \dots, t_m are the taxa exposed to such compartment. As it can be seen in Table 2(4), increasing biodiversity in a compartment results in lower ecotoxicity values, and hence higher EcoRR scores. For example, the ecotoxicity of chlorpyrifos to 39 aquatic organisms (Ecotox Wa) in runoff waters of areas off-farm is 46. Reducing the biodiversity of each taxon by half renders an ecotoxicity value of $92 = 46 \times 2$, as in fact happens in irrigation waters on-farm where only 19 species are affected. However, increasing or reducing the number of species in a single taxon does not have a linear effect (Fig. 2B), because that change depends not only on the proportional contribution of such taxon to the biodiversity of the compartment but also on its absolute Tgm values. Indeed, the fractional components $\text{Tgm taxa}_i / (S_i / N)$ approach the taxa geometric mean values in the case of dominant taxa, whereas in poorly represented taxa such fraction is much higher than their respective Tgm.

$$\begin{aligned} \frac{\text{Tgm taxa}}{(1/N)} &\gg \text{Tgm taxa}, & \text{when } S = 1 \\ \frac{\text{Tgm taxa}}{(1/2)} &= 2 \times \text{Tgm taxa}, & \text{when } S = \frac{N}{2} \\ \frac{\text{Tgm taxa}}{(S/N)} &\sim \text{Tgm taxa}, & \text{when } S \sim N \end{aligned}$$

The intended consequence of this procedure is to give more weight to dominant taxa in a compartment, so the final EcoRR scores will be influenced by the

ecotoxicity to the most diverse taxa, which obviously are more representative of the ecosystem and contain a wider range of sensitivities for all species included. In effect, this procedure avoids the use of conservative endpoint values unless a taxon is well represented in the ecosystem. On purpose, this procedure does not make any consideration of the most sensitive species, which do not represent the toxicity of complex ecosystems (Cairns and Niederlehner, 1987) nor are necessarily the functional ‘keystone’ species: the latter are more likely to be found among the dominant taxa.

2.3. Step 3: relative risk assessment

In the final step of the relative risk assessment, the EcoRR scores for each compartment are calculated as the exposure values (X_C) over the corresponding ecotoxicity values (Ecotox C), with the total EcoRR for a particular area estimated as the sum of EcoRR scores in each compartment.

$$\text{Air : EcoRR}_A = \frac{X_A}{\text{Ecotox A}}$$

$$\text{Soil : EcoRR}_S = \frac{X_S}{\text{Ecotox S}}$$

$$\text{Vegetation : EcoRR}_V = \frac{X_V}{\text{Ecotox V}}$$

$$\text{Water (aquatic org.) : EcoRR}_{Wa} = \frac{X_{Wa}}{\text{Ecotox Wa}}$$

$$\text{Water (terrestrial org.) : EcoRR}_{Wt} = \frac{X_{Wt}}{\text{Ecotox Wt}}$$

$$\text{Groundwater : EcoRR}_{GW} = \frac{X_{GW}}{\text{Ecotox GW}}$$

$$\text{Sediment : EcoRR}_{SD} = \frac{X_{SD}}{\text{Ecotox SD}}$$

$$\text{Total EcoRR off-farm} = \sum \text{EcoRR}_C \text{ off-farm}$$

Because of the aggregated structure of the model, separate EcoRR scores for terrestrial and aquatic environments can be obtained by adding the respective EcoRR values from their integrating compartments:

$$\text{EcoRR terrestrial} = \text{EcoRR}_A + \text{EcoRR}_S + \text{EcoRR}_V$$

$$\begin{aligned} \text{EcoRR aquatic} &= \text{EcoRR}_{Wa} + \text{EcoRR}_{Wt} \\ &+ \text{EcoRR}_{GW} + \text{EcoRR}_{SD} \end{aligned}$$

and

$$\begin{aligned} \text{Total EcoRR off-farm} &= (\text{EcoRR terrestrial} \\ &+ \text{EcoRR aquatic}) \text{ off-farm} \end{aligned}$$

Notice that the water compartment has been subdivided into two components, as explained in step 2: one for the aquatic species and another for terrestrial species that feed or drink from the water compartment. Groundwater (GW) was excluded from this paper, as no taxa were exposed to residues in such compartment on site (see Tables 2 and 3). Using separate scores for either group facilitates the assessment in the water compartment by helping pinpoint the animal groups at risk and their routes of exposure. In fact, the same could be done in the sediment compartment if required, as the EcoRR composite scores allow flexibility in this regard.

2.4. Case study

A simulation of relative risk assessment for 37 pesticides using the above EcoRR model was performed so as to provide an example where comparison of ecotoxicological risks among pesticides could be referred to a site-specific situation. The setting was a new irrigated cotton development in a floodplain adjacent to an area of high biological value, the Macquarie Marshes Nature Reserve, a Ramsar-listed wetlands located in central-north New South Wales, Australia. Soils in the floodplain are heavy grey clays, prone to form deep cracks when drying, and the water table at the site is located about 7–9 m down the profile, eventually resurfacing in the marshes. Vegetation is governed by the frequency of flooding, and comprises a mosaic of 21 plant communities in permanent swamps, semi-permanent riverine forested wetlands, ephemeral wetland plants and dryland vegetation types. The fauna of the marshes is rich and varied, home to important breeding colonies of waterbirds in the country, and is threatened by the progressive shortage of water due mainly to increasing demand by agricultural developments (Kingsford and Thomas, 1995).

The site consists of 300 ha of irrigated cotton cropping area surrounded by riverine ecosystems and grazing land. The irrigation system on-farm comprises 3 km of 5 m wide channels and a water storage with capacity for 156 ML, with levees around the crop and

Table 3

Final procedure to calculate EcoRR scores, using the insecticide chlorpyrifos as an example^a

	Air, X_A	Soil, X_S	Vegetation, X_V	Water aquatic, X_{Wa}	Water terrestrial, X_{Wt}	Sediment, X_{SD}
Exposure = $D \times P \times t_{1/2} \times BCF$						
Buffer	5	122	274	4171	4171	526
Off-farm	2	531	1227	538	538	526
	Ecotox A	Ecotox S	Ecotox V	Ecotox Wa	Ecotox Wt	Ecotox SD
Ecotoxicity = $\sum C/N$						
Buffer	0.4	275	27	92	18	342
Off-farm	0.1	93	16	46	12	141
	EcoRR _A	EcoRR _S	EcoRR _V	EcoRR _{Wa}	EcoRR _{Wt}	EcoRR _{SD}
EcoRR = $X_C / \text{Ecotox } C$						
Buffer	12.0	0.4	10.2	45.5	233.1	1.5
Off-farm	18.8	5.7	76.5	11.7	43.8	3.7

^a Groundwater compartment excluded (see text and Table 2).

irrigation system ensuring that all runoff water from irrigation or storms (tailwaters) would be contained on-farm, with most of this water being located on the storage. Recirculation of tailwaters on-farm is a requirement of best management practices for irrigated cotton farms in Australia (Williams, 1997). For the purpose of this paper, the simulation study attempted to evaluate the relative risk of those pesticides on-farm and the wetlands reserve only, but the same model can be used to compare risks to the nearby grazing land.

Based on statistics from cotton farms in the region during five seasons, the most commonly used pesticides were selected for this simulation: two fungicides, seven herbicides, 21 insecticides, two plant-growth regulators and three defoliant. Both fungicides are applied as coating the cotton seeds and incorporated into the soil at planting time. Two insecticides (aldicarb and phorate) and one herbicide (norflurazon) are applied as granules also at planting time or immediately after. All other herbicides are applied by ground-rig spray booms, and the remaining insecticides, defoliant and plant-growth regulators are applied from aircraft. The extent of the drift zones for both types of spray applications was determined using drift models and data from trials in cotton fields (Woods et al., 2001), an example of which is illustrated in Fig. 1. Areas affected by drift cover 36 ha in the buffer, 608 ha for ground-rig booms and 1330 ha for aerial sprays, with the total potential affected area (including cropping fields) es-

timated in 1660 ha. In this simulation, the assessment of the on-farm area included the buffer zone.

Concentrations of all pesticides in air, soil, vegetation, runoff water, groundwater and sediment were estimated by fugacity level II, based on the recommended application rates indicated in commercial product's labels. Chemical data on vapour pressure, water solubility, K_{ow} , half-lives in soil, water and degradation in plant material, were obtained from Hornsby et al. (1996) and Tomlin (1997). Half-lives in air for all pesticides were estimated assuming that rates of degradation in air were twice as fast as in the water compartment. The bioconcentration factors were calculated using Chiou's QSAR (1977). Probabilities and routes of exposure were determined as described in the chlorpyrifos example above (Tables 1 and 2). Data on frequency of wind and its direction, as well as flooding were obtained from 40 years weather records for the site (Australian Bureau of Meteorology).

Toxicity data for surrogate species in mammals (rat, rabbit), birds (quails, duck), fish (rainbow trout, bluegill, carp) and crustaceans (water flea) were obtained from Tomlin (1997), complemented with data on other species of fish, crustaceans, and amphibians obtained from AQUIRE and some data on Australian species from Warne et al. (1998). The biodiversity of the off-farm areas included 290 species of wildlife vertebrates (12 fish, 15 frogs, 48 reptiles, 16 mammals

and 199 birds), plus six orders of crustaceans, whereas only 109 species recorded within the cotton farm were considered in the assessment on-farm, the most conspicuous being some 30 species of waterbirds that used the irrigation system as a feeding site.

EcoRR scores were calculated for on- and off-farm areas, terrestrial and aquatic environments, during the main spraying period (i.e. November to March) coinciding with the irrigation season in Australian summer in what was considered a normal growing scenario. The EcoRR scores can also be calculated for each month of the year, thus obtaining a more accurate picture of what risk would be expected at a given time; however, for the sake of brevity only the seasonal approach is shown in this paper. Scores for a flooding scenario were also calculated and compared to those obtained under normal scenarios. An eval-

uation of the adequacy of these relative risk scores was made by comparing EcoRR scores in aquatic and terrestrial environments with EPA quotients (Urban and Cook, 1986) for selected taxa, using acute LC₅₀ endpoints for the aquatic taxa and acute oral LD₅₀ for terrestrial taxa. A comparison of the terrestrial environment with chronic quotients, using NOEL endpoints for mammals surrogate (rat), was also done.

3. Results

EcoRR scores obtained for all 37 pesticides in five compartments off-farm are shown in Fig. 4. For most chemicals, the highest risk was identified on surface runoff waters, particularly with carbamate and organophosphorous insecticides, but risk was

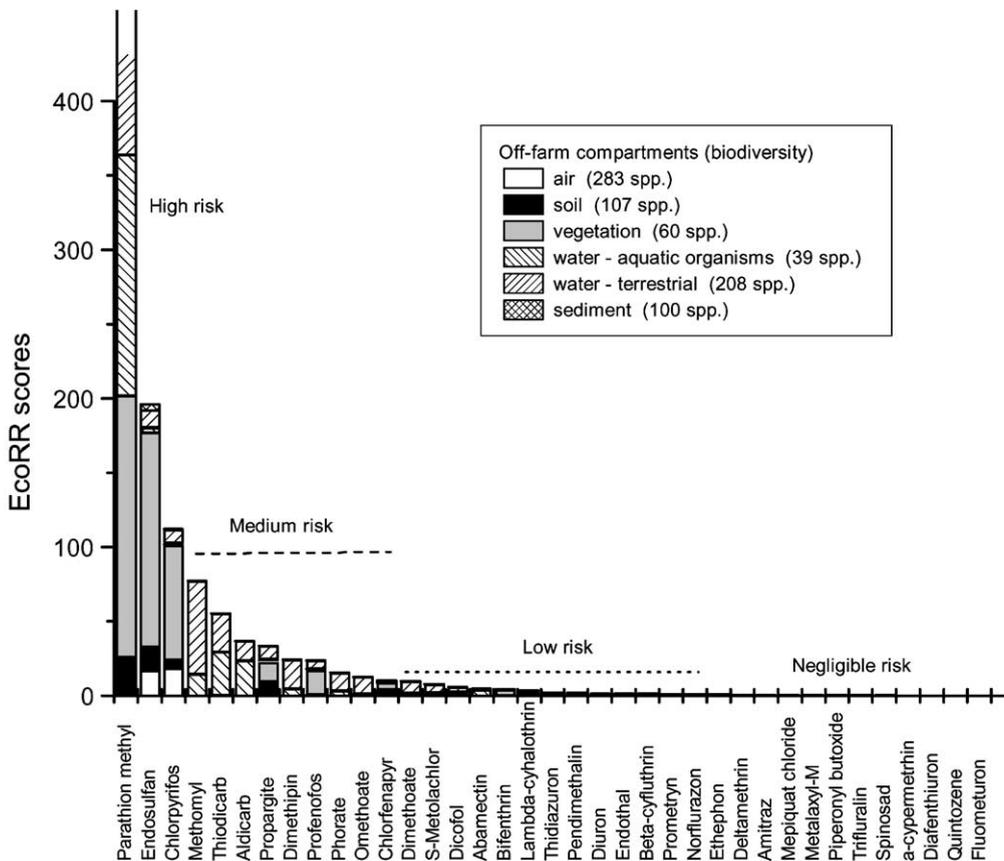


Fig. 4. Relative risk off-farm of 37 pesticides in five environmental compartments, expressed by EcoRR scores in a simulation study of an irrigated cotton farm. The biodiversity of each compartment refers to a wetland ecosystem in Australia.

also high in vegetation contaminated with parathion methyl, endosulfan and chlorpyrifos insecticides. Soil and sediment compartments posed some risk in the case of parathion methyl, endosulfan, propargite and chlorfenapyr, all moderately persistent insecticides of high toxicity except chlorfenapyr which is considered a very persistent insecticide ($t_{1/2S}$ about 150 days). Risk through inhalation of airborne residues was negligible for all compounds and apparently low in the case of volatile compounds such as endosulfan and chlorpyrifos.

The EcoRR scores of most compounds in the aquatic environment on-farm are higher than in the area outside the farm, particularly in the case of herbicides, as can be seen for some examples in Table 4. A similar picture is obtained on the farm buffer, where the water compartment is represented by the irrigated system channels around the cropping fields and the water storage on-farm. In general, the highest scores in aquatic environments were obtained either with pesticides of high toxicity to crustaceans and fish or with soluble and persistent herbicides such as diuron. However, synthetic pyrethroids, diafenthiuron, and abamectin, all of which are extremely toxic to fish and crustaceans, had very low scores in such environment both on- and off-farm areas. The highest EcoRR scores in the aquatic environments in any area correspond to parathion-methyl and methomyl, the risk of the latter insecticide confined mainly to terrestrial taxa exposed through feeding and drinking in the farm contaminated waters. Not surprisingly, methomyl is the most toxic to birds of all pesticides considered in this study. In terrestrial environments,

on the contrary, off-farm EcoRR scores for most pesticides were slightly higher than on-farm and buffer zones, as the affected area outside the farm was much larger and more species of all taxa were potentially exposed to residues, however small they might be.

The simulation of a flood was done only for areas off-farm, as the fields on-farm were supposedly protected by levee banks (see case study). It implied that residues in soil from areas affected by drift could be re-dissolved in the huge amount of water expected to flow over them. Thus, the great dilution expected is to some extent offset by the removal of a large amount of residues which otherwise would be locked in the soil compartment. Under this scenario, PECs of all pesticides were estimated for a sheet of water 30 cm over the farm land, using also a fugacity model level II. Although no consideration was given to the dynamics of the situation, it was assumed that such residue concentrations would move inevitably into the neighbouring wetlands and have an impact on their rich ecosystems. From the modelled data, off-farm EcoRR scores resulted higher during a flood than in a normal farming scenario for all pesticides considered (Fig. 5). The increase was steeper for those pesticides of great toxicity to aquatic organisms such as synthetic pyrethroids and several organophosphates.

PECs in the surface water runoff and contaminated vegetation in the off-farm area were also used to calculate quotients ($Q = \text{PEC}/\text{toxicity endpoint}$) for crustaceans, fish, frogs, birds and mammals. Quotient results for each taxa were compared to EcoRR scores in aquatic and terrestrial environments, and the logistic correlations of their full datasets are shown in Fig. 6.

Table 4

Comparative risk assessment (EcoRR scores) of eight pesticides to aquatic and terrestrial environments for both on- and off-farm affected areas

Compound	On-farm			Off-farm wetlands			Ratio off-farm/on-farm
	Aquatic EcoRR	Terrestrial EcoRR	Total EcoRR	Aquatic EcoRR	Terrestrial EcoRR	Total EcoRR	
Methomyl	726.0	<0.1	726.0	77.3	<0.1	77.3	0.11
Endosulfan	133.4	58.8	192.2	19.5	177.0	196.5	1.02
Chlorpyrifos	64.0	36.6	100.7	12.0	100.9	112.9	1.12
Diuron	40.7	0.1	40.8	0.2	1.4	1.6	0.04
Prometryn	3.9	<0.1	3.9	1.1	0.1	1.2	0.31
Bifenthrin	0.4	0.9	1.3	0.4	3.8	4.2	3.20
Metalaxyl-M	0.8	<0.1	0.8	0.6	NA ^a	0.6	0.74
Diafenthiuron	<0.1	<0.1	<0.1	<0.1	0.1	0.1	3.68

^a Not applicable.

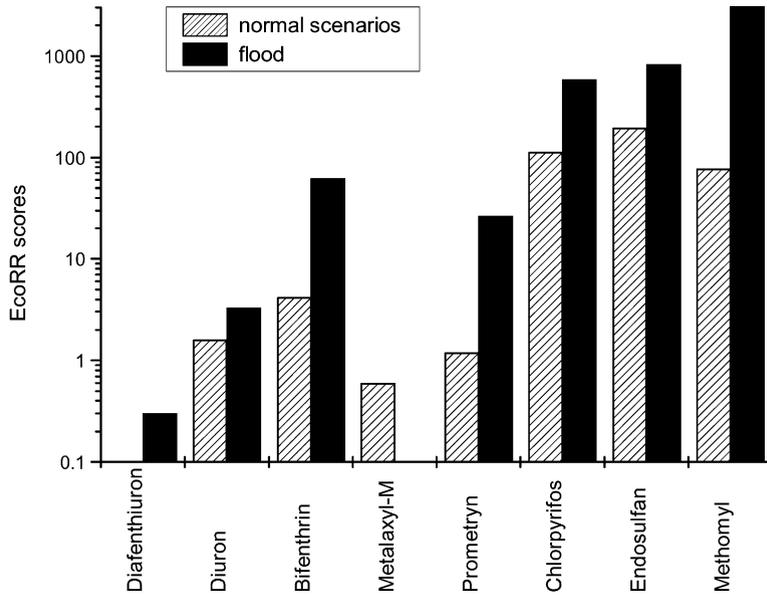


Fig. 5. Comparison of EcoRR scores obtained for eight pesticides under normal cropping and flood scenarios in the simulation study.

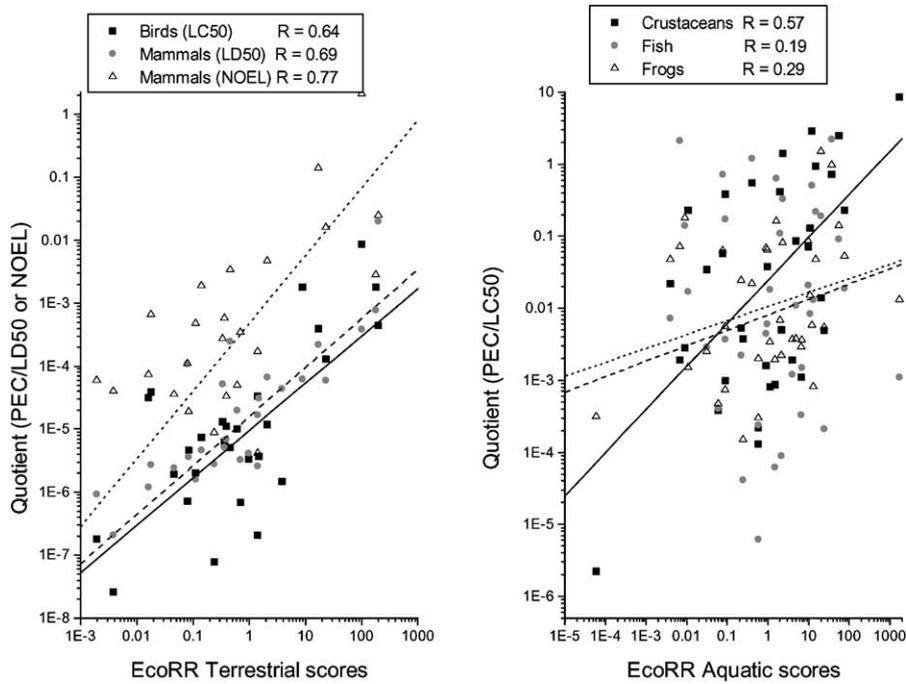


Fig. 6. EcoRR scores compared to quotients for several aquatic and terrestrial taxa in off-farm areas of the case study.

Table 5
Risk ranking based on the correspondence between quotient values (Q) for particular taxa and EcoRR scores for ecosystems

Ranking categories	Q	EcoRR
Very high risk	>1	>1000
High risk	1	100–1000
Medium risk	0.1	10–100
Low risk	0.01	1–10
Negligible risk	<0.01	<1

In the aquatic environment, only the quotient for crustaceans showed some correlation ($r = 0.57$) with EcoRR scores in the runoff water compartment. However, better correlations were observed between terrestrial EcoRR scores and quotients for birds ($r = 0.64$) or mammals, in the latter case using both acute ($r = 0.69$) and chronic toxicity data ($r = 0.77$). Exclusion of a few outliers from the full set resulted in better correlations in all cases except in fish and frogs taxa.

Based on such correlations, the risk levels expressed by EcoRR scores can be ranked in categories, bearing in mind that for each Q value there are several EcoRR scores depending on the taxa considered. Thus, EcoRR risk categories are better defined by a range of values as suggested in Table 5.

4. Discussion

The EcoRR model has been proven effective and reliable in predicting the potential risk that chemicals applied to a site-specific environment have in the surrounding ecosystem. Its approach of aggregating scores allows to identify specific areas, compartments or groups of organisms (e.g. aquatic, terrestrial) with potential risks due to chemical residues. At the same time, it gives flexibility in the way such aggregations may be done in particular assessments. It must be emphasised, before commenting on the results of the case study, that EcoRR scores are only relative measurements of environmental risk which can be very useful to compare risk among sets of chemicals applied to the same site, and are by no means absolute risk values in the ordinary sense of a risk assessment. On the other hand, EcoRR is not a proper index system either, since the scores obtained are valid to establish comparisons at specific sites but not in general.

Here, the multiple factors considered in both the exposure and toxicity modules are evaluated in view of the results obtained from the simulation of 37 pesticides applied to an irrigated cotton farm. All factors are responsible for the variations in score values, but in assessing the importance of each factor in the final EcoRR score it is evident that some are variable and others are constant depending on whether different compartments, areas or groups of organisms are considered. Thus, (i) chemical properties of a substance such as the BCF are constant, as are also the toxicities to various taxa; (ii) in a compartment, the half-life of a chemical is constant, whereas the dose applied, probability of exposure and biodiversity are variable; and (iii) in a specified area, probabilities of exposure, biodiversity and volumes of soil, air, vegetation and water are constant, but the dose varies depending on the mode and rate of application of a chemical.

The dose of chemical residues depends not only on the rate of application, which the farmer can vary within certain limits, but also on the application technique. As shown in Fig. 4, among the 10 pesticides with highest risk on areas off-farm eight were applied by aircraft, simply because their total amount of drift residues is larger compared to those pesticides applied by ground-rig booms. To prove the case, not all of these were insecticides of high toxicity as the defoliant dimethipin was also among them. Herbicides, which are usually applied by ground-rigs, received much lower scores on off-farm areas than other pesticides, with the highest risk being for S-metolachlor (rank 14). Aware of the fact that fugacity models overestimate PECs in runoff water (Di Guardo et al., 1994; Baskaran et al., 2001), EcoRR scores in the water compartment on-farm may have been inflated, particularly in the case of very soluble substances such as carbamate insecticides, dimethipin, triazines, urea herbicides and defoliants which are prone to leaching. One reason for this overestimation is that leaching is not considered in fugacity models, and excess residues are assigned to the runoff compartment to balance the mass equations when in reality such residues move down the field soil profile.

Persistence of a chemical is a constant factor in a compartment, but it varies between compartments. It would be expected that chemicals produce higher EcoRR scores in the compartments where they persist longer, and this seems to be the case with endosulfan,

chlorpyrifos and parathion methyl in vegetation and sediments, chlorfenapyr in soil, or dimethipin, aldicarb and most herbicides in water. In off-farm areas where pasture and fodder could be ingested by livestock animals (sheep, cattle), the risk scores of the latter insecticides are well related to their residues appearing in meat (Beck et al., 1966). Inevitably, livestock and wildlife animals do not understand the warnings given by farmers and applicators regarding the dangers of spray drift (Carson, 1963). Persistence is absent from EPA quotients, thus explaining the discrepancy found between EcoRR scores of persistent chemicals such as dimethipin (half-life >100 days in any compartment) and its quotient value. It should not be forgotten that DDT was banned in most countries, not because of its toxicity (four times more toxic to mammals and about 10 times more toxic to birds than dimethipin), but rather because its extremely long persistence in the environment and bioaccumulation in organisms (Dunlap, 1981), causing chronic effects in ecosystems which were unforeseen when first launched to the market. At the other end of the persistence spectrum, those chemicals experiencing fast degradation in any compartment have very low EcoRR scores: for instance, very volatile chemicals such as thiodicarb, trifluralin or pendimethalin produced insignificant EcoRR scores in air because their short half-lives in this media prevented them from causing an effective harm through inhalation. Similarly, highly toxic insecticides as diafenthiuron produced almost a nil EcoRR score in most compartments because of its apparently high rate of dissipation in all media.

Probabilities of exposure are lowest in the air compartment, and this explains why so few pesticides pose a risk to non-target organisms by the inhalation route. Although very volatile chemicals such as endosulfan and chlorpyrifos had the highest EcoRR scores in air, their values were low when compared to scores in other compartments. A similar outcome is obtained with residues in the sediment compartment, where relatively high concentrations of many chemicals (e.g. parathion-methyl, norflurazon, diuron) was not reflected in their low scores obtained, indicating that sediments are not very accessible by most organisms on site, and therefore its environmental risk should be limited. In irrigated crops, as in this simulation study, the water compartment on-farm has the highest probability of exposure, and consequently most residues

found in irrigation waters pose a high risk even for chemicals of relatively little toxicity as dimethipin, norflurazon or S-metolachlor. In fact, all of the 10 pesticides with highest risk on-farm had their highest scores in water, including of course those with highest toxicity either to aquatic taxa (endosulfan, aldicarb, chlorpyrifos) or to birds and mammals (methomyl, thiodicarb, aldicarb, omethoate, dimethoate). Because of the latter, ecotoxicological risks to terrestrial fauna through feeding and drinking of highly toxic waters such as tailwaters should be given a priority in risk assessments of farm chemicals: the attractiveness of large water bodies on farming regions can be a deadly lure for terrestrial wildlife. For instance, some studies on waterbirds in the cotton regions of Australia have shown that many predators (herons, egrets, darters, etc.) frequently obtain their prey in the water dams/storages located on cotton farms, but disappear from there as soon as the pesticide spraying season begins (Broome and Jarman, 1983), presumably as a result of the toxic residues to which they are continuously being exposed. Because the estimated probability of exposure to runoff waters off-farm was about 15 times lower than on the irrigation system, pesticides had much lower scores outside the farm areas despite their PECs being slightly higher in runoff than on-farm: e.g. methomyl's aquatic EcoRR is nine times lower off-farm and diuron's about 200 times (see Table 4).

The toxicity of a chemical was crucial in determining the highest scores in both on- and off-farm areas. Among the 10 highest total EcoRR scores were found the six most toxic chemicals to crustaceans, three to fish and frogs, eight to birds and seven to mammals. The only missing pesticides in the top list were all the synthetic pyrethroids, abamectin and diafenthiuron, which despite of their extremely high toxicity to fish had very low scores in the water compartment. This result may be explained by the low water solubility and high adsorption of these insecticides to soil and sediment particles, therefore presenting very low probability of exposure and hence a low EcoRR score. Insecticides of great toxicity such as aldicarb and phorate are usually applied as granules and incorporated into the soil at planting; for this reason, their risk through exposure to seed-feeding birds and other animals is minimised (Bunyan et al., 1981; Best and Fischer, 1992). However, their predicted high residues

in water gave them high EcoRR scores, indicating their potential risk in this compartment at least on-farm grounds. In the case of aldicarb, this risk seems to apply also to runoff waters outside the farm, perhaps as a result of a combination of factors of which its high persistence in water is the most notorious. Complementary models that determine the likelihood of leaching (Gustafson, 1989; Pestemer and Günther, 1995) also indicate that aldicarb should be regarded as a highly dangerous substance in irrigated agricultural crops, consistent with well known problems it has caused to human populations in the past (Mirkin et al., 1990).

Finally, the higher than normal EcoRR scores under a flooding scenario highlighted the importance of multifactorial models like this, which override the apparent weak effect of diluted residue concentrations in huge amounts of water by considering other crucial factors such as persistence, bioaccumulation and biodiversity. In these circumstances, the effective risk of small residues to biologically rich surrounding areas receiving a direct impact of a flood must increase, and this is recognised by the higher EcoRR scores obtained in such scenarios (Fig. 5).

4.1. Reliability of EcoRR scores

The good correlation between EcoRR scores and acute and chronic quotients to terrestrial taxa, as well as crustaceans in the aquatic environment (Fig. 6) is a guarantee of its reliability in predicting risk in ecosystems. The scale of EcoRR scores is, however, larger than that of the quotients, and this gives the wrong impression that EcoRR scores may indicate high risks where the quotient does not. In reality, most residues of pesticides found in agricultural areas are small enough to reassure ecotoxicologists that there is no apparent risk. However small they may be, the plain fact is that animals feeding in the vicinity of cotton farms show some residues of pesticides in their stomach contents (Sánchez-Bayo et al., 1999). What their effects would be to ecosystems in the long-term is something that remains unknown, but persistence and bioaccumulation may have unforeseeable effects in future, as history has demonstrated it in the case of DDT and other organochlorines.

The advantages of using the EcoRR model is that all taxa and environmental compartments can be assessed simultaneously, allowing comparisons of environmen-

tal risk among a set of chemicals by a range of characteristics other than the mere toxicity, as the quotient does. Specifically, persistence and bioaccumulation—two important features of environmental residues—are integrated in the EcoRR scores whereas unfortunately are missing in the quotients. Most importantly, as risk implies probability of exposure EcoRR scores are true expressions of risk whereas quotients indicate only hazards but not risk in the proper sense. Attempts to correct the inadequate values obtained by quotients in birds are cumbersome (Tiebout and Brugger, 1995) and of doubtful practical application.

As with any other model, the EcoRR methodology relies fully on the accuracy of the data used, particularly PEC estimates, half-lives and toxicity data. If estimates of residue concentrations and half-lives can be validated with measurements in the field, toxicities worked out under laboratory conditions can sometimes be very different from those measured in field situations (Leeuwangh et al., 1994). Specific data for a site, such as the timing of pesticide applications, the extent of drift and its direction within a given property, etc. must be obtained from local sources.

4.2. Management implications

While toxicity, persistence and chemical characteristics are specific features of a chemical, the other two major factors influencing risk in the EcoRR model—quantity applied and method of application—are subject to management. For management to be effective in minimising the adverse impact of agricultural pesticides in the environment, growers should be advised of which compartments are most at risk when using a particular chemical. In this context, knowing there is a risk it may be possible to find solutions that minimise it. For instance, levees built around the crop fields can effectively reduce or eliminate the off-farm risk of highly hazardous chemicals such as aldicarb during a large storm event or in a flood. As shown by our flood simulation, levees avoided the movement of metalaxyl-M residues into the wetlands (Fig. 5), and the same applied to quinterozone and other pesticides buried in the field as granules (aldicarb, phorate and norflurazon). As a modelling tool, EcoRR allows one to estimate the risk in both protected or unprotected field scenarios, giving the growers a quantitative index of the relative risk involved in each case. Like

all environmental problems, the magnitude of this risk would differ from one setting to another, and since there is not a single solution to avoid risks in all farms these management strategies should be applied on a case-by-case basis.

5. Conclusion

In summary, the EcoRR model provides an objective method of quantifying and comparing the relative risk amongst different hazardous chemicals applied on agricultural farms. The flexibility of EcoRR allows to detect any variation in the environmental conditions of a site, as these will certainly change the EcoRR scores by altering any of the multiple factors involved in their calculation. Thus, risk can be assessed for different seasons of a year, or under scenarios such as the flood described in this paper. The relative risk scores obtained will assist decision making, allowing a more responsible environmental choice of pesticides, and may help design management strategies with the aim of lowering the risk of certain chemicals with major impacts outside the farm (Raschke and Burger, 1997). In this context, the EcoRR model has proved to be a flexible expression which promises ample scope for modelling ecological risk assessment, and can be used as a tool in farm management.

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