Available online at www.sciencedirect.com
SCIENCE DIRECT®
Agriculture, Ecosystems and Environment 103 (2004) 45–58
Agriculture Ecosystems & Environment
www.elsevier.com/locate/agee

Estimating pesticide environmental risk scores with land use data and fugacity equilibrium models in Misiones, Argentina

Jorge Ares*
National Patagonic Center, Boulvd. Brown s/n, Casilla 76, 9120 Puerto Madryn, Argentina

Received 25 February 2003; received in revised form 10 October 2003; accepted 27 October 2003

Abstract

In the Province of Misiones (NE Argentina), traditional agriculture was based on industrial crops like mate tea, tea and tobacco, which still occupy 93% of the cultivated land. Recently, a fast crop re-conversion process with citrus plantations intended for direct consumption began. This re-conversion implies a number of changes in the agricultural systems. In particular, an intensification in the use of agrochemical pesticides to control bacterial, fungic and parasitic (mites, flies, scales, etc.) citrus pests is to be expected, unless effective Integrated Pest Control Programs (IPCPs) are simultaneously and successfully implemented. In order to maintain environmental risks at current levels, an adequate timing of crop replacement, pesticide use and progress of IPCPs is required. Methods and results of the analysis of prospective increases in pesticide environmental risk derived from agricultural re-conversion in scenarios with and without IPCPs at various scales of land use units are presented. The results indicate that some spatial scales of citrus cropping imply an estimated 530–790% increase of the exposure of local residents to pesticides as compared to present levels, and 66–110% increases in average regional human exposures. A successful IPCP that would ameliorate the effect of crop re-conversion maintaining present risk scores should accomplish a reduction of 75% of the risk posed by pesticides used in citrus crops within the next 20 years. This would compensate for an estimate 9% annual crop re-conversion rate. The techniques and concepts used here to arrive to these estimates could be extended to the analysis of environmental risks posed by agricultural re-conversion processes in other regions where similar processes occur.
© 2003 Elsevier B.V. All rights reserved.

Keywords: Pesticides; Agrochemical risks; Agriculture intensification; Fugacity modeling; Integrated pest control; Argentina

1. Introduction

The Province of Misiones in Argentina is located within the 25°28′S–28°10′S and 53°38′W–56°03′W at the north-eastern border of the country (Fig. 1). Traditional agriculture in the region was based in industrial crops like mate tea, tea and tobacco, which still occupy 93% of the cultivated land (SAGPyA, 2000). In recent years, citrus crops (tangerine, lemon, orange) have attracted the interest of farmers because their products find better export markets than those of older crops. At present, citrus crops demand intensive use of pesticides to control their many pests. Accordingly, a replacement of traditional crops like tea, tobacco or mate tea is expected to produce increasing levels of environmental exposure to these products of non-target organisms, including man. Citrus crops,

* Tel./fax: +54-2965-451021.
E-mail address: joares@arnet.com.ar (J. Ares).

0167-8809/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.agee.2003.10.005

Fig. 1. Situation of Misiones Province (Argentina) in the South American continent.

however, produce larger benefits to the farmers than traditional alternatives, and this prompts the interest to investigate forms and procedures to attain higher citrus productivity while maintaining environmental and production quality.

The environmental exposures that a set of agrochemical treatments applied to a crop system can produce depend on the chemical properties of the active ingredients, those of the dispersing agent, the form and doses of application, and the environmental characteristics of the site where the applications take place (Lewis et al., 1997a). Factors affecting the mobility and persistence of agrochemicals are related to the precipitation regime, the intensity of surface water runoff, the average thermal regime, etc. (Knisel and Davis, 2000). The vulnerability of non-target organisms depends on the spatial structure and distribution of biodiversity in the area (Ares, 2003).

A number of techniques including simulation modeling (MacKay et al., 1997; Pederson et al., 2001) can be used to perform a screening analysis of the use of pesticides in direct (crop protection) or indirect (channel maintenance, pre-emergence soil preparation) applications in order to formulate guidelines to achieve minimum environmental exposures (Roberts and Kearney, 1995; Henriques and Dixon, 1996). Tiered approaches to the estimation of pesticide exposure in tropical environments based on quantitative structure–activity relations (QSARs) have been applied by Freire-Gaspar and De-Lamonica (2001).

Modern pest control in crops relies on the development of Integrated Pest Control Programs (IPCPs) (Speight et al., 1999). During a successful IPCP, the relative importance of biological and cultural (Herzog and Funderburk, 1986) controls over pests increases and the need to use chemical pesticides decreases. However, the effective implementation of an IPCP in perennial crops may take extended periods of time (5–15 years), during which the cultivated area of infected crops can increase faster than the capacity to develop biological controls of their pests. Even those IPCPs considered to be successful might not allow a complete suppression of all chemical pesticides in use. In any case, a realistic scenario of pest control in newly introduced perennial crops should consider a gradual replacement of chemical by biological and cultural controls of pests and a simultaneous increase in the area cultivated with the crop. The combination of these trends would result in varying environmental risks to humans due to pesticides.

The objectives of this study were: (1) To summarize available information on the pesticides applied to traditional crops (tea, tobacco, mate tea) and to citrus crops in Misiones. (2) To score environmental risks to residents in areas dedicated to these crops through a screening procedure based on fugacity modeling. (3) To identify possible future trends of these risks in scenarios where the area cultivated with citrus may increase with simultaneous increase in the application of successful IPCPs. (4) To quantify the degree of success that IPCPs should attain in order to maintain present levels of environmental risks in scenarios of crop re-conversion.

According to these ideas, the re-conversion of cropping systems in Misiones was inspected in terms of the possible increment of the areas devoted to citrus crops during the next few years, and feasible goals of simultaneous IPCP implementation. Possible future cropping scenarios were inspected by means of fugacity modeling (Mackay and Paterson, 1991) and crop projection matrices (Hood, 2002) based on projected modal crop size, crop location, the pesticides used and the average meteorological conditions.

2. Materials and methods

2.1. Study area

The relief of Misiones is characterized by gentle slopes and small hills resulting from past intense erosion. Average altitudes are from 800 m (a.s.l.) at the NE to 100 m (a.s.l.) in the S. Gently sloping plains crossed by wide fluvial valleys occupy most of the area. The climate is subtropical warm with abundant precipitation (1500–2000 mm per year) and no marked dry season. The average air temperature is 20–21 °C, with 11 °C annual amplitude. This combination of continuous humid conditions and elevated temperatures produces vigorous growth of many plant species as well as parasitic and predating pests. Organic pollutants tend to decompose at a fast rate because of the elevated temperatures. Environmental transport of water-soluble substances and metabolites is also rapid. Most soil types in Misiones derive from basalt rocks, with minor representation of other soil groups originated from sandy sedimentary deposits and fluvial sediments. Most citrus crops occupy nearly flat or gently sloping areas in the numerous valleys crossing the territory, usually on Entic Rhodudalfs, Kanhapludalfs, Typic Udorthents, Entic and Lithic Hapludolls and Rhodic Kandiudulth soils (Soil Survey Staff, 1999).

2.2. Scenarios of agricultural production

According to previous descriptions from SAGPyA (2000), three scenarios were considered in this study in order to estimate environmental risks during crop re-conversion in Misiones. Scenario 1: this corresponds to farmers recently incorporated to citrus production. There are about 900 of this type of farmers operating over 3000 ha, assisted by a special fund raised on taxes upon the tobacco consumption all over the country. Most of them manage production units of about 5 ha, with moderate introduction of modern agricultural technology and equipment. Scenario 2: this corresponds to a small group of family properties of large citrus crops (about 400 ha each). These farmers usually have access to improved agricultural techniques and equipment. Scenario 3: this corresponds to farmers that do not cultivate citrus, but traditional crops: tea, mate tea, tobacco, etc. in usually large production units (400 ha). These latter correspond to about 93% of the cultivated area in Misiones. Standard metric dimensions for these scenarios were estimated from various sources and geometrical relations (Table 1).

2.3. Pesticides used: amounts and chemical characteristics

Pesticide types and amounts used in the various crops in Misiones were compiled based on data supplied by experts and consulting agronomists in the area. Table 2 shows the summary of the most common formulations and pesticide types used in various crops. Table 3 shows some environment-relevant chemical characteristics of the pesticides as needed to formulate fugacity models.

2.4. Human environmental exposure and risk score assessment

Environmental concentrations of chemical pesticides and human exposures were estimated with a modified version of the fugacity-based model described by Paterson and MacKay (1989). The "fugacity capacity" can be intuitively defined as the tendency of a substance to abandon an environmental phase (air, water, soils, sediments, organisms). The fugacity paradigm assumes that the equilibrium (i.e. long-term) concentration of substances in various phases of the environment depends on their fugacity capacity. Equilibrium concentrations of pesticide chemicals are computed by assuming that their emission to the environment is nearly constant, that first order decay processes and advection movements in the aqueous and air phases occur and that there is no impediment for the diffusive transport between environmental phases. The concentration of substances in organisms including man is also estimated through this approach and depends on their diet and lipidic content. Terrestrial animals and man are exposed through inhalation and dietary habits, while aquatic organisms are exposed through ingestion and the partition of the pollutants between water and their body lipids. The procedure conforms the assumptions of

Table 1
Dimensions of crop scenarios in Misiones Province

Scenario no.	Description	Air[a] (m^3)	Water[b] (m^3)	Soil[c] (m^3)	Sediment[d] (m^3)	Aquatic organisms[e] (m^3)	Air advection[f] residence time (days)	Water advection[g] residence time (days)	Observations
1	Small citrus farms	5×10^8	5×10^4	4.5×10^5	2.5×10^3	5×10^{-1}	1×10^{-3}	1×10^{-2}	Modal area: 5 ha[h]
2	Large citrus farms	4×10^9	4×10^6	4×10^8	2×10^5	4×10	1×10^{-2}	1×10^{-1}	Modal area 400 ha
3	Large farms, mixed traditional crops[i]	4×10^9	4×10^6	4×10^8	2×10^5	4×10	1×10^{-2}	1×10^{-1}	Modal area: 400 ha; mate tea (76%), tea (14%), tobacco (10%)[j]

[a] Average depth of atmospheric mixing layer: 10^3 m.
[b] Corresponds to a free water surface equivalent of 10% of farm area, 10 m average depth.
[c] Corresponds to 10 m average soil water percolation depth.
[d] Corresponds to 0.5 m average sediment depth.
[e] Based on estimated total fish catch with bulk density = $1\,t\,m^{-3}$.
[f] Average annual wind speed: $10\,km\,h^{-1}$. Residence time (day) = air flow (m^3 per day)/compartment volume (m^3). Air flow (m^3 per day) = wind speed (m per day) × lateral surface of scenario (m^2) × 0.5.
[g] Average annual water flow speed: $2\,km\,h^{-1}$.
[h] 1 ha = 10,000 m^2.
[i] Pesticides used: dimethoate, dicofol, $BrCH_3$, methalaxil, diazinon, acephate, carbaryl, zineb and flumethralin.
[j] Corresponds to proportions of land use in Misiones Province (1997).

Table 2
Pesticide types and amounts commonly used in various crops in Misiones Province[a]

Crop	Recommended treatment	No. of treatments per year	Active product	Annual dose[b] (kg ha^{-1})	Comments	Average annual dose[c] (kg ha^{-1})
Mate tea	"Rulo" of mate tea	3	Dimethoate (50%)	1.66 × 3		2.49
Tea	Mite	2	Dicofol (21-7)	11 × 2		4.62
Tobacco	Insects	8	Diazinon (56%)	0.62 × 8		2.77
		8	Acephate (80%)	0.65 × 8		4.16
		8	Carbaryl (85%)	0.6 × 8		4.08
	Fungii	8	Zineb (75%)	2.33 × 8		14.0
Cítrus	Fungii	7	$CuOH_2$ (77%)	15.5 × 7	Average	83.5
	Fruit fly	5	Mercaptothion (100%)	3.82 × 5	Average after fourth year	19.1
	Insects	8	Chlorpyrifos (48%)	1 × 8	After fourth year	3.84
	Fungii	1	Ziram (98%)	1	In first year	0.98
		8	Mancozeb (80%)	15 × 8	Every year	96
		8	Carbendazim (75%)	4 × 8	Average after fourth year	24
	Mining worm	8	Abamectin	$9.5 \times 10^{-4} \times 8$		0.007
	Herbicide	8	Glyphosate (48%)	3.4 × 8	Every year	13.1
		8	2-4-D (100%)	3.4 × 8	After third year	27.2
	Ant control	1	Mirex (100%)	3	From first to fourth year	3

[a] Unpublished data from H. Barbosa and J. Krauseman.
[b] As commercial product. Expert estimates of the applied doses indicate that these can vary considerably from case to case, depending on the equipment used, personal criteria and other factors. Accordingly, the numbers presented here should be considered as educated guesses of the actual amounts used. In all cases, 700 l/ha application volumes are assumed.
[c] As active product. Estimated on the basis of a 30-year crop cycle.

the so-called Fugacity Level II approach (Paterson and MacKay, 1989; see also Appendix A).

The computer code of the model was modified in order to introduce the metric dimensions listed in Table 1 as required by the model code. The fugacity model also requires input data relative to each of the pesticides used: name, molecular mass, vapor pressure, water solubility and octanol–water partition ratio, half-life in air, water, soil and organisms. Application rates as indicated by the usual agronomic practices as well as estimated inflow rates to the modeled area by air advection based on long-term average wind speeds and water advection based on average water current speeds must also be estimated. Additionally, the model requires parameters to evaluate possible adverse effects to organisms, like human acceptable daily intake (ADI) or daily reference dose (RfD) (LaGrega et al., 1994) data for each pesticide.

Resident human exposure was estimated by the equilibrium concentration of pesticides in diet items and inhaled air, assuming standard diet component amounts (vegetables: $3.5 \times 10^{-4}\,m^3$ per day; meat: $3 \times 10^{-4}\,m^3$ per day; dairy products: $3 \times 10^{-4}\,m^3$ per day; fish: $5 \times 10^{-5}\,m^3$ per day; water: $2 \times 10^{-3}\,m^3$ per day; air: $20\,m^3$ per day). Scores of pesticide environmental risks to human residents in each scenario were estimated by comparing the individual pesticide intakes resulting from diet (water + dairy products + fish + vegetables + air breathing) with their ADI or RfD, whichever the lowest (EXTOXNET, 2002).

2.5. Evolution of crop areas, relative success of IPCPs and resulting environmental risks

Feasible future changes of the crop area dedicated to traditional crops (mate tea, tea, tobacco), their replacement with citrus crops and the resulting risks thereof were explored by means of a matrix projection simulation routine (Hood, 2002). The procedure was adapted to solve the following basic equations:

$$C_{i,t} = C_{i,t-1} \times (1 + r_i) \qquad (1)$$

Table 3
Chemical properties[a] of pesticides used in Misiones

Compound	Molecular weight (g)	Vapor pressure (Pa)	Water solubility ($g\,m^{-3}$)	log K_{ow}	Half-life air (days)	Half-life water (days)	Half-life soils (days)	Hal-life sediments (days)	Half-life biotica (days)	ADI, RfD[b] (mg per day)
2-4-D	221.0	0.5	900	2.7	15	25	10	50	10	7×10^{-1}
Abamectin	>500	1×10^{-7}	7×10^{-3}	≅4.0	1	5	30	20	0.2	$\cong 1 \times 10^{2}$
Acephate	183.2	2.3×10^{-4}	7.9×10^{-1}	−1.9	<1	<1	6	<1	6	3.5×10^{-1}
Carbendazim	191.2	1.0×10^{-6}	15	1.5	100	60	150	70	50	2.1[c]
$CuOH_2$	63.54	0	2.9×10^{5}	2.0	1×10^{25}	1×10^{25}	1×10^{25}	1×10^{25}	1×10^{25}	0.2[d]
Carbaryl	201.2	2×10^{-4}	120	2.3	0.5	12	10	30	22	4
Chlorpyrifos	350.6	2.5×10^{-3}	1.5	4.9	0.3	10	170	90	15	0.2
Diazinon	304.3	1.2×10^{-2}	40	3.8	0.5	150	190	120	5	6.3×10^{-3}
Dicofol	370.5	1×10^{-6}	8×10^{-1}	4.3	0.01	70	60	150	700	1.4×10^{-1}
Dimethoate	229.3	1.1×10^{-3}	3.0×10^{4}	0.75	0.01	200	70	90	3	1.4
Glyphosate	169.1	3×10^{-5}	1.2×10^{4}	−3.0	0.01	60	40	65	60	1.4×10^{2}
Mercaptothion	330.4	1×10^{-3}	150	2.9	0.3	50	20	40	10	2.1×10^{1}
Mancozeb (ETU)[e]	266.3	1×10^{12}	6	<1	5	2	7	7	7	2.1×10^{-1}
Mirex	545.5	2.5×10^{-4}	3×10^{-3}	6.50	0.2	5	3×10^{3}	5×10^{3}	1×10^{3}	–
Zineb (ETU)[f]	265	1×10^{-7}	10	1.78	5	16	16	16	16	1.4×10^{-1}
Ziram	≅270	1×10^{-7}	6.5	<1	5	5	5	5	5	1.4

[a] MacKay et al. (1997), EXTOXNET (2002).
[b] Lowest of ADI, RfD for a 70 kg human.
[c] Codex Alimentarius, Food and Agriculture Organization (FAO).
[d] Estimated as 1/100 TLV (ACGIH, 2003).
[e] Mancozeb discomposes fast to ethylen-thio-urea (ETU), a compound to which contribution to thyroid disorders and theratogenesis are attributed (EXTOXNET, 2002).
[f] Zineb see Mancozeb (footnote 18).

$$R_{i,t} = \sum^{j} C_{i,t} \times R_{i,j} \quad (2)$$

or

$$R_{i,t} = \sum^{j} (C_{i,t} \times R_{i,j}) - RR_{i,t,\mathrm{IPCP}}$$

If an IPMP is applied. The boundary condition is: $C_{\text{non-c}} + C_{\text{c}} =$ constant, and t: 0.20 (years). $C_{i,t}$ is the area cultivated with crop i at time t, r_i the annual rate of change of the area dedicated to crop i, $R_{i,t}$ the total environmental risk attributable to pesticides $1, \ldots, j$ in crop i, $R_{i,j}$ the risk characteristic of pesticide j in crop i at a given spatial scale and $RR_{i,t,\mathrm{IPCP}}$ the feasible risk reduction attained in crop i at time t as a result of the application of an IPCP to that crop. The boundary condition implies a crop re-conversion process. Since financial and climatic circumstances can influence both r_i and $RR_{i,\mathrm{IPCP}}$, these rates are assumed to be stochastically (normally) distributed with estimated mean and spread values. A feasible mean degree of IPMPs success to be attained during a period of 20 years that would result in a reduction of pesticide use equivalent to a 75% reduction of risk scores was tested for consistency within the crop re-conversion scenarios (mean $RR_{i,\mathrm{IPCP}} = 0.0375$, S.D. $= 0.0375$). The choice of these parameters seems in reasonable agreement with available experience in the area and reported results of similar programs (Ward et al., 1999; McCoy et al., 2003). According to the experience of local planners, a 9% annual increase in the area dedicated to citrus can be expected to occur during the next 20 years in Misiones, depending on financial and climatic scenarios. Occasionally this rate could be duplicated or re-conversion could cease at unfavorable years. Some newly installed or old citrus crops could be lost due to unfavorable climatic or pest conditions. Based on these, the rate of increase of the area with citrus was simulated by means of a stochastic variable (mean $r_{\text{citrus}} = 0.09$, S.D.: 0.09).

3. Results

Fig. 2 illustrates the estimated equilibrium mass partitions among major environmental compartments of some of the pesticides used in traditional (tea,

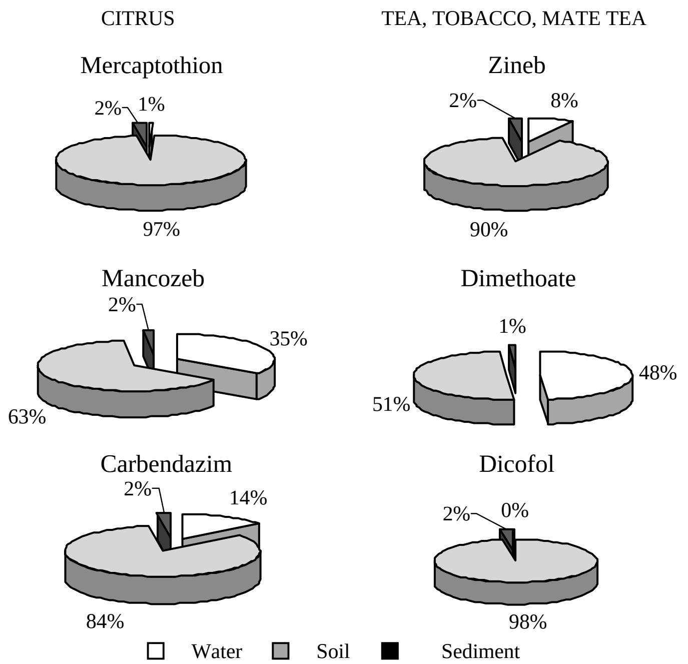

Fig. 2. (Left) Equilibrium mass partition of common pesticides used in citrus crops in Misiones. (Right) Same in traditional crops (tea, tobacco, mate tea).

tobacco, etc.) and in citrus crops in Misiones. The partition estimates result from the chemical characteristics of the substances as listed in Table 3 and the relative size (Table 1) of the environmental compartments in the respective crop scenarios. Some of the pesticides, like glyphosate, dimethoate and mancozeb tend to be solved in water in equilibrium with soils and sediments, while others like mercaptothion, dicofol and zineb remain bound to the soil organic matter because of their lipophilic nature. The mass fractions in other environmental compartments than those shown in Fig. 2 are less important (<1%) in all cases, either because of the low partition coefficient of the compound into

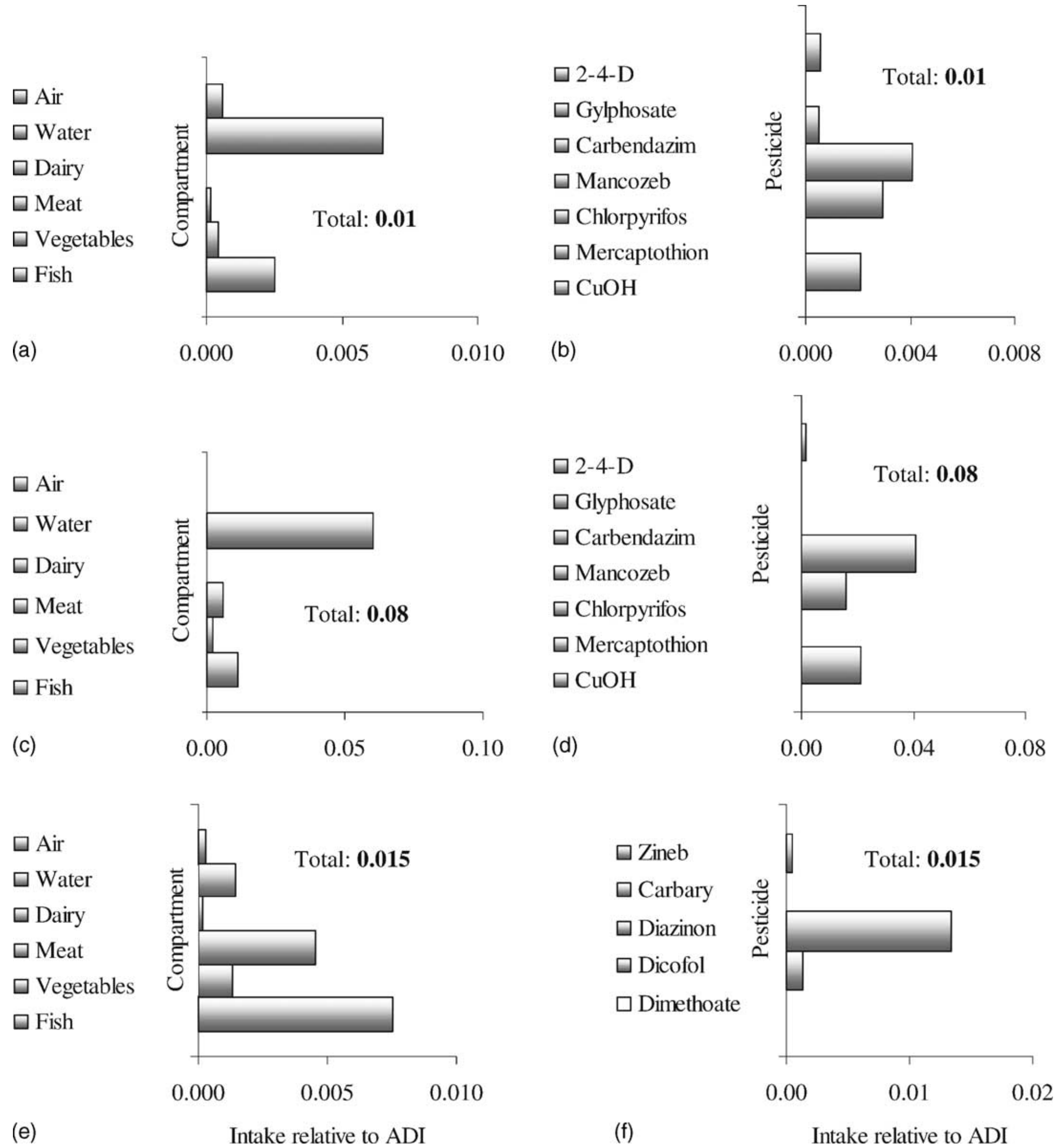

Fig. 3. (a) Human intake exposures relative to ADIs by various food items in areas with small citrus crops (5 ha); (b) same discriminated by pesticides used in these crops. (c) and (d) Respectively same as '(a) and (b)' in areas of large (400 ha) citrus crops. (e)–(f): Respectively same as '(a) and (b)' in areas of large (400 ha) traditional crops.

them (air) or because of the low compartment size (organisms).

The concentration of pesticides in environmental compartments (including those conforming the human diet) also depends on the agronomic practices used in each crop type (i.e. the quantity of pesticide used per unit area per year). Additionally, concentrations can be reduced by un-polluted air and water advection into the area. Fig. 3 shows the estimated human diet intakes relative to ADI discriminated by diet component (left) and by pesticide (right). Note that the horizontal scales in insets c and d (large citrus crops) are 10 times higher than those in the other sections of Fig. 3 (a and b: small citrus crops; e and f: large traditional crop farms). Considering citrus crops of different size (compare Fig. 3c and d with Fig. 3a and b) the difference in exposures is accounted by the different residence times of air and water advection (see Table 1). The ratio of the sum of all intakes in large citrus to those in small citrus units is 7.9. In comparing citrus crops of large size (400 ha) with traditional crops (tea, tobacco, etc.) over similar areas (see Fig. 3c and d vs. Fig. 3e and f) the differences in exposure result from the more intensive use of pesticides in citrus as compared to traditional crops (see Table 2). The sum of all intakes in Fig. 3c and d (large citrus crops) is 5.3 times higher than that in large traditional crops (Fig. 3e and f).

A further analysis of human exposures to pesticides in the different crop systems represented in Fig. 3 indicates that water is the main route of exposure in systems of citrus crops, while dairy–meat–milk are the main routes in scenarios of traditional crops. This is a consequence of the higher representation of pesticides that tend to partition in water vs. those that tend to partition in organic matter in each of the systems (see K_{ow} values in Table 3) and of their ADI rating. Fig. 3 also shows that for those farmers re-converting from small to large citrus crops (without simultaneously implementing effective IPCPs, see later) *local* risks would increase by 790% and for those shifting from large traditional to large citrus crops by 530% (reaching 0.08 ADI in both cases).

Fig. 4 shows three stochastic realizations of the process of crop replacement during the period 2002–2022 and that of the resulting risks to humans from environmental exposure to pesticides. Crop replacement is assumed to occur in large production units at the expense of similarly large areas with traditional crops. Different time projections were formulated depending on the implementation of effective IPCPs that would reduce risks from exposures to pesticides down to 25% of their present levels. If a series of years with favorable conditions occur (Fig. 4a) the area for citrus crops

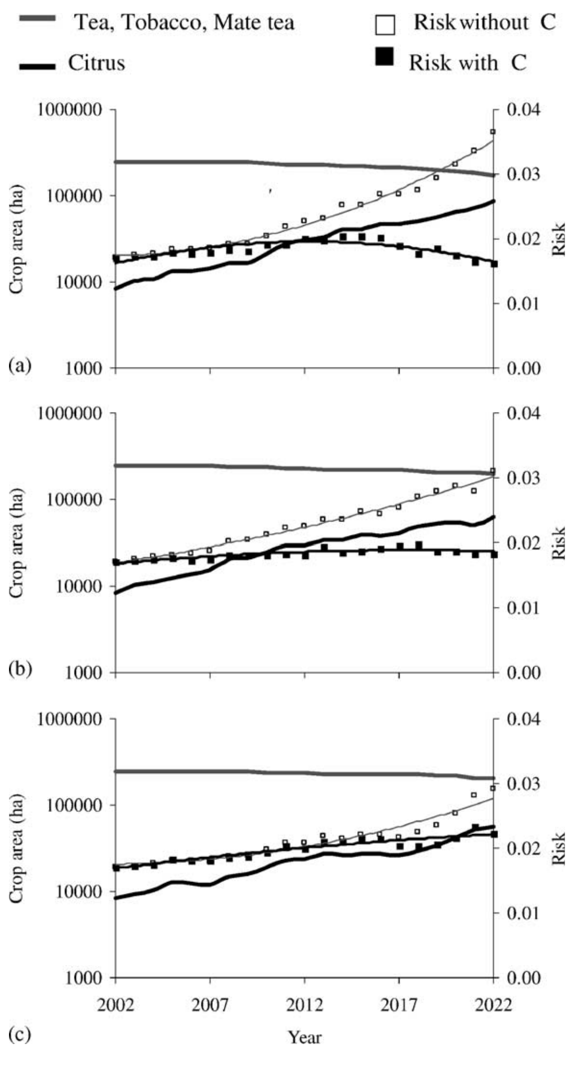

Fig. 4. The projected evolution of the areas devoted to citrus and traditional crops in Misiones and the estimated change of average environmental risks to residents from exposure to pesticides depending on the implementation of effective Integrated Pest Controls Programs (IPCPs). (a)–(c) Insets describe three realizations of a stochastic model where the area dedicated to citrus increases at a mean annual rate = 0.09 (S.D.: 0.09) and an IPCP program produces a reduction of pesticide risks at an average annual rate: 0.0375 (0.75 in 20 years, S.D.: 0.0375). Risk trends were fitted with a second-degree polynomial to ease visualization.

could be expected to increase up to about 90,000 ha by 2022. In the absence of an effective IPCP, the weighed average human risk from exposure to pesticides in Misiones would increase from 0.018 to 0.038 ADI or about 110% during the same period. If an effective IPCP is implemented at year 2002 and maintained through 2022, average human risks in Misiones could be kept at their present levels or be eventually reduced. Other possible scenarios with less effective development of citrus production (15,000–18,000 ha by year 2022) would imply risk increases of 66% (from 0.018 to 0.03, Fig. 4b). In some cases (Fig. 4c) risks could increase even under low-moderate success of citrus crops, because of a defective or incomplete implementation of IPCPs. Note that the assumption that large citrus units would replace similar extensions of traditional crops constitutes a worst-case scenario, because risks in large units are greater than at small units, and citrus could increase in middle sized or even in many small units. However, a worst-case assumption might prove realistic, since traditional farmers on large production units are in better position and more likely to become investors in crop re-conversion.

4. Discussion

4.1. Pesticide risk scores

Various approaches have been developed to build evaluation systems that would encompass the wide range of effects implied in pesticide effects on non-target organisms, including man. Pesticide scoring methods are usually based on a weighed appreciation of their effect on a number of damage functions (Field, 1995, pp. 169–172). Lewis et al. (1997b) proposed a method that uses scores derived from label information (presence/absence of anticholinesterase compound, game/bird/bees/fish toxicity, flammability, etc.) and from the physico-chemical characteristics of the pesticides (water solubility, partition in organic solvent, soil half-life). Inherent in this and similar approaches (Hart, 1997) is estimating the intensity of damage functions related to human and ecosystem risks. These systems may rank pesticides in differing orders depending on the criteria used to estimate risks, the characteristics of the site or the management practices at the farm system (Reus et al., 2002). The approach used in the present study is based on fate-exposure-risk scores. While being more consistent with the procedure used for the pesticide authorization (Reus and Leendertse, 2000) computer modeling and a certain degree of expertise are required. These could limit its application by farmers and other public users, but seems convenient for farm and human health policy planning, eco-auditing, etc.

As in this study, human intake in relation to estimated safe limits has frequently been inspected as a (relevant) surrogate or partial indicator of environmental risk (Alcock, 2000; Margni et al., 2002; Skibniewska, 2003). Although conceptually similar, RfDs and ADIs are estimated through slightly different procedures that in some cases can result in different recommendable limits for human daily exposure. A striking example of this is mancozeb (ADI: 0.03 mg kg^{-1} per day, RfD: 0.003 mg kg^{-1} per day) where adopting the lowest of both seems a conservative choice, as done in this study. It should also be noted that safety factors in the range of orders of magnitude are imbedded in deriving ADI/RfD from laboratory evidence on small mammal toxicity (LaGrega et al., 1994). As a consequence of this, risk estimates based on ratios involving these parameters should be better regarded as scaling scores of relative environmental safety. This meaning departs to a certain extent from the usually accepted definition of risk as an expression of the probability of occurrence of some adverse outcome to some organism (Warren-Hicks and Moore, 1998, p. 25), although it has been widely adopted (Reus and Leendertse, 2000; Sánchez-Bayo et al., 2002). It is also important to note that consequent to the procedures used to estimate ADI/RfDs, pesticide and diet intake scores based on risk-ratios tend to span over several orders of magnitude, as contrasting with scores based on relative rankings (Lewis and Tzilivakis, 1998), combined decision rules including fuzzy parameters (van der Werf and Zimmer, 1998), or combinations of chemical properties and application practices (Brüggeman and Halfon, 1995). This has several implications. First, risk-ratios seem better suited to convey the degree of precision about toxicity that derives from estimates of ADI-RfD or similar maximum permissible thresholds. A second aspect is related to the problem of evaluating the risks posed by mixtures of pesticides on the basis of toxicity risks based on exposures to single active products. While this is to a great extent an unresolved toxicological issue, it is illustrative to consider current criteria in the accepted practice to evaluate risky exposures in industrial systems outside the agricultural sector. Whenever evidence on the contrary is not available, some expert panels would admit that an estimate of total risk might be obtained through a weighed summation of partial risks (ACGIH, 2003). In other cases, experts might not accept this concept (DFG, 2003). In recent applications in the agriculture industry, sums of partial risk-based pesticide scores have been used as a means to estimate total risks (Sánchez-Bayo et al., 2002) and this approach has also been applied in this study. Adding up relative pesticide scores might not find a better justification and would certainly produce different rankings as those obtained by summing up risk scores.

4.2. *Fugacity modeling applied to the estimation of pesticide environmental risk*

Fugacity modeling (Mackay, 2001) has evolved during the last two decades into a standard technique to evaluate the distribution of chemicals in multi-medial environments, including pesticides (MacKay et al., 1997; Sánchez-Bayo et al., 2002). Since the concentration of chemicals in the environment depends on the local size of its different phases (air, water, organisms, etc.) the use of fugacity multi-medial models to derive pesticide risk scores requires defining evaluative environments that would mimic the proportions of different media in the agricultural scenarios. In doing this, it should be noted that the relations describing transfers among environmental phases do not vary proportionally to the size of the production units being modeled. In particular, advective in/outflows of pesticides through air and water are proportional to the size of the areas bounding these phases. In three-dimensional environments, the areas bounding large phases are proportionally smaller in relation to the bounded phase volume, resulting in increased residence times of the pollutants inside large production units as compared to small farms (Ares, 2003). The results shown in this study further illustrate this point.

It should also be considered that Level II fugacity modeling supplies estimates of environmental pesticide concentrations assuming an equilibrium of pesticide fugacities among compartments is attained. This might not hold in situations where short-lived pesticides are applied only once in a growing season, and an equilibrium among all phases might never be reached before the pesticide decomposes or is transported to neighbor environments. The case here presented does not seem to fall within these limitations. Citrus and traditional crops in Misiones receive repeated applications of pesticides during the growing season (see Table 2) and a quasi-continuous inflow of them can be assumed at a first screening level, as here done.

4.3. *Estimating crop re-conversion scenarios*

An estimate of shifting risks in agricultural scenarios in Misiones during the next decades must consider the partial replacement of traditional crops for citrus crops under increasing adoption of IPCPs. However, agricultural systems can only be modeled/predicted with a considerable level of uncertainty. Uncertainty arises from imperfect knowledge of the bio-economic inputs and inaccuracies in mathematical modeling, the effect of chemical and biological control instruments, and the variability of climate conditions (Bor, 2003). Also, the need to practice pest control or use pesticides is to a great extent dictated by the highly dynamic behavior of predator–prey systems that can vary in time within wide limits (Ares, 2003). Present approaches to modeling agricultural systems integrate the treatment of their biophysical and economic components (Bouzaher et al., 1995; Belcher et al., 2004). Since integrated agricultural systems depend on external forcing variables of uncertain behavior, stochasticity is introduced to inspect system internal dependencies and most probable future outcomes. Rainfall and external markets are typically formulated as stochastic components (Belcher and Boehm, 2002; Lien, 2003).

In this study, a stochastic matrix projection model of traditional × citrus crop replacement in scenarios with/without simultaneous implementation of IPCPs was formulated in simple terms. The aim of the model was exploring the interdependencies between feasible IPCP goals and the evolution of environmental risks resulting from increasing acreage dedicated to citrus crops. The model risk reduction goal is consistent with reported experience in this type of programs (Speight et al., 1999). Since both the success of the IPCP and the increase in the area dedicated to citrus could vary depending on financial and climatic circumstances, different alternatives could result from the stochastic variation of both. Stochasticity was introduced in a heuristic rather than mechanistic way through variables describing the rate of crop type change and the rate of reduction in risk resulting from diminishing pesticide use.

Since incipient IPCPs are being implemented in Misiones, the results obtained with the model described in Eqs. (1) and (2) point to the relevance of conducting a continuing evaluation of the relative success of these programs in terms of the extent of reduction in pesticide use, discriminated by their different classes. These activities could be framed in organized diagnosis-advisory rules, as shown by Mahaman et al. (2003). Since both the success of IPCPs and commercial crops might depend on financial and climatic circumstances, adequate margins of stochasticity in their development must be expected and identified in their projected time course.

5. Conclusions

The re-conversion from traditional (tea–tobacco, etc.) crop systems to pest-sensitive citrus crops in Misiones Province (Argentina), could potentially increase the average environmental risks to human residents during the next 20 years. Depending on the type and spatial arrangement of the re-conversion process, the relative success of the new crops and the efficacy of implemented IPCPs, increases in risk by 66–110% could result. Present average levels of risk due to pesticide use could be maintained while enlarging the area with citrus crops up to 90,000 ha during the next 20 years if effective Integrated Pest Control Programs (IPCPs) are simultaneously implemented. Whatever the IPCP to be implemented to control citrus pests in Misiones, its effectiveness should result in a risk reduction (as defined in this study) of about 75% in 20 years in order to be commensurate with planned increases in the areas dedicated to citrus. For those re-converting from small to large citrus crops (without implementing effective IPCPs) local risks would increase by 790% and for those shifting from large traditional to large citrus crops by 530%. Re-conversion in small citrus production units relatively isolated from each other should be promoted in comparison with the same arranged in large, un-fragmented production areas. Monitoring the success of IPCP programs in terms of the reduction of pesticide use attained is necessary to allocate effort to an effective control of environmental risks. The concepts and methods here presented can be used to evaluate environmental conditions in similar crop re-conversion processes in other areas of perennial crops.

Acknowledgements

This research was conducted in the frame of a contract with the Secretary of Agriculture, Animal Husbandry, Fisheries and Nutrition and co-funded by the National Council for Scientific and Technological Research (CONICET), PIP 956/99, Argentina.

Appendix A

A.1. Principles and theory of fugacity modeling[1]

A primary objective in environmental chemistry is to forecast the concentrations of pollutants in the environments with respect to space and time variables. Our knowledge of the behavior of pollutants can be used to model the space and time domains of pollutants once emissions are known or estimated. Fugacity models are distribution based models incorporating all environmental compartments, and are based on steady-state fluxes of pollutants across compartment interfaces.

Fugacity is defined as the chemical activity of a gas, and expresses the escaping tendency from a compartment. Fugacity is linearly related to concentration at dilute concentrations via:

$$C_{i,j} = Z_{i,j} f_{i,j}$$

$C_{i,j}$ is the concentration of pollutant i in compartment j (mol m^{-3}); $Z_{i,j}$ the fugacity capacity of pollutant i in compartment j (mol m^{-3} Pa^{-1}); $f_{i,j}$ the fugacity of pollutant i in compartment j (Pa).

Fugacity may also be expressed for any environmental compartment or phase, and represents

[1] For a complete description of environmental modeling techniques based on the fugacity concept, see Mackay D, 2001.

equivalent gas phase fugacity. At equilibrium between two or more phases:

$$f_{A,1} = f_{A,2}$$

$$\frac{C_{A,1}}{Z_{A,1}} = \frac{C_{A,2}}{Z_{A,2}}$$

Z constants are usually derived from Raoult's law:

$$f_{i,j} = C_{i,j} v_j \gamma_{i,j} f_R$$

where $f_{i,j}$ and $C_{i,j}$ are as above and v_j is the phase molar volume of compartment (mol m^{-3}) and $\gamma_{i,j}$ the activity coefficient of pollutant i in compartment j. Conventionally, f_R the reference fugacity (Pa) of the liquid state vapor pressure of the organic pollutant.

A.2. Setting up a fugacity model

A usual procedure in setting up a fugacity model is defining a so-called "unit" environment, containing relative proportions of environmental phases similar to the system to be modeled. Phase volumes (m^3) are then estimated for all relevant compartments and sub-compartments. A decision is then taken about the level of complexity to be introduced in the model in relation to the existence of equilibrium among phases, in/outflows of material and biophysical processes modifying the pollutant concentrations other than the in/outflow of the pollutant itself (biodegradation, photolysis, redox transformations, etc.). A complexity Level II assumes the existence of these reactions in a context of a constant emission at a known rate (mol/time) and the occurrence of advective movements of the pollutant among compartments. Adequate constants describing these physical properties are obtained and the Z constants for all relevant compartments and sub-compartments are then calculated. The computer code also incorporates output subroutines with additional calculations incorporating exposure estimates, summarizing values discriminated for each phase, etc.

References

ACGIH (American Conference of Governmental Industrial Hygienists), 2003. Documentation of the Threshold Limit Values and Biological Exposure Indices, 7th ed. American Conference of Governmental Industrial Hygienists, Cincinnati, OH.

Alcock, R.E., 2000. The environment and health: a new challenge. Environ. Int. 26, 3–5.

Ares, J., 2003. Time and space issues in ecotoxicology: populations models, landscape pattern analysis and long range environmental chemistry. Environ. Toxicol. Chem. 22, 95–957.

Belcher, K.W., Boehm, M., 2002. Evaluating agroecosystem sustainability using an integrated model. In: Rapport, D.J., Lasley, B.L., Rolston, D.E., Nielsen, N.O., Qualset, C.O., Damania, A.B. (Eds.), Managing for Healthy Ecosystems. CRC Press, Boca Raton, Florida, pp. 103–132.

Belcher, K.W., Boehm, M.M., Fulton, M.E., 2004. Agroecosystem sustainability: a system simulation model approach. Agric. Syst. (in press).

Bor, Y.J., 2003. Uncertain control of dynamic economic threshold in pest management. Agric. Syst. 78, 105–118.

Bouzaher, A., Cabe, R., Johnson, S.R., Manale, A., Shogren, J.F., 1995. CEEPES: an evolving system for agroenvironmental policy. In: Milon, J.W., Shogren, J.F. (Eds.), Integrating Economic and Ecological Indicators: Practical Methods for Environmental Policy Analysis. Praeger Publishers, Westport, CT, pp. 101–124.

Brüggeman, R., Halfon, E., 1995. Theoretical base of the program 'Hasse'. GSF-Bericht 20/95, Forschungszentrum für Umwelt und Gesundheit, München-Neuherberger.

DFG (Deutschen Forschungsgemeinschaft), 2003. MAK-und BAT-Werte-Liste 2003. Wiley–VCH, Weinheim, 260 pp.

EXTOXNET, 2002. URL: http://pmep.cce.cornell.edu/profiles.

Field, B., 1995. Economía Ambiental. McGraw-Hill, Buenos Aires, 587 pp.

Freire-Gaspar, E., De-Lamonica, E.M., 2001. Contaminaçao do ambiente aquático por pesticidas: estudo do caso: aguas usadas para consumo humano em Primavera do Leste, Mato Grosso-Analise Preliminar. Quim. Nova 24, 27–36.

Hart, A., 1997. Key characteristics of pesticide risk indicators used as policy tools: a comparison of 11 indicators. In: Report of the OECD Workshop on Pesticide Risk Indicators, Copenhagen, April 21–23, 1997.

Henriques, W.D., Dixon, K.R., 1996. Estimating spatial distribution of exposure by integrating radiotelemetry, computer simulation and geographic information system (GIS) techniques. Human Ecol. Risk Assess. 2, 527–538.

Herzog, D.C., Funderburk, J.E., 1986. Ecological bases for habitat management and pest cultural control. In: Kogan, M. (Ed.), Ecological Theory and Integrated Pest Management Practice. Wiley, New York, pp. 217–250.

Hood, G., 2002. Poptools-TPMath Software. URL: http://www.cse.csiro.au/poptools.

Knisel, W.G., Davis, F.M., 2000. Groundwater loading effects of agricultural management systems. USDA-Agricultural Research Service, Pub. No. SEWRL-WGK/FMD-050199, Washington.

LaGrega, M.D., Buckingham, P.L., Evans, J.C., 1994. Hazardous Waste Management. McGraw-Hill, New York.

Lewis, K.A., Newbold, M.J., Hall, A.M., Broom, C.E., 1997a. Eco-rating system for optimizing pesticide use at farm level. J. Eng. Res. 68, 271–279.

Lewis, K.A., Newbold, M.J., Hall, A.M., Broom, C.E., 1997b. Eco-rating system for optimizing pesticide use at farm level. Part 2. Evaluation, examples and piloting. J. Eng. Res. 68, 281–289.
Lewis, K.A., Tzilivakis, J., 1998. Evaluating a technique used to measure environmental performance within agriculture—case studies. Eco-manage. Auditing J. 5, 126–135.
Lien, G., 2003. Assisting whole-farm decision-making through stochastic budgeting. Agric. Syst. 76, 399–413.
Mackay, D., Paterson, S., 1991. Evaluating the multimedia fate of organic chemicals: a Level III fugacity model. Environ. Sci. Technol. 25, 427–436.
Mackay, D., 2001. Multimedia Environmental Models: The Fugacity Approach. Lewis Publishers, Boca Ratón, FL.
MacKay, D., Shiu, W.Y., Ma, K., 1997. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals: Pesticide Chemicals, vol. V. Lewis Publishers, Boca Ratón, FL.
Mahaman, B.D., Passam, H.C., Sideridis, A.B., Yialouris, C.P., 2003. DIARES-IPM: a diagnostic advisory rule-based expert system for integrated pest management in Solanaceous crop systems. Agr. Syst. 76, 1119–1135.
Margni, M., Rossier, D., Crettaz, P., Jolliet, O., 2002. Life cycle impact assessment of pesticides on human health and ecosystems. Agric. Ecosyst. Environ. 93, 379–392.
McCoy, C.W., Nigg, H.N., Timmer, L.W., Futch, S.H., 2003. Florida Citrus Pest Management Guide: Use of Pesticides in Citrus IPM. Entomology and Nematology Department, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida, CPMG-03, Florida, 8 pp.
Paterson, S., MacKay, D., 1989. A model illustrating the environmental fate, exposure and human uptake of persistent organic chemicals. Ecol. Model. 47, 85–114.
Pederson, B.M., Thibodeaux, L.J., Valsaraj, K.T., Reible, D.D., 2001. Testing a multimedia compartmental model with monitoring data. Environ. Toxicol. Chem. 20, 2114–2121.
Reus, J., Leendertse, P.C., 2000. The environmental yardstick for pesticides: a practical indicator used in the Netherlands. Crop Protect. 19, 637–641.
Reus, J., Leendertse, P., Bockstaller, C., Fomsgaard, I., Gutsche, V., Lewis, K., Nilsson, C., Pussemier, L., Trevisan, M., van der Werf, H., Alfarroba, F., Blümel, S., Isart, J., McGrath, D., Seppälä, T., 2002. Comparison and evaluation of eight pesticide environmental risk indicators developed in Europe and recommendations for future use. Agric. Ecosyst. Environ. 90, 177–187.
Roberts, T.R., Kearney, P.C., 1995. Environmental Behavior of Agrochemicals, vol. 9. Progress in Pesticide Biochemistry. Wiley, New York.
SAGPyA, 2000. Secretaría de Agricultura, Ganadería, Pesca y Alimentación. Proyecto de Fortalecimiento de los Servicios Fitosanitarios de la Prov. de Misiones. Documento Principal. SAGPyA, Buenos Aires.
Sánchez-Bayo, F., Baskaran, S., Kennedy, I.R., 2002. Ecological relative risk (EcoRR): another approach for risk assessment of pesticides in agriculture. Agric. Ecosyst. Environ. 91, 37–57.
Skibniewska, K.A., 2003. Diet monitoring for assessment of human exposure to environmental pollutants. Environ. Int. 28, 703–709.
Soil Survey Staff, 1999. Soil Taxonomy. A basic system of soil classification for making and interpreting soil surveys. Agriculture Handbook, vol. 436. United States Department of Agriculture, Natural Resources Conservation Service, Washington, 871 pp.
Speight, M., Hunter, M., Watt, A.D., 1999. Ecology of insects: concepts and applications. Blackwell Science, Oxford, 350 pp.
van der Werf, H.M.G., Zimmer, C., 1998. An indicator of pesticide environmental impact based on a fuzzy expert system. Chemosphere 36, 2225–2249.
Ward, C.R., Wachter, S., English, L.M., Feather, F., 1999. Integrated Pest Management in the Western Region. University California Report, Riverside, 6 pp.
Warren-Hicks, W.J., Moore, D.R.J., 1998. Uncertainty analysis in ecological risk assessment. In: Proceedings of the Pellston Workshop on Uncertainty Analysis in Ecological Risk Assessment, August 23–28, 1995. Society of Environmental Toxicology and Chemistry (SETAC), Pellston, MI, Pensacola, 314 pp.