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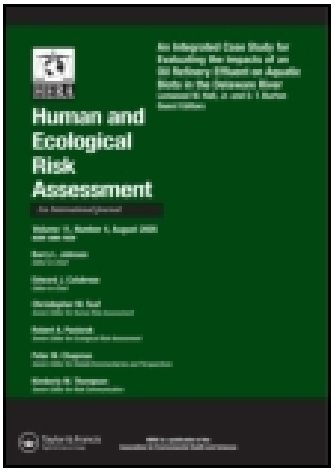

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Environmental Risk of Pesticides: Applying the DelAzulPestRisk Model to Freshwaters of an Agricultural Area of Argentina

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Environmental Risk of Pesticides: Applying the DelAzulPestRisk Model to Freshwaters of an Agricultural Area of Argentina

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ABSTRACT

DelAzulPestRisk is a risk-based chemical ranking model based on human and local biota toxicities that estimates the integrated risk of pesticides in water from their extensive (concentration, risk) and intensive (persistence, bioaccumulation) chemical properties. The model is built on two modules: human health risk factor (estimated based on the probabilistic cancer and non-cancer health risk by using U.S. Environmental Protection Agency models applied to a bathing exposure scenario) and biota health risk factor (quantified on the basis of the probabilistic toxicity exposure ratio –PEC/PNEC– for three local representatives of water biota multiplied by an amplification factor supported by the persistence and bioaccumulation potential). The model was applied to shallow creeks of Tres Arroyos County, Argentina, which flow across wheat and soybean agricultural lands, and in whose waters were detected many organochlorine pesticides (α, γ, y, δ-HCH, aldrin, heptachlor, γ-chlordane, endosulfan, endosulfan sulphate, dieldrin, and DDD). Dieldrin, aldrin, and heptachlor generated the worst potential effects—due mainly to the cancer and non-cancer dermal health risk—although this was not a significant environmental threat. DelAzulPestRisk is a screening assessment tool for water management purposes that become useful in countries lacking efficient water quality control systems.

Key Words: water management, risk-based chemical ranking system, pesticides, Argentina.

INTRODUCTION

The application of pesticides is still the most effective and accepted way to protect crops against plagues, thereby contributing significantly to improved crop yields

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(Finizio and Villa 2002). However, the greater use in Argentina of chemical fertilizers and pesticides has increased the presence of these substances in the environment, causing pollution in diverse degrees of severity. The assessment of the pesticides in water environments is very important not only for estimating their threat to exposed human users (bathers, nautical sport players, *etc.*) and to local biota. Assessment is also valuable for promotion of changes in agricultural practices.

There are numerous examples in the literature of integrated models for water quality analysis based on variables related to different aspects of the environmental threat (Halfon and Reggiani 1986; Gustafson 1989; Kovach *et al.* 1992; Galassi *et al.* 1996; Halfon *et al.* 1996; Swanson *et al.* 1997; Finizio *et al.* 2001; Maud *et al.* 2001; Finizio and Villa 2002; Grammatica and Di Guardo 2002; Reus *et al.* 2002; Sanchez-Bayo *et al.* 2002; Russom *et al.* 2003; Ares 2004; Padovani *et al.* 2004; Palma *et al.* 2004; De Smet *et al.* 2005; Kookana *et al.* 2005; Yazgan and Tanik 2005; Greitens and Day 2007; Juraske *et al*. 2007; Tixier *et al.* 2007; Boriani *et al*. 2010; Feola *et al.* 2011). These integrated assessment systems frequently are algorithms that weigh and combine parameters of a diverse nature (toxicity, routes, times and scenarios of exposure, persistence, bioconcentration, mobilization and transport, *etc.*).

We have developed DelAzulPestRisk, a model whose purpose is to estimate the environmental risk caused by pesticides in superficial waters as a tool that allows ranking chemicals according to the severity of their potential environmental effects (Peluso *et al.* 2012b). This risk-based model was built taking into account the toxicity of the pesticides to humans and local biota, and their persistence and bioaccumulation. Originally, the model was developed to be applied to waters of Del Azul Creek, an area of recreational use in Argentina, known to be contaminated with pesticides.

The goals of this study were to further develop the DelAzulPestRisk method and to assess the environmental risk of organoclorine pesticides in creeks of Tres Arroyos County's superficial waters (200 km distant from Del Azul Creek) by applying the model, and to discuss similarities and differences between the results with those obtained in the Del Azul study area.

METHODOLOGY

Area of Study

Tres Arroyos County is located in the southeast of Buenos Aires province, (38°22'46"S - 60°16'38"W at a central point), in the south of the Chaco Pampean Region, about 490 km distant from the capital city of Argentina. This district covers an area of 5,861km^2 and has a population of 58,179 people. It plays a very important role in the country's economy due to the large tracts of land dedicated to intensive agricultural and cattle-ranching activities (Carbone and Píccolo 2002; Carbone 2004). The main crops in the district are wheat, soybean, sunflower, and maize with 142,300, 112,700, 61,600, and 9,100 Ha sowed, respectively, according to 2011 annual campaign data (Directorate of Provincial Statistics of Buenos Aires Province 2012). These crops are all highly dependent on the use of agrochemicals.

The surface drainage network of the study area belongs to a 3,017 km^2 basin (Martinez *et al.* 2008), containing three creeks (first, second, and third branches of Tres Arroyos Creek) that flow through the city of Tres Arroyos, capital town

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of the district. Downstream from the city, these streams meet, forming a single water course (Claromecó Creek) that runs throughout the county in a north–south direction until discharged into the Argentino Sea. These water courses are typical streams of pampean plains: narrow (from 5 to 20 m), shallow (from 0.50 to 1.50 m), and slow-flowing (water flow between 0.6 to 1.6 m^3s^{-1} during low-waters, according to Martinez *et al.* (2008).

Water runoff from agricultural soils may drain into these creeks. Because many of the creeks' areas are used as bath resorts during summer, the water quality is frequently analyzed by monitoring for the presence of heavy metals and pesticides. Since hazardous substances have been detected in these waters, their health risk for recreational bathing has been estimated (Peluso *et al.* 2012a). However, this analysis by itself, did not allow a full evaluation of the water quality in a broad sense since others negative environmental effects were not considered (*e.g.*, biota toxicity, persistency, bioconcentration, mobility).

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Description of the DelAzulPestRisk Model

The algorithm, presented in Eq. (1), was based on those of the CHEM-1 model (Swanson *et al.* 1997).

$$\mathrm{ERF} = \mathrm{HHRF} + \mathrm{BHRF} \tag{1}$$

where ERF = Environmental Risk Factor; HHRF (Human Health Risk Factor) = $\sum$ risk values for chronic cancer and non-cancer effects; BHRF (Biota Health Risk Factor) = $\sum$ risk values for chronic toxicity to local representative organisms, multiplied by a Biota Amplification Factor (BAF) = $\sum$ aquatic persistence and bioconcentration potential of the pesticides. The methods used to calculate each term of the model are described in detail below.

Calculation of Human Health Risk Factor (HHRF)

Model's description

This overview is based on Peluso *et al.* (2012b). The health risk is an estimate of the likelihood that a chemical will generate cancer or non-cancer effects in exposed people (USEPA 1989). For the risk to human health, the calculation was based on the dose of exposure to the pesticides according to USEPA models. The estimation of exposure quantifies the contact dose between the substance and a human target depending on the routes of contact, scenarios, and duration of the event (USEPA 1992). The potential effect estimation to human health was performed by applying a probabilistic risk analysis for the exposure to pesticides during recreational bathing on waters of the study area (Peluso *et al.* 2012b). The risk was quantified for a 10-year-old child bather by considering two possible routes of exposure: accidental water ingestion and dermal contact. In both cases, USEPA models were used (1992, 2007), by applying Eqs. (2) and (3), respectively.

$$\mathrm{ADDI} = [\mathrm{Conc} * \mathrm{Ir} * \mathrm{EF} * \mathrm{ED}]/[\mathrm{Bw} * \mathrm{AT}] \tag{2}$$

$$\mathrm{ADDS} = [\mathrm{DAevent} * \mathrm{ESA} * \mathrm{EF} * \mathrm{ED} * \mathrm{FC}]/[\mathrm{Bw} * \mathrm{AT}] \tag{3}$$

where ADDI = Average daily dose by accidental intake (mg kg^{-1} day^{-1}); ADDS = Average daily dose by skin contact (mg kg^{-1} day^{-1}); Conc = Concentration of the

pesticide in water (mg L^{-1}); Ir = Daily water accidental intake rate (L day^{-1}); EF = Exposure frequency (days $year^{-1}$); ED = Exposure duration (year); BW = Weight of the exposed human (kg); AT = Correction factors of average time for chronic exposure (ED * 365 days for non-cancer risk estimation, 70 years * 365 days for cancer risk estimation); DAevent = Absorbed dose per event (mg cm^{-2} $event^{-1}$) calculated based on USEPA (2007); ESA = Exposed Skin Area (cm^2); FC = Correction factor for surface and volume units (10,000 cm^2 m^{-2} * 0.001 L cm^{-3}).

In the DelAzulPestRisk model, both cancer and non-cancer effects are considered. The non-cancer risk (NCR) calculation was performed based on the ratio between ADD and the chemical specific non-cancer toxicological safe dose (RfD) for the route of exposure (USEPA 1989). If the risk scores are less than 1.0, the NCR is assumed to be negligible (USEPA 1989). The cancer risk (CR) (incremental lifetime cancer risk) was calculated by multiplying ADD by the chemical-specific cancer toxicological reference value, the Slope Factor (SF), which is also specific for each exposure pathway (USEPA 1989). We assumed $1.00E^{-05}$ as the CR safe limit (Peluso *et al.* 2012a,c).

The RfDs and SFs used for accidental water intake risk calculation were obtained from the USEPA IRIS database (2012). The RfDs and SFs for dermal risk calculation were estimated based on USEPA (2007), following Eqs. (4) and (5), because chemical-specific dermal toxicity factors are not available.

$$\text{RfDderm} = \text{RfDint} * \text{ABSGi} \tag{4}$$

$$\text{SFDerm} = \text{SFint}/\text{ABSGi} \tag{5}$$

where RfDderm and SFderm: Dermal reference dose (mg kg^{-1} day^{-1}) and dermal slope factor (mg kg^{-1} $day^{-1})^{-1}$; RfDint and SFint: Intake reference dose (mg kg^{-1} day^{-1}) and intake slope factor (mg kg^{-1} $day^{-1})^{-1}$; ABSGi: Fraction of contaminant absorbed in the gastrointestinal tract (dimensionless) in the critical toxicity study.

The pesticides' RfD, SF, and ABSGi are presented in Table 1. The DelAzulPestRisk model estimated the potential effect to human health using both NCR and CR measures, as further explained.

Concentration of the hazardous substance in water

A preliminary study made between January of 2007 and February of 2011 had revealed the presence of organoclorine pesticides in waters of the three branches of the Tres Arroyos Creeks and Claromecó Creek (α, γ, and δ-hexaclorociclohexane [HCH], aldrin, heptachlor, γ-chlordane, endosulfan, endosulfan sulphate, dieldrin, and diclorodifenildicloroetane [DDD]). The complete group of pesticides was larger, but excluded those for which concentrations never exceeded the analytic detection limit. A more detailed description of the field methods for the pesticide survey of Tres Arroyos waters is available in Peluso *et al.* (2012a).

The health and biota risks were estimated probabilistically based on the probability distributions of the pesticide concentration fitted with Crystal Ball (Decisioneering 2007). Each probability distribution was truncated at the minimum and maximum values of the measured concentrations. The probability model and parameters for each pesticide concentration are available in Table 1.

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Table 1. Probability distribution models and statistics of the concentration of the pesticides; their non-cancer and cancer toxicological referential values for intake and dermal routes; fraction of contaminant absorbed in gastrointestinal tract, 95th percentile of the absorbed dose per event and their predicted non-effect concentration for the selected organisms.

								RfD[6]		SF[9]						
Substances	CAS	P. Curve	Min[1]	Max[2]	AM[3]	SD[4]	95th P[5]	Int[7]	Derm[8]	Int	Derm	ABS_{GI}[10]	95th P Dae[11]	PNEC A[12]	PNEC D[13]	PNEC C[14]
α - HCH	319–84–6	Max Extreme	6.00	2.78	6.87	3.60	1.36	3.00	3.00	6.30	6.30	1.00	1.60	2.67	2.22	2.24
			E^{-07}	E^{-05}	E^{-06}	E^{-06}	E^{-05}	E^{-04}	E^{-04}	E^{+00}	E^{+00}	E^{+00}	E^{-09}	E^{-01}	E^{-01}	E^{-01}
δ - HCH	319–86–8	Min Extreme	4.00	6.23	2.11	1.07	4.03	3.00	3.00	1.30	1.30	1.00	1.05	2.67	2.22	2.24
			E^{-08}	E^{-07}	E^{-07}	E^{-07}	E^{-07}	E^{-04}	E^{-04}	E^{+00}	E^{+00}	E^{+00}	E^{-10}	E^{-01}	E^{-01}	E^{-01}
γ - HCH	58–89–9	Pareto	5.00	2.79	8.46	1.05	8.48	3.00	3.00	1.30	1.30	1.00	8.08	2.67	2.22	2.24
			E^{-07}	E^{-06}	E^{-07}	E^{-09}	E^{-07}	E^{-04}	E^{-04}	E^{+00}	E^{+00}	E^{+00}	E^{-11}	E^{-01}	E^{-01}	E^{-01}
Aldrin	309–00–2	Log	2.00	4.94	1.67	7.34	3.05	3.00	3.00	1.70	1.70	1.00	1.55	2.96	3.00	1.60
			E^{-07}	E^{-06}	E^{-06}	E^{-07}	E^{-06}	E^{-05}	E^{-05}	E^{+01}	E^{+01}	E^{+00}	E^{-08}	E^{-03}	E^{-03}	E^{-03}
γ - chlordane	5566–34–7	Min Extreme	4.00	2.55	1.07	4.23	1.82	5.00	4.00	2.50	4.38	8.00	4.76	2.04	2.14	1.10
			E^{-07}	E^{-06}	E^{-06}	E^{-07}	E^{-06}	E^{-04}	E^{-04}	E^{-04}	E^{-01}	E^{-01}	E^{-08}	E^{-03}	E^{-03}	E^{-03}
DDD	72–54–8	Min Extreme	1.00	4.52	2.01	6.47	3.22	5.00	5.00	1.60	1.60	1.00	1.06	1.11	1.01	8.70
			E^{-07}	E^{-07}	E^{-07}	E^{-08}	E^{-07}	E^{-04}	E^{-04}	E^{+01}	E^{+01}	E^{+00}	E^{-08}	E^{-02}	E^{-02}	E^{-03}
Dieldrin	60-57-1	Beta	1.00	1.16	3.15	2.15	7.33	2.00	2.00	2.40	2.40	1.00	5.47	3.06	2.80	2.51
			E^{-06}	E^{-04}	E^{-05}	E^{-05}	E^{-05}	E^{-03}	E^{-03}	E^{-01}	E^{-01}	E^{+00}	E^{-11}	E^{-02}	E^{-02}	E^{-02}
Endosulfan	115–29–7	Min Extreme	1.00	1.47	4.84	2.44	9.17	6.00	6.00	N.A.	N.A.	1.00	3.65	1.06	1.52	1.51
			E^{-07}	E^{-06}	E^{-07}	E^{-07}	E^{-07}	E^{-03}	E^{-03}			E^{+00}	E^{-08}	E^{+00}	E^{+00}	E^{+00}

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Table 1. Probability distribution models and statistics of the concentration of the pesticides; their non-cancer and cancer toxicological referential values for intake and dermal routes; fraction of contaminant absorbed in gastrointestinal tract, 95th percentile of the absorbed dose per event and their predicted non-effect concentration for the selected organisms.*(continued)*

								RfD[6]		SF[9]						
Substances	CAS	P. Curve	Min[1]	Max[2]	AM[3]	SD[4]	95th P[5]	Int[7]	Derm[8]	Int	Derm	ABS_{GI}[10]	95[th]P Dae[11]	PNEC A[12]	PNEC D[13]	PNEC C[14]
Endosulfan sulphate	1031-07-8	Min Extreme	2.50	1.16	5.86	1.93	9.16	6.00	6.00	N.A.	N.A.	1.00	8.48	1.33	1.21	1.18
			E^{-06}	E^{-05}	E^{-06}	E^{-06}	E^{-06}	E^{-03}	E^{-03}			E^{+00}	E^{-10}	E^{-01}	E^{+00}	E^{+00}
Heptachlor	76–44–8	Min Extreme	1.17	2.81	1.63	2.95	2.16	5.00	5.00	4.50	4.50	1.00	3.82	1.53	1.64	1.60
			E^{-05}	E^{-05}	E^{-05}	E^{-06}	E^{-05}	E^{-04}	E^{-04}	E^{+00}	E^{+00}	E^{+00}	E^{-10}	E^{-01}	E^{-01}	E^{-01}

[1–5]Minimum, maximum, arithmetic mean, standard deviation, and 95th percentile, respectively, of the concentrations of the pesticides in water (mg L^{-1}); [6]reference dose (mg kg^{-1} d^{-1}); [7]intake; [8]dermal; [9]slope factor (mg kg^{-1} $d^{-1})^{-1}$; [10]fraction of contaminant absorbed in gastrointestinal tract (dimensionless); [11]95th percentile of the absorbed dose per event (mg cm^{-2} $event^{-1}$); [12–14]predicted non-effect concentration (PNEC, in mg L^{-1}) for green algae, *Daphnia sp.* and *Cyprinus carpio*, respectively.

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Other parameters in Eqs. (2) and (3)

It had previously been mentioned that the health risk was calculated by considering a 10-year-old child as a representative exposed individual during bathing. The accidental ingestion rate of water was assumed as 0.05 L per hour of the bath event duration according to USEPA (1989). The duration of the bath event (tevent, in minutes), relevant for the absorbed dose per event calculation (DAevent in Eq. (3)) and event frequency during the year (EF, common to Eqs. (2) and (3)), were probabilistically estimated based on a questionnaire administered by the authors conducted at the Del Azul bath resort during the summer of 2010–2011 (Peluso *et al.* 2012a,b,c). Although the survey was performed at 200 km from this study area, the summer climatic conditions relevant for bathing activities (temperature, wind, rain, *etc.*) are not so different between both study locations. Further, the demographic and socioeconomic characteristics of the population of Tres Arroyos city are not so different from those of Azul city. Therefore, Del Azul study results were applied due to the absence of local data.

The duration of exposure (ED, common to Eqs. (2) and (3)) was probabilistically treated, assuming a triangular probability distribution of 1 and 30 years as lower and upper limits, and 15 as mode (Peluso *et al.* 2012a,c).

The probability distribution models and their descriptive parameters of the bodyweight (BW from Eq. (2)) and body height (necessary to estimate the Exposed Skin Area) were based on Lejarraga and Orfila (1987). The exposed skin area (ESA from Eq. (3)) was calculated using the DuBois and DuBois (1916) equation, corrected by a factor called bath pattern (Eq. (6)). This factor measures the fraction of the skin surface effectively submerged in the water depending on the duration of the recreational event (Peluso *et al.* 2012a,c).

$$\mathrm{ESA} = (\mathrm{H}^{0.725*}\mathrm{BW}^{0.425*}0.007184) * \mathrm{BP} \tag{6}$$

where ESA: Exposed skin area (cm^2); H: Body height (cm); BW: Bodyweight (kg); BP: Bath pattern (dimensionless). Parameters related to the bath event and exposed skin area (tevent, EF, ED, H, BW, and BP) are presented in Table 2.

The absorbed dose per event (DAevent from Eq. (3)) was estimated based on a steady state approach from USEPA that calculates the absorbed dose through the skin according to a substance's concentration, the permeability of the stratum corneum, and the duration of the recreational event (USEPA 2007). A detailed description of the application of this method is available in Peluso *et al.* (2012a,c). The 95th percentiles (95thP) of the absorbed dose per event of each substance are presented in Table 1.

Aggregated human health risk estimation

The ADDI and ADDS calculations were made by applying Monte Carlo for simple random sampling for 5000 trials using Crystal Ball 7.1 software (Decisioneering 2007). Although the accidental ingestion and dermal contact risk models were described separately, NCR and CR were calculated for each substance for both contact ways simultaneously. This aggregated health risk was calculated using an additive model (USEPA 1989, 2007), as shown in Eqs. (7) and (8). As was stated by USEPA, this is a valid approach for health risk assessments of initial prospecting, or as

Table 2. Probability distribution model and descriptive statistics of the parameters inputs to ADD calculation: Duration of the bath event, frequency of bathing days, bodyweight, height and surface, bath pattern, and exposed skin area.

Param	Fitted Distributions	Min	Max	AM	SD	95th P	Others	
t_{event} [1]	Min[2] Extreme	0.00	30.00 E^{+01}	18.81 E^{+01}	25.38	27.77 E^{+01}	Like[3] 21.82 E^{+01}	Sc[4] 62.24
EF[5]	Gamma	0.00	54.00	19.91	14.34	47.59	Loc[6] 0.11	Sc 34.58
ED[7]	Triang[8]	1.00	30.00	15.00				
BW[9]	Normal	23.50	44.50	33.56	5.00	41.72		
H[10]	Normal	125.00	149.00	136.00	5.00	145.00		
BSA[11]	Normal	91.79 E^{+02}	13.34 E^{+03}	11.26 E^{+03}	72.59 E^{+01}	12.40 E^{+03}		
BP[12]	Triang	0.07	1.00	0.49	0.19	0.83	Mo[13] 0.40	
ESA[14]	Beta	83.84 E^{+01}	12.01 E^{+03}	55.26 E^{+02}	22.17 E^{+02}	94.35 E^{+03}	α 2.36	β 3.95

[1]Duration of the bath event (min); [2]minimum extreme; [3]likeliest; [4]scale; [5]exposure frequency (days years^{-1}); [6]location; [7]exposure duration (years); [8]triangular; [9]bodyweight (kg); [10]body height (cm); [11]body skin area (cm^2); [12]bath pattern (dimensionless); [13]mode; [14]exposed skin area (cm^2).

a screening model (USEPA 1989, 2007). This methodology also justified in the case when data on the toxicology of the mixture, or similar condition, are unavailable (Mumtaz *et al*. 2007).

$$\text{NCRAggr} = \text{ADDI}/\text{RfDint} + \text{ADDS}/\text{RfDint} \quad (7)$$

$$\text{CRAggr} = \text{ADDI} * \text{SFint} + \text{ADDS} * \text{SFderm} \quad (8)$$

where NCRAggr = Non-cancer aggregated risk (dimensionless); CRAggr = Cancer aggregated risk (dimensionless).

The addition procedure was conducted iteration by iteration; consequently, the output was a new probabilistic distribution of aggregated risk values, on which descriptive statistics were calculated for subsequent analysis.

The DelAzulPestRisk model estimated the potential effects to human health from each pesticide as the addition of the probabilistic NC aggregated risk and the ratio between the probabilistic distribution of CRAggr and the CR safe criteria, as shown in Eq. (9).

$$\text{HHRF} = \text{NCRAggr} + \text{CRAggr}/\text{CRSL} \quad (9)$$

where HHRF = Human Health Risk Factor (dimensionless); CRSL = Cancer risk safe limit (dimensionless). The limit of significance for HHRF was set at 1.

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Calculation of Biota Health Risk Factor (BHRF)

This description is based on Peluso *et al.* (2012b). DelAzulPestRisk estimates the risk to biota as in Eq. (10).

$$\mathrm{BHRF} = \mathrm{BR} * \mathrm{BAF} \tag{10}$$

where BHRF = Biota health risk factor; BR = Biota risk; BAF = Biota aggravating factor. BHRF, BR, and BAF are dimensionless.

The Biota Risk is measured as the ratio between a pesticide's concentration in water and the toxicological safe threshold for the selected organism. These are representatives of the local aquatic biota. The Toxicity Exposure Ratio (Finizio *et al.* 2001), is often also referred to as the ratio between the Predicted Environmental Concentration and the Predicted Non-Effect Concentration or PEC/PNEC (USEPA 2004). If PEC/PNEC <1, no toxic effects are expected to occur in the organism. The PEC values used were the probabilistic pesticide concentrations and the PNEC values were the chronic NOEC (No Observable Effects Concentration) toxicity value. Due to the wide variability in experimental data on toxicity, the NOEC was estimated as the acute LC50 or EC50 (which are the concentrations that causes mortality or the maximum biological response to 50% of the exposed organisms in the toxicological test, respectively). LC50 and EC50 were obtained with ECOSAR software (USEPA 2011a), which uses the structure–activity relationship (SAR) to predict the aquatic toxicity of a substance based on its structural similarity to related substances for which toxicity data exist (USEPA 2011a). Although experimental toxicity data are preferable to SAR data, the availability of experimental data is limited. On the other hand, SAR methodology is recognized as a valid tool for analysis, interpretation, and visualization of heterogeneous datasets from various sources (Wang *et al.* 2012) and that can be used in risk assessments (Eriksson *et al.* 2003). The acute to chronic toxicity ratio (ACR) was applied for estimating the chronic NOECs from the acute LC50 or EC50. This procedure is extensively used to estimate the chronic toxicity of chemicals for which acute exposure toxicity data are available but for chronic exposure are either limited or absent (Raimondo *et al.* 2007).

The groups of organisms used as representatives of freshwater biota in the study area were: green algae, Chlorophyta Chlorophyceae (in 96 hs EC50 toxicity test); *Daphnia sp.*, "Water fleas," Arthropoda Crustacea, (in 48 hs LC50 toxicity test); and *Cyprinus carpio*, "Common carp," Chordata Actinopteyigii (in 96 hs LC50 toxicity test). These organisms were selected because of their presence in the waters of the study area. The ACR values used were 5.4, 7.0, and 10 for green algae, *Daphnia sp.*, and *Cyprinus sp.*, respectively, and were extracted from Ahlers *et al.* (2006). The PNECs of the pesticides are presented in Table 1.

The risk of potential toxic effects on biota was estimated as the addition of the ratio PEC/PNEC for these three organisms, as presented in Eq. (11)

$$\mathrm{BR} = \mathrm{PEC/PNECA} + \mathrm{PEC/PNECD} + \mathrm{PEC/PNECC} \tag{11}$$

where BR = Biota risk; PEC = Predicted environmental concentration (mg L^{-1}); PNECA = Predicted non-effect concentration for green algae; PNECD = PNEC for *Daphnia sp.*; PNECC = PNEC for *Cyprinus carpio*. The unit of PNEC is mg L^{-1}.

The addition procedure was conducted iteration by iteration obtaining as output a distribution of biota risk values on which descriptive statistics were calculated for later analysis. The limit of significance for BR was set at 1.

Estimation of Biota Amplification Factor (BAF)

This description is based on Peluso *et al.* (2012b). BAF plays the role of enhancer of the potential effects of the pesticides on the biota, as could be appreciated in Eq. (10). This factor responds to Eq. (12).

$$\text{BAF} = \text{Persistence} + \text{Bioconcentration} \tag{12}$$

The persistence was estimated as a single parameter by applying EPISUITE 4.1 (USEPA 2011b). This digital tool has different calculation modules in which, from the identification of the molecule and the amount of substance released into the environment, were estimated to be the mass percentage share based on the fugacity (Mackay and Paterson 1981, 1991; Mackay *et al.* 1996a,b), and also the half-life in different environmental compartments, based on a calculation module called BIOWIN. This model estimates the probability of rapid aerobic and anaerobic biodegradation of the compound in the presence of mixed populations of environmental microorganisms (Boethling and Sabljic 1989; Boethling *et al.* 2004). This calculation module scales the results of half-life in each compartment as a series of decreasing values depending on their duration. This would be approximately: 1 (half-life measured in years), 2 (in months), 3 (in weeks), 4 (in days), and 5 (in hours). Since the half-life results are obtained on a decreasing scale of severity (the higher the value, the lower the potential environmental impact), the scale had to be reversed to fulfill their role as "enhancer." This was done according to Eq. (13), where half-life is the value calculated with EPISUITE for the aquatic compartment, and measured in hs.

$$\text{Persistence} = 5 - \text{Half-Life} \tag{13}$$

The bioconcentration potential (BCF) was also estimated as the log BCF (in L kg^{-1}) by the BCFBAF module of EPISUITE, which estimates BCF of an organic compound using the compound's log octanol-water partition coefficient (Kow), as presented in Eq. (14), based on Meylan *et al.* (1999).

$$\text{LogBCF} = 0.66 \log \text{Kow} - 0.33 + \text{Correction} \tag{14}$$

Thus, BAF was set as Eq. (15).

$$\text{BAF} = (5 - \text{Half-Life/UCF1}) + \log \text{BCF/UCF2} \tag{15}$$

where UCF1 = Unit conversion factor 1, equal to 1 hs; UCF2 = Unit conversion factor 2, equal to 1 L^{-1}. BAF is dimensionless. Given the role that BAF plays in the model we have decided to disregard the units, only considering the absolute values making it a biota risk multiplier. The maximum value of persistence is 5, and 5 is an extreme value for log BCF. BAF; in situations of high persistence and high BCF, could increase up to 10 times the risk to biota. However, BAF will only be applied when BR $\geq$ 1. When BR $<$ 1, BAF = 1.

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Estimation of Environmental Risk Factor (ERF)

As can be appreciated in Eq. (1), ERF was estimated by the addition of HHRF and BHRF, a procedure conducted iteration by iteration. The limit of significance for ERF was set at 1. USEPA stated for human health risk that if the value is higher than the significance limit means that adverse health effects are more likely to occur, and some remedial action is needed (USEPA 1989). ERF and the other risk estimations also act as indicators about whether the effects are likely to occur; in other words, whether the pesticides present in the aquatic environment could generate environmental damage, for human or for biota.

Statistical Analysis

All simple statistical calculations such as means, standard deviations, 95th percentiles (95thP), minimums, and maximums were estimated using Crystal Ball (Decisioneering 2007), as outputs of the Monte Carlo procedure. To determine whether the risk scores of the most environmentally risky substances were statistically different, we applied the Kruskal-Wallis test. This method tests the difference between the arithmetic means of three or more independent non-normal subgroups (nonparametric test). The null hypothesis is that the mean ranks of the k groups will not significantly differ. In our study, p-values $< .05$ were considered to indicate a significant difference between the compared subgroups. This analysis was conducted using Statistica 7.0 (Statsoft 2004).

Sensitivity Analysis

This analysis allows knowing which parameter generates the highest uncertainty in the results based on estimating the contribution of each of them to the variance of the probabilistic results. This estimation calculates the rank correlation coefficients between every parameter of the model and the results while the simulation is running. This procedure was performed using Crystal Ball 7.1. (Decisioneering 2007), and performed on the probabilistic distribution of ERF of the most risky pesticide to know the contributions of HHRF and BHRF and, subsequently, it was applied to the majority of them to test their components contributions.

RESULTS

Tres Arroyos Study Area

Shown in Tables 3 and 4 are the results for each pesticide's HHRF, NCR, and CR. Dieldrin presented the highest values of NCRAggr and CRAggr/CSFL, showing the greatest human health risk, both for accidental intake and for dermal contact. In neither case did the aggregated risk reach the significance risk level (1.0), even when considering the maximum of the probabilistic distribution of the risk values (dieldrin NCRAggr max: $1.00E^{-02}$; CRAggr/CSFL max: $7.29E^{-01}$). The maximum value of the probabilistic distribution of HHRF was $7.61E^{-01}$, which is quite close to the CRAggr/CSFL result. While it is true that this risk score was very close to the limit of significance established, it must be acknowledged that the maximum value of a probabilistic distribution of risk is extremely conservative. If the analysis of the

Table 3. Probabilistic results of non-cancer human health risk for accidental intake, dermal and aggregated pathways of exposure.

Substances	NCR[1] Int				NCR Derm				NCR Aggr[2]			
	AM	SD	Max	95th P	AM	SD	Max	95th P	AM	SD	Max	95thP
α - HCH	5.72 E^{-06}	6.41 E^{-06}	6.27 E^{-05}	1.86 E^{-05}	2.25 E^{-05}	2.62 E^{-05}	2.93 E^{-04}	7.45 E^{-05}	2.82 E^{-05}	3.19 E^{-05}	3.40 E^{-04}	9.17 E^{-05}
δ - HCH	1.71 E^{-07}	1.93 E^{-07}	1.56 E^{-06}	5.59 E^{-07}	1.13 E^{-06}	1.31 E^{-06}	1.30 E^{-05}	3.68 E^{-06}	1.30 E^{-06}	1.48 E^{-06}	1.44 E^{-05}	4.21 E^{-06}
γ - HCH	6.98 E^{-07}	6.26 E^{-07}	3.46 E^{-06}	1.96 E^{-06}	2.42 E^{-06}	2.26 E^{-06}	1.43 E^{-05}	6.99 E^{-06}	3.12 E^{-06}	2.80 E^{-06}	1.67 E^{-05}	8.76 E^{-06}
Aldrin	1.40 E^{-05}	1.51 E^{-05}	1.39 E^{-04}	4.32 E^{-05}	2.33 E^{-03}	2.55 E^{-03}	2.47 E^{-02}	7.45 E^{-03}	2.35 E^{-03}	2.56 E^{-03}	2.48 E^{-02}	7.49 E^{-03}
γ - chlordane	5.24 E^{-07}	5.50 E^{-07}	4.06 E^{-06}	1.68 E^{-06}	1.25 E^{-04}	1.38 E^{-04}	1.16 E^{-03}	4.08 E^{-04}	1.25 E^{-04}	1.39 E^{-04}	1.16 E^{-03}	4.09 E^{-04}
DDD	2.49 E^{-08}	2.47 E^{-08}	2.31 E^{-07}	7.46 E^{-08}	2.15 E^{-06}	2.22 E^{-06}	1.89 E^{-05}	6.47 E^{-06}	2.17 E^{-06}	2.24 E^{-06}	1.91 E^{-05}	6.54 E^{-06}
Dieldrin	1.57 E^{-04}	1.98 E^{-04}	1.58 E^{-03}	5.49 E^{-04}	2.60 E^{-03}	3.44 E^{-03}	3.17 E^{-02}	9.51 E^{-03}	2.76 E^{-03}	3.61 E^{-03}	3.29 E^{-02}	1.00 E^{-02}
Endosulfan	1.93 E^{-08}	2.13 E^{-08}	1.59 E^{-07}	6.31 E^{-08}	3.74 E^{-08}	4.32 E^{-08}	3.54 E^{-07}	1.21 E^{-07}	5.67 E^{-08}	6.25 E^{-08}	5.03 E^{-07}	1.78 E^{-07}
Endosulfan sulphate	2.38 E^{-07}	2.39 E^{-07}	1.78 E^{-06}	7.36 E^{-07}	3.21 E^{-07}	3.36 E^{-07}	2.95 E^{-06}	9.90 E^{-07}	5.59 E^{-07}	5.54 E^{-07}	4.42 E^{-06}	1.65 E^{-06}
Heptachlor	8.10 E^{-06}	7.55 E^{-06}	4.68 E^{-05}	2.38 E^{-05}	5.57 E^{-04}	5.36 E^{-04}	3.72 E^{-03}	1.65 E^{-03}	5.65 E^{-04}	5.43 E^{-04}	3.76 E^{-03}	1.67 E^{-03}

[1]Non-cancer risk (dimensionless); [2]aggregated.

risk results was made based on the 95thP in a semi-conservative approach, which is more adequate for management purposes, the results were much lower compared to the maximum (95thP of HHRF of dieldrin: 1.88E^{-01}). Aldrin posed the second highest risk values (HHRF max: 2.80E^{-01}; 95thP: 9.63E^{-02}), followed by heptachlor (HHRF max: 2.77E^{-01}; 95thP: 9.19E^{-02}).

It is interesting to point out that the pesticides had higher values generated by cancer risk (measured as the ratio to the limit value of 1.00E^{-05}) than by non-cancer risk, and by dermal contact in respect to the accidental intake exposure pathway.

It can be appreciated from Table 5 that dieldrin and aldrin also posed the highest values of 95thP of BR but almost two orders of magnitude lower than the 95thP value of HHRF (7.87E^{-03} vs. 1.96E^{-01} and 4.13E^{-03} vs. 1.04E^{-01} for dieldrin and aldrin, respectively). Further, the 95thP of BR for chlordane (the third largest BR value) was slightly higher than that of HHRF (3.35E^{-03} vs. 2.10E^{-03}). Endosulfan and endosulfan sulphate also generated slightly higher biota risk than those for human health. When the risk is considered by organism of BR, it can be appreciated that each 95thP risk value was around 2 to 3 E^{-03} for dieldrin and 1 to 2 E^{-03} for aldrin. In other words, the three risk components of BR were not so different between them and their addition only slightly increased the BR value.

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Table 4. Probabilistic results of cancer human health risk for accidental intake, dermal and aggregated pathways of exposure, and of the Human Health Risk Factor.

Substances	CR/CRSL[1] Int				CR/CRSL Derm				CR/CRSL Aggr				HHRF[2]			
	AM	SD	Max	95th P	AM	SD	Max	95th P	AM	SD	Max	95th P	AM	SD	Max	95th P
α - HCH	2.37 E^{-04}	3.00 E^{-04}	2.86 E^{-03}	8.12 E^{-04}	9.31 E^{-04}	1.21 E^{-03}	1.29 E^{-02}	3.28 E^{-03}	1.17 E^{-03}	1.48 E^{-03}	1.55 E^{-02}	4.04 E^{-03}	1.20 E^{-03}	1.50 E^{-03}	1.57 E^{-02}	4.13 E^{-03}
δ - HCH	1.46 E^{-06}	1.88 E^{-06}	2.03 E^{-05}	5.25 E^{-06}	9.61 E^{-06}	1.25 E^{-05}	1.32 E^{-04}	3.46 E^{-05}	1.11 E^{-05}	1.42 E^{-05}	1.48 E^{-04}	3.91 E^{-05}	1.24 E^{-05}	1.55 E^{-05}	1.59 E^{-04}	4.30 E^{-05}
γ - HCH	5.98 E^{-06}	6.20 E^{-06}	4.36 E^{-05}	1.87 E^{-05}	2.07 E^{-05}	2.22 E^{-05}	1.72 E^{-04}	6.57 E^{-05}	2.67 E^{-05}	2.77 E^{-05}	2.09 E^{-04}	8.27 E^{-05}	2.98 E^{-05}	3.02 E^{-05}	2.22 E^{-04}	9.04 E^{-05}
Aldrin	1.57 E^{-04}	1.89 E^{-04}	1.94 E^{-03}	5.34 E^{-04}	2.60 E^{-02}	3.14 E^{-02}	2.48 E^{-01}	8.91 E^{-02}	2.62 E^{-02}	3.15 E^{-02}	2.49 E^{-01}	8.97 E^{-02}	2.86 E^{-02}	3.38 E^{-02}	2.80 E^{-01}	9.63 E^{-02}
γ - chlordane	2.02 E^{-06}	2.42 E^{-06}	1.90 E^{-05}	7.00 E^{-06}	4.80 E^{-04}	6.06 E^{-04}	5.39 E^{-03}	1.69 E^{-03}	4.82 E^{-04}	6.08 E^{-04}	5.41 E^{-03}	1.70 E^{-03}	6.07 E^{-04}	7.35 E^{-04}	6.57 E^{-03}	2.10 E^{-03}
DDD	2.62 E^{-07}	2.96 E^{-07}	2.67 E^{-06}	8.59 E^{-07}	2.26 E^{-05}	2.67 E^{-05}	3.08 E^{-04}	7.57 E^{-05}	2.29 E^{-05}	2.70 E^{-05}	3.10 E^{-04}	7.65 E^{-05}	2.50 E^{-05}	2.90 E^{-05}	3.26 E^{-04}	8.23 E^{-05}
Dieldrin	2.72 E^{-03}	3.78 E^{-03}	3.48 E^{-02}	1.00 E^{-02}	4.53 E^{-02}	6.61 E^{-02}	6.99 E^{-01}	1.70 E^{-01}	4.81 E^{-02}	6.94 E^{-02}	7.29 E^{-01}	1.80 E^{-01}	5.08 E^{-02}	7.27 E^{-02}	7.61 E^{-01}	1.88 E^{-01}
Endosulfan													5.67 E^{-08}	6.25 E^{-08}	5.03 E^{-07}	1.78 E^{-07}
Endosulfan sulphate													5.59 E^{-07}	5.54 E^{-07}	4.42 E^{-06}	1.65 E^{-06}
Heptachlor	4.00 E^{-04}	4.30 E^{-04}	3.19 E^{-03}	1.30 E^{-03}	2.75 E^{-02}	3.04 E^{-02}	2.71 E^{-01}	8.92 E^{-02}	2.79 E^{-02}	3.08 E^{-02}	2.74 E^{-01}	9.05 E^{-02}	2.85 E^{-02}	3.13 E^{-02}	2.77 E^{-01}	9.19 E^{-02}

[1]Cancer risk/cancer risk safe level (dimensionless); [2]Human Health Risk Factor (dimensionless).

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Table 5. Probabilistic results of PEC/PNEC ratios for green algae, *Daphnia sp.* and *Cyprinus carpio*, and for the biota risk.

Substances	PEC/PNECA[1]				PEC/PNECD[2]				PEC/PNECC[3]				BR[4]			
	AM	SD	Max	95th P	AM	SD	Max	95th P	AM	SD	Max	95th P	AM	SD	Max	95th P
α - HCH	2.57 E^{-05}	1.36 E^{-05}	9.73 E^{-05}	5.13 E^{-05}	3.09 E^{-05}	1.63 E^{-05}	1.17 E^{-04}	6.17 E^{-05}	3.07 E^{-05}	1.62 E^{-05}	1.16 E^{-04}	6.13 E^{-05}	8.73 E^{-05}	4.61 E^{-05}	3.30 E^{-04}	1.74 E^{-04}
δ - HCH	8.00 E^{-07}	4.04 E^{-07}	2.25 E^{-06}	1.52 E^{-06}	9.62 E^{-07}	4.85 E^{-07}	2.70 E^{-06}	1.82 E^{-06}	9.56 E^{-07}	4.82 E^{-07}	2.69 E^{-06}	1.81 E^{-06}	2.72 E^{-06}	1.37 E^{-06}	7.64 E^{-06}	5.15 E^{-06}
γ - HCH	3.16 E^{-06}	3.98 E^{-09}	3.20 E^{-06}	3.17 E^{-06}	3.80 E^{-06}	4.78 E^{-09}	3.85 E^{-06}	3.81 E^{-06}	3.78 E^{-06}	4.75 E^{-09}	3.82 E^{-06}	3.79 E^{-06}	1.07 E^{-05}	1.35 E^{-08}	1.09 E^{-05}	1.08 E^{-05}
Aldrin	5.68 E^{-04}	2.56 E^{-04}	1.65 E^{-03}	1.07 E^{-03}	5.61 E^{-04}	2.53 E^{-04}	1.63 E^{-03}	1.06 E^{-03}	1.05 E^{-03}	4.75 E^{-04}	3.06 E^{-03}	1.99 E^{-03}	2.18 E^{-03}	9.84 E^{-04}	6.35 E^{-03}	4.13 E^{-03}
γ - chlordane	5.17 E^{-04}	2.05 E^{-04}	1.24 E^{-03}	8.80 E^{-04}	4.92 E^{-04}	1.95 E^{-04}	1.18 E^{-03}	8.37 E^{-04}	9.58 E^{-04}	3.80 E^{-04}	2.30 E^{-03}	1.63 E^{-03}	1.97 E^{-03}	7.79 E^{-04}	4.71 E^{-03}	3.35 E^{-03}
DDD	1.80 E^{-05}	5.70 E^{-06}	3.80 E^{-05}	2.83 E^{-05}	1.97 E^{-05}	6.25 E^{-06}	4.16 E^{-05}	3.10 E^{-05}	2.30 E^{-05}	7.28 E^{-06}	4.85 E^{-05}	3.61 E^{-05}	6.08 E^{-05}	1.92 E^{-05}	1.28 E^{-04}	9.54 E^{-05}
Dieldrin	1.04 E^{-03}	7.07 E^{-04}	3.75 E^{-03}	2.38 E^{-03}	1.14 E^{-03}	7.71 E^{-04}	4.09 E^{-03}	2.59 E^{-03}	1.27 E^{-03}	8.60 E^{-04}	4.56 E^{-03}	2.89 E^{-03}	3.45 E^{-03}	2.34 E^{-03}	1.24 E^{-02}	7.87 E^{-03}
Endosulfan	4.48 E^{-07}	2.24 E^{-07}	1.31 E^{-06}	8.51 E^{-07}	3.12 E^{-07}	1.56 E^{-07}	9.14 E^{-07}	5.93 E^{-07}	3.14 E^{-07}	1.57 E^{-07}	9.17 E^{-07}	5.95 E^{-07}	1.07 E^{-06}	5.37 E^{-07}	3.14 E^{-06}	2.04 E^{-06}
Endosulfan sulphate	4.38 E^{-05}	1.48 E^{-05}	8.64 E^{-05}	6.92 E^{-05}	4.80 E^{-06}	1.62 E^{-06}	9.47 E^{-06}	7.58 E^{-06}	4.95 E^{-06}	1.67 E^{-06}	9.76 E^{-06}	7.81 E^{-06}	5.36 E^{-05}	1.81 E^{-05}	1.06 E^{-04}	8.46 E^{-05}
Heptachlor	1.07 E^{-04}	1.92 E^{-05}	1.75 E^{-04}	1.41 E^{-04}	9.95 E^{-05}	1.79 E^{-05}	1.63 E^{-04}	1.32 E^{-04}	1.02 E^{-04}	1.84 E^{-05}	1.68 E^{-04}	1.35 E^{-04}	3.08 E^{-04}	5.56 E^{-05}	5.06 E^{-04}	4.08 E^{-04}

[1–3]Predicted environmental concentration/predicted non-effect concentrations for green algae, *Daphnia sp.* and *Cyprinus carpio* (dimensionless); [4]biota risk (dimensionless).

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Dieldrin had a high value of BAF (7.47), the fourth in importance, after chlordane (9.06), aldrin (8.24), and heptachlor (7.75), as is shown in Table 6. However, since no pesticide presented a BR value higher than 1, BAF was considered equal to 1, meaning that it does not play a role as an enhancer of the biota risk (BHRF = BR).

As stated above, due to the differences between the highest values of HHRF compared to those of BHRF, the ERF values were very close to HHRF. This means that no pesticide reaches the significance risk level, even considering the maximum of the probabilistic distribution of the risk results. According to Table 6 dieldrin presented the highest ERF value, close to 1 but only for the maximum value of the risk results (ERF max: $7.70E^{-01}$; 95thP: $1.95E^{-01}$). Obviously, aldrin and heptachlor had the second and third highest H+BHF values (ERF max: $2.77E^{-01}$ and $2.74E^{-01}$; 95thP: $9.93E^{-02}$ and $9.22E^{-02}$, respectively). Despite the similarity of the statistical parameters of the probabilistic results of these substances, the Kruskall-Wallis test was applied to test the statistical significance of the differences between them. According to this analysis, dieldrin, aldrin, and heptachlor ERF results were significantly different. For aldrin-heptachlor comparison, despite the similarity between them, the Kruskall-Wallis p-value was $2.4E^{-5}$, very much lower than the significance level of $p < .05$.

The results of the sensitivity analysis, carried out on dieldrin's ERF, indicated the importance of each probabilistic parameter on the results, measured as their contribution to the variance. Shown in Table 6 is the percentage of the contribution of HHRF and BHRF to their variance. It is clear that HHRF generated the major contribution (more than 80%). Analyzing the percentage of the contribution of the main exposure parameters of HHRF to their variance, the frequency of exposure and the concentration of dieldrin together explained more than 80% of the whole variance.

Comparison of Tres Arroyos vs. Del Azul Results

No pesticide substance would produce health effects in the Tres Arroyos human population, not even considering cancer or non-cancer effects, which had already been evidenced by Peluso *et al.* (2012a). The original DelAzulPestRisk application tested the environmental risk generated by pesticides in Azul County freshwaters, obtaining the same outcome. Although the organochlorine pesticides are not strictly the same between both studies, 8 of the 10 match. As well, dieldrín and DDD were undetectable in Del Azul waters, β-HCH was in those of Tres Arroyos.

According to the 95thP of the probability distribution of the HHRF results, aldrin and heptachlor, second and third most dangerous substances in this study, had higher values with regard to those of Azul County: almost 30 and 1.5 times, respectively. Chlordane also generated higher human risk than in Del Azul (almost 5 times higher), but for the remaining pesticides, the situation was reversed. α-HCH, the organochlorine pesticide with higher HHRF value in the Del Azul study, was almost 10 times higher than in Tres Arroyos.

As in the Tres Arroyos study, in Azul freshwaters the BHRF was much lower than the HHRF. But, in this case, the difference between HHRF and BHRF for the highest HHRF pesticide was almost 600 times. Aldrin was the highest BHRF of the organochlorine pesticides of Azul, but was 7 times lower than in Tres Arroyos.

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Table 6. Probabilistic results of the biota amplification factor and components and of the environmental risk factor. Percentage contributions from HHRF and BHRF to the variance of ERF, and from HHRF parameters to their variance.

Substances	BAF[1]			ERF[2]				cvHHRF[3]				
	Per[4]	Log BCF[5]	BAF	AM	SD	Max	95th P	EF[6]	Con[6]	BP[8]	Tev[9]	Oth[10]
α - HCH	3.48 E^{+00}	2.40 E^{+00}	5.88 E^{+00}	1.29 E^{-03}	1.52 E^{-03}	1.59 E^{-02}	4.24 E^{-03}					
δ - HCH	3.48 E^{+00}	2.40 E^{+00}	5.88 E^{+00}	1.50 E^{-05}	1.61 E^{-05}	1.65 E^{-04}	4.67 E^{-05}					
γ - HCH	3.48 E^{+00}	2.40 E^{+00}	5.88 E^{+00}	4.06 E^{-05}	3.02 E^{-05}	2.32 E^{-04}	1.01 E^{-04}					
Aldrin	4.28 E^{+00}	3.96 E^{+00}	8.24 E^{+00}	3.07 E^{-02}	3.42 E^{-02}	2.77 E^{-01}	9.93 E^{-02}					
γ - Chlordane	4.94 E^{+00}	4.12 E^{+00}	9.06 E^{+00}	2.57 E^{-03}	1.25 E^{-03}	9.94 E^{-03}	4.94 E^{-03}					
DDD	3.35 E^{+00}	3.64 E^{+00}	6.99 E^{+00}	8.61 E^{-05}	3.92 E^{-05}	4.26 E^{-04}	1.58 E^{-04}					
Dieldrin	4.33 E^{+00}	3.14 E^{+00}	7.47 E^{+00}	5.43 E^{-02}	7.38 E^{-02}	7.70 E^{-01}	1.95 E^{-01}	46.6	37.70	6.30	1.40	8.00
Endosulfan	4.38 E^{+00}	2.19 E^{+00}	6.57 E^{+00}	1.13 E^{-06}	5.69 E^{-07}	3.35 E^{-06}	2.13 E^{-06}					
Endosulfan Sulphate	4.41 E^{+00}	2.08 E^{+00}	6.49 E^{+00}	5.37 E^{-05}	1.81 E^{-05}	1.07 E^{-04}	8.51 E^{-05}					
Heptachlor	4.47 E^{+00}	3.28 E^{+00}	7.75 E^{+00}	2.88 E^{-02}	3.13 E^{-02}	2.74 E^{-01}	9.22 E^{-02}					
cvHHRF[11]						83.00						
cvBHRF[12]						16.90						

[1]Biota Amplification Factor (dimensionless); [2]Environmental Risk Factor (dimensionless); [3]percentage of the contribution of the exposure parameters to the variance of HHRF; [4]persistence value (measured as 5 – half-life (hs.)); [5]log of bioconcentration potential (L kg^{-1}); [6]frequency of exposure; [7]pesticide concentration; [8]bath pattern; [9]duration of the event of bath; [10]others; [11] and [12]percentage of the contribution of HHRF and BHRF to the variance of ERF.

Comparing both studies, the most risky organochlorine pesticide according to H+BHRF results was almost 5 times higher in Tres Arroyos than in Azul ($1.95E^{-01}$ vs. $4.34E^{-02}$). Although not applicable in both studies, it can be mentioned that BAF for dieldrin was 1.27 times higher than for α-HCH.

Beyond the results from this comparison, it is clear that the DelAzulPestRisk model allows setting up differences in the environmental conditions based on the list of the pesticides present in each study area and their concentrations. The model identifies the level of the severity of the potential environmental effects, pointing out which pesticides generate the worst condition.

DISCUSSION

DelAzulPestRisk is a risk-based model that allows assessing the potential effects on an aquatic ecosystem based on toxicological, ecotoxicological, and physico-chemical properties of the pesticides. As with other models (Swanson *et al.* 1997; Boriani *et al.* 2010), DelAzulPestRisk was built in integrated modules. We wanted to develop a tool that would allow providing a screening view of the likelihood of potential environmental effects on an aquatic environment in an integrated and broad approach; in other words, to be used as a comprehensive warning system of the pollution caused by toxic substances in freshwaters.

The DelAzulPestRisk model, while close in its overall structure to those of Swanson *et al.* (1997), differs in how it estimates the human or the biota risk and is therefore more similar to those of Boriani *et al.* (2010), which calculate both types of risks using specific risk assessment methodologies. Other aspects related with the risk estimation were further discussed below.

Estimating the human risks as was done by applying this model implies accepting uncertainty and variability, which play a significant role on the results. Beyond the analysis of the roles of the variability and uncertainty of each parameter of the model, Peluso *et al.* (2012a,c) commented about several sources of uncertainty remaining in our studies. But the uncertainty and variability increases in the case of a tool whose purpose is to assess the risk to the biota. Obviously three organisms do not represents the whole aquatic biota in the study area. Further, the availability of experimental toxicity data is uneven (toxicity experimental data are limited or absent; when available, there is a great variability among the organisms tested and toxicity endpoints, *etc.*). This is the reason that led us to build the Biota Health Risk Factor based on toxicological data of only three species, and using QSAR toxicity data rather than experimental data, prioritising the comparability of the results in the context of a tool for screening purposes. With increased availability of experimental toxicity data, the model could adopt them easily. In addition, it would be interesting to incorporate new trophic levels into the algorithm to become more biota comprehensive (*e.g.*, microorganisms, other invertebrates, macrophytes, aquatic amphibians, reptiles, birds, and mammals).

The "Biota Amplification Factor" of the DelAzulPestRisk model is comparable to the "Exposure Factors" of the CHEMS-1 model (Swanson *et al.* 1997) or to the "Environmental Fate and Transport Index" of the ERICA model (Boriani *et al.* 2010). The persistence and bioconcentration potential of the pesticides were included frequently in the models (*e.g.*, Finizio *et al.* 2001; Sanchez-Bayo *et al.* 2002; Swanson

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et al. 2007, Boriani *et al.* 2010). The mobility or transport of the substances, on the other hand, is less frequent (*e.g.*, Sanchez-Bayo *et al.* 2002; Ares 2004; Padovani *et al.* 2004; Kookana *et al.* 2005). We discarded all aspects related with pesticide mobility because we focus on the potential environmental effects *in situ*. For this reason the point of departure of DelAzulPestRisk is the concentration of the pesticides measured in the water for which the quality we are attempting to assess.

To develop the best integrated index entails facing up to how to include and weigh a wide range of environmental parameters to achieve a balance between the large amount of information and the real possibilities of obtaining it (Levitan 1995, 1997). Due to the cost and time required to achieve it, many chemical ranking methodologies are screening assessments that, at least, allow providing fairly immediate preliminary answers (Swanson *et al.* 1997; Finizio *et al.* 2001; Padovani *et al.* 2004; De Smet *et al.* 2005). The DelAzulPestRisk algorithm was built trying to depend on a limited number of variables for which such data were available and updatable.

Furthermore, there are two important requirements for a chemicals ranking system: it should give information about the real risk of a substance and it should give separate scores for different environmental effects (Padovani *et al.* 2004). Related to the first issue, the most frequent approaches of a chemical ranking system in literature tend to ignore a fundamental parameter to estimate the risk: the amount of substance present in the environment compartment, for example, the substance's concentration (Peluso *et al.* 2012b). In the cases where it is considered, this parameter is very often estimated indirectly by models of fugacity (Sanchez-Bayo *et al.* 2002; Ares 2004; Padovani *et al.* 2004); or models based on the amounts of substances released into the environment (Swanson *et al.* 1997; Finizio *et al.* 2001; De Smet *et al.* 2005; Yazgan and Tanik 2005), or on transport models (Padovani *et al.* 2004; Kookana *et al.* 2005). Without this parameter, it is impossible to delineate directly the exposure, and thus, the analysis does not reflect the risk generated by the substances, but their hazard (MacKay *et al.* 2001). This approach results in outputs with less power for the decision-makers (Peluso *et al.* 2012b). The literature states that it is desirable to estimate the "risk" within the meaning of "technical concept of risk"; that is, considering the potential extent of damage (Maud *et al.* 2001) according to the local conditions. This cannot be done with a chemical ranking system based on the threat of the substances based only on molecular characteristics. The DelAzulPestRisk model is a risk-based chemicals ranking model that allows estimating the exposure to the hazardous substances directly, not indirectly from data of emissions to the environment and transport models (Peluso *et al.* 2012b). In addition, to the uncertainties inherent in estimation models (of which the DelAzulPestRisk model is not exempt as was stated early) should be added uncertainties about the use of pesticides (formulations, emission rates, *etc.*). This information is not easily obtained locally in developing countries such as Argentina, as highlighted by Feola *et al.* (2011) in his study on the selection of an index to be applied in Colombia (Peluso *et al.* 2012b). However, comparative analysis systems based on risk usually focus either only on the human risk (Ares 2004) or on ecotoxicological risk (Palma *et al.* 2004). As in few other models (Boriani *et al.* 2010) DelAzulPestRisk focuses on both in an integrated manner and based on local conditions.

However, it should be clarified that the final output offered by the DelAzulPestRisk model cannot be considered a formal measurement of risk but an indication of it.

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The model integrates variables that are genuine risk measures (those obtained for human and biological modules) with others that are not (the half-life and the bioaccumulation potential). That makes the model not a true "risk" model but a "risk-based" one (Peluso *et al.* 2012b). In other words, the ERF value warns whether the pesticides present in the aquatic environment could generate an environmental damage, for humans or for biota, according to the conditions and exposure scenarios tested. Furthermore, an ERF value greater than 1 does not imply that the environmental damage really occur; but only points to the possibility of its occurrence. DelAzulPestRisk, then, acts as a warning system that may justify further studies more detailed on the aquatic environment (Peluso *et al.* 2012b).

The way that the DelAzulPestRisk model was built allows fulfilling the second remark of Padovani *et al.* (2004), which states that a requirement of a chemicals ranking system is to provide separate scores for different environmental effects. The modular structure of the model allows an analysis of the effects by environmental compartments (human, biota), by environmental behavior of the substances (persistence, bioaccumulation), or by their overall environmental risk.

The model was validated only by a comparison between two applications of the model. However, we agree with Reuss *et al.* (2002, p. 186) with the need for validation. However, "this kind of validation is extremely complicated and can only be carried out if indicators produce output that can be measured in the field," which is not the case for the DelAzulPestRisk model. For this reason, we consider essential, as stated by Reuss (2002, p. 186), "make the calculations behind an indicator transparent and subject to expert judgment and peer review." That is what we are pursuing with this work.

Maud *et al.* (2001, p. 72) present a list of the desirable characteristic of a chemical ranking system. Briefly, these are: use available data; be simple; be transparent; do not include contentious weighting schemes; have a large potential range of scores that allow clear differentiation between products; explicitly exclude risk to humans and concentrate on risk to the environment; be more analogous to the technical concept of risk. Although the simplicity of our method could be discussed (particularly with respect to the probabilistic analysis), DelAzulPestRisk is a practical, accessible, and updateable tool that respects most of the listed desirable characteristics.

The environmental agencies of Argentina do not possess adequate tools to assess the potential effects of the pesticides in freshwaters. Consequently, although DelAzulPestRisk is also a screening method as many of those cited in this paper, it should allow environmental managers to count with an integrated view of the environmental risks that the pesticides or other toxic chemicals could generate. On the other hand, the system could allow estimating the limit concentrations of substances that would present a threat to bathers or aquatic organisms, and that could be used as an early warning system (Peluso *et al.* 2012b).

CONCLUSIONS

DelAzulPestRisk is a risk-based chemical ranking model based on human and local biota toxicity that estimates the potential environmental effects of pesticides in aquatic environments. The model was applied on creeks of Tres Arroyos County,

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Argentina, in which waters were detected organochlorine pesticides (α, γ y δ-HCH, aldrin, heptachlor, γ-chlordane, endosulfan, endosulfan sulphate, dieldrin, and DDD).

Dieldrin, aldrin, and heptachlor generated the worst potential environmental effects, although they did not reach the risk threshold. The human health risk module produced the higher values, mainly due to the cancer and non-cancer dermal health risk. Dieldrin, aldrin, and chlordane were the three main biota-risky pesticides, but with values almost two orders of magnitude lower than those of human health risk. Although was not applied, Dieldrin had a high value of the biota amplification factor, remaining the fourth in importance.

The DelAzulPestRisk model can highlight differences in the severity of the environmental conditions based on the list of the pesticides present in each water body, their concentrations, their human and biota toxicities, and their persistence and potential for bioconcentration. Based on models from the literature, we took into account most of the characteristics listed as "desirables" for a chemical ranking system according the literature.

In summary, the DelAzulPestRisk model provides a screening tool to the environmental managers that can generate an integral view of the environmental risk caused by hazardous substances allowing their ranking and prioritization.

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