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Health Risk by Chlorinated Pesticides in Water Bodies Used for Recreational Bathing in Argentina

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1. Introduction

The Buenos Aires province, located in Central Eastern Argentina, has an area of 307,571 km², which represents more than 10% of the total surface of the country. It is the province with the largest population (14 million inhabitants, according to Provincial Direction of Statistics, 2010) and accounts for 35 % of the Gross Domestic Product of the country.

The province is one of the main agricultural producers of the country, representing 40 % of the national production (MAA, 2004). The most prominent crops are: soybean, with 3.7x10⁶ Ha sowed; wheat, with 2.9x10⁶ Ha, sunflower with 1.1x10⁶ Ha, and maize, with 0.8x10⁶ Ha, according to the 2005/2006 harvest figures (Provincial Direction of Statistics, 2010).

These volumes are the result of a process of agriculturization started in the 1970s and 1980s, in which, the expansion of the agricultural frontier, the conversion of grassland into agricultural lands, and the bigger technification of the activity, brought about an increasing usage of input, mainly herbicides and insecticides (Pengue, 2000; Pengue, 2001). Considering the whole Argentinian territory, soybean is the crop with the greatest surface increase, from barely 37,700 Ha in 1970 (Pengue, 2001), to more than 16x10⁶ Ha in 2005 (ISAAA, 2010).

The increase in the use of pesticides (from 73 to 236 million kilograms between 1995 and 2005, according to CASAFE (2007)) triggered arguments on the environmental impacts of this productive process. Stemming from this, many studies have revealed the presence of biocides in the environment in different compartments of Argentina: water environments (Zubillaga et al., 1987, Janiot et al., 1994, Loewy et al., 1999, Menone et al., 2000, 2001, Rovedatti et al., 2001, Miglioranza et al., 2004, Jergentz et al., 2005, Silva et al., 2005, Marino & Ronco, 2005, Peruzzo et al., 2008, Arias et al., 2010), soils (Miglioranza et al., 1999, 2002, 2003a, 2003b, Peruzzo et al., 2008, Gómez et al., 2009), biota, (Miglioranza et al., 1999,

Menone et al., 2000, 2006, Cataldo et al., 2001, Jergentz et al., 2004, Andrade et al., 2005, De la Torre et al., 2005, Martín & Ronco, 2006, Cid et al., 2007, Carriquiriborde et al., 2007, Jofré et al., 2008), humans (García Fernández, 1974, Muñoz de Toro et al., 2006), and agricultural or stockbreeding products (Lenardón et al., 1994, Maitre et al., 1994, Loewy et al., 2003, Ruíz et al., 2008).

The protection of the population from pesticides in Argentina is based on several national regulations (FARN, 2005), both general with implicit references to pesticides, and specific with explicit references to pesticides. One example of a general regulation is the amendment in 1994 of the 41th article of the National Constitution, establishing the right to all inhabitants to enjoy a healthy environment. Another example is Law 25675/2002, or General Law of the Environment, which established the minimal requirements to accomplish sustainable and adequate management of the environment, assuring preservation, conservation, recovery, and improvement of the quality of environmental resources (Congress of Argentina, 2002).

More specific regulations related to the protection from pesticides include Law 18284, or National Food Code (National Government of Argentina, 1969) and Regulatory Decree 2126 (National Government of Argentina, 1971). This decree established the conditions under which the production and sale of food products are authorized, determining the highest allowed concentrations of pesticide residues in food (FARN, 2005). These regulations, which are under constant revision, stipulate that all elaborated, fractioned, conserved, transported, distributed or displayed food, spices, beverages, their raw materials or food additives must comply with these requirements.

The aforementioned Code, in chapter VII, establishes the requisite characteristics for drinking water (ANMAT, 2010). Pesticides are listed in a group of substances labeled as "organic contaminants":

Aldrin + Dieldrin, max.: 0.03 $\mu\text{g L}^{-1}$;

Chlordane, max.: 0.30 $\mu\text{g L}^{-1}$;

DDT (Total + Isomers), max.: 1.00 $\mu\text{g L}^{-1}$;

Heptachlor + Heptachloroepoxide, max.: 0.10 $\mu\text{g L}^{-1}$;

Lindane, max.: 3.00 $\mu\text{g L}^{-1}$;

Metoxichlor, max.: 30.0 $\mu\text{g L}^{-1}$;

2,4 D, max.: 100 $\mu\text{g L}^{-1}$;

Metil Parathion, max.: 7 $\mu\text{g L}^{-1}$;

Parathion, max.: 35 $\mu\text{g L}^{-1}$;

Malathion, max.: 35 $\mu\text{g L}^{-1}$;

A bad quality of recreational water is associated with the possibility of contracting pulmonary, sensory organs (eyes, ears), skin and, particularly, gastrointestinal diseases. Among these diseases, the latter (vomits, diarrhea, nauseas) are the most studied as regards water quality and the presence of indicator bacteria which cause such diseases. Prüss (1998) analyzed 22 scientific papers which studied the causal relationship between gastrointestinal symptoms and recreational water quality evaluated from the concentrations of indicator bacteria. In 19 papers, a strong statistical association was verified. WHO (1998), in *Guidelines for Safe Recreational-water Environments: Coastal and Freshwaters* described the impact of water quality on recreational use, placing special stress on fecal contamination with pathogenic microorganisms. Subsequently, general evaluation and monitoring guidelines of the microbiological quality of recreational water were established through the *Annapolis Protocol*

(WHO, 1999). Moreover, 2 chapters were specifically dedicated to the methodology of evaluation of water microbiological quality in *Monitoring Bathing Waters - A Practical Guide to the Design and Implementation of Assessments and Monitoring Programmes* (WHO, 2000). The bacteriological recounts as indicators of recreational water quality have a preferential place when analyzing bathing waters.

Regarding chemical contamination of waters that can be used with recreational purposes, WHO (1998) explains that the occurrence of health risk is much less likely. However, the risk must not be minimized and, hence, bathers' health must be ensured, though how to achieve this is not mentioned. In some cases, the guidelines of quality evaluation of drinking water can be used as evaluation tools, as explained in *WHO Guidelines for drinking-water Quality* (2008).

In Argentina, water quality of superficial aquatic environments with recreational usage and direct contact is evaluated following the *National Guide Levels for Water Quality for Human Recreation*, written by the National Undersecretary of Hydrological Resources (NUHR, 2007). However, only microbiological parameters are established as quality guidelines.

Several projects funded by different Argentinian governmental agencies conducted, among other activities, monitoring of water bodies of the Buenos Aires Province, analyzing for the presence of pesticides among other substances. Given the fact that pesticides have been detected in water, and that the monitored water bodies could potentially be or are currently used with recreational purposes, it is necessary to evaluate the danger of using such water bodies for the formerly mentioned activities since there are no adequate management tools in the environmental legal framework of Argentina. The objective of the hereby work is to evaluate this danger employing Health Risk Analysis (HRA) as a way to replace the lack of other analytical tools.

HRA are management tools that allow establishing, based on the available scientific information, if the chemical substances with particular toxic characteristics present in an environment represent a threat for people's health in accordance with the way in which the exposure to such substances is conducted (NRC, 1983). The risk, according to the USEPA model, is a function of the toxicity of the hazardous substance and the magnitude of the exposure to it, being the latter a measure of the "quality and quantity" of the contact between the substance and the exposed organism (USEPA, 1989, 1992a). The exposure quantifies the relationship between the causal agent of the risk and an organism taking into account contact pathways, scenarios, and time exposure (USEPA, 1992a). The use of HRA for the analysis of bathing waters has few antecedents in Argentina (for example Peluso et al., 2009, 2010), and they have not been recognized in any legal framework as a management tool.

2. Experimental methods and procedures

2.1 Description of the study area

Different investigation projects, whose area of study involves the Buenos Aires province, focus their attention on the quality of water resources and have conducted pesticide monitoring. The following can be mentioned:

Tools for the Sustainable Management of the Water Resources in a Plain Basin (ANPCyT, 2005), which conducted 5 pesticide monitorings at Del Azul creek between January 2005 and December 2007; Monitoring of Organochlorine Pollutants in Buenos Aires Shallow Lakes: Assessment of the Impact on the Ichthyofauna. Implications and Perspectives of

Management (CONICET, 2005), which conducted 4 series of sampling per shallow lake between July 2005 and July 2008 (the shallow lakes were: La Barrancosa, La Salada, El Chifle, San Antonio, Del Estado, Quilla Lauquén, El Paraíso, La Brava, De los Padres, La Peregrina, El Carpincho, Blanca Chica, La Sirena y Monte); Development of Criteria and Guidelines for the Management of Water Resources in Plain Areas (ANPCyT, 2007) which, between January 2008 and July 2010, conducted 5 series of sampling in the 1st, 2nd and 3rd branches of Tres Arroyos creek, Claromecó, Cristiano Muerto, and Quequén Salado creeks. These projects provided information on the presence of organochlorine pesticides used as basis for the risk analysis applied in this work. Figure 1 presents the geographic location of the analyzed environments.

All these water bodies are located in agricultural areas where pesticides are applied to a greater or lesser extent. Table 1 presents a list of the water bodies, indicating the county of the province where they are located, and the surface and sowed area for the four most important crops (soybean, wheat, maize, and sunflower).

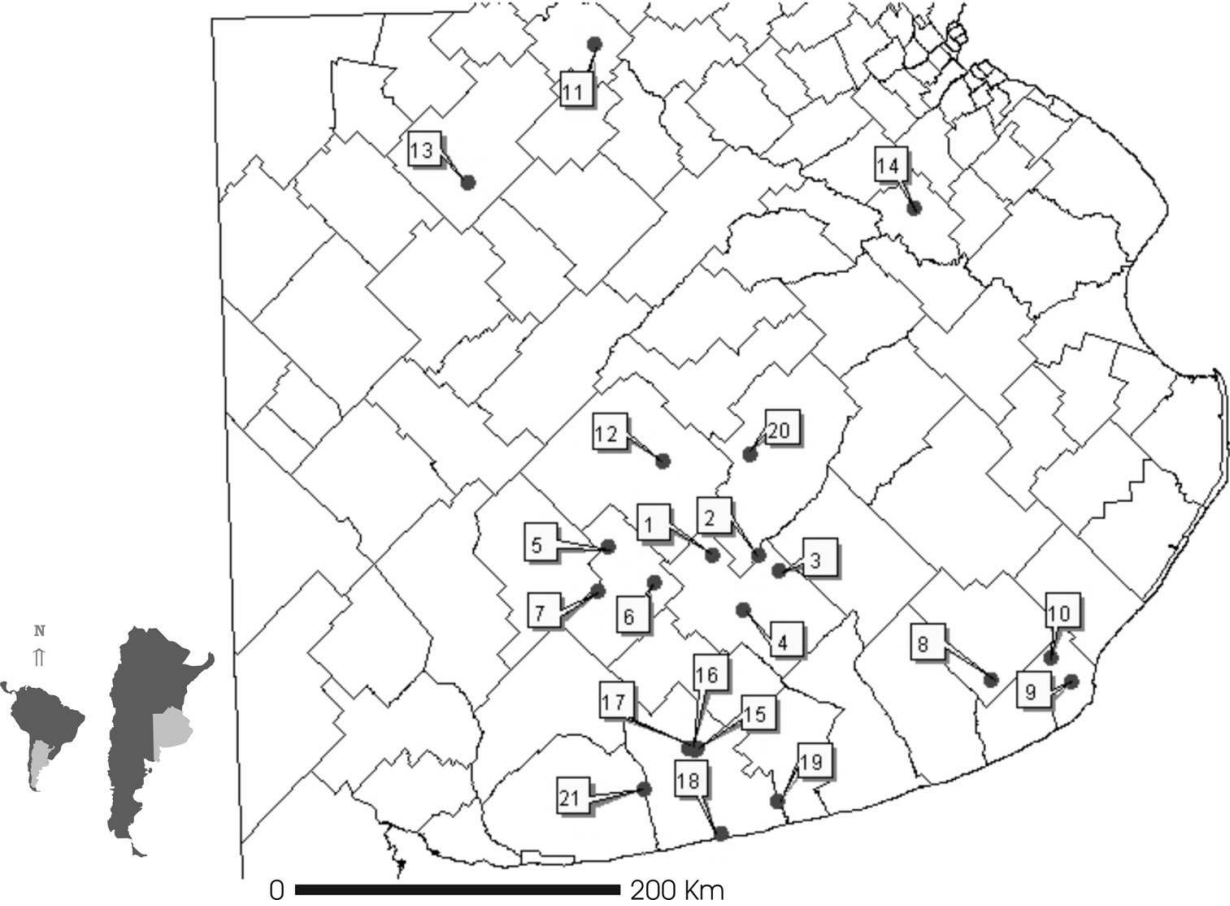


Fig. 1. Geographical location of studied water bodies

Water body	County	County area (in Km ²)	Area sowed by county (2006-2007) (in Ha) based in CITAB (2010)			
			Soybean	Wheat	Sunflower	Maize
La Brava SL	Balcarce	4120	40000	70600	25500	11500
El Chifle SL	Benito Juárez	5285	47600	45000	15500	7000
La Barrancosa SL	Benito Juárez					
La Salada SL	Benito Juárez					
San Antonio SL	Benito Juárez	5772	106500	33360	3000	18900
La Sirena SL	Lincoln					
De los Padres SL	General Pueyrredón	1460	16700	22000	5500	3800
La Peregrina SL	General Pueyrredón					
El Carpincho SL	Junín	2260	107900	20500	500	25000
Del Estado SL	Laprida	3440	16000	13000	4000	4000
El Paraiso SL	Laprida					
Quilla Lauquen SL	Laprida					
Monte SL	Monte	1890	18600	6000	700	6000
Blanca Chica SL	Olavarría	7715	69000	15500	5000	10000
Del Azul C	Azul	6615	71000	57000	12000	13000
Quequén Salado C	Coronel Dorrego	5818	56500	191690	58000	6500
Cristiano Muerto C	San Cayetano	3004	41400	112430	70000	7500
1st branch of Tres Arroyos C	Tres Arroyos	5861	97000	228450	150000	12000
2nd branch of Tres Arroyos C	Tres Arroyos					
3rd branch of Tres Arroyos C	Tres Arroyos					
Claromecó C	Tres Arroyos					

Table 1. Studied water bodies indicating the county of location in the province and its area. Moreover, sowed surfaces of soybean, wheat, sunflower and maize are presented. References: SL: shallow lake, C: creek.

2.2 Concentration of hazardous substances in water

The different studies mentioned before were planned so as to obtain spatial and temporal representative water samples according to prefixed objectives in each project. In all cases, sampling consisted of taking one or more representative water samples, obtained by means of mixing a group of subsurface subsamples from different points in the water bodies. The samples were collected according to standard techniques for the analytical determinations to

be carried out (amber glass bottles with internal Teflon tops) and they were refrigerated (4-8 ° C) until analysis, which was carried out in a private laboratory certified by the application authority in environmental issues from the Buenos Aires Province (Reg. 017 Res. 640/02 of the *Provincial Organism for Sustainable Development*. Table 2 presents the substances, their abbreviations for this work, their identification codes according to the Chemical Abstract Service (CAS, 2010) and the applied analytical technique and limit of detection for their determination.

Pesticide	Abbreviation	CAS	Techn. Code	Detect. Lim.
Hexachloro Ciclo Hexane, alpha isomer	α - HCH	319-84-6	EPA SW 846 M 8081	6.00E-07
Hexachloro Ciclo Hexane, gamma isomer	γ - HCH	58-89-9	EPA SW 846 M 8081	5.00E-07
Hexachloro Ciclo Hexane, delta isomer	δ - HCH	319-86-8	EPA SW 846 M 8081	4.00E-08
Chlordane, gamma isomer	γ - Clor	57-74-9	EPA SW 846 M 8081	4.00E-07
Acetochlor	Acet.	34256-82-1	EPA 3510	1.00E-04
Aldrin	Aldr.	309-00-2	EPA SW 846 M 8081	2.00E-07
dichlorodi- phenyldichloroethane (4,4'-DDD)	DDD	72-54-8	EPA SW 846 M 8081	1.00E-07
Dichlorodiphenyltrichloroethane (4,4'-DDT)	DDT	50-29-3	EPA SW 846 M 8081	8.80E-06
Endosulfan, alpha isomer	α - Endo.	959-98-8	EPA SW 846 M 8081	1.00E-07
Endosulfan, beta isomer	β - Endo.	33213-65-9	EPA SW 846 M 8081	9.00E-07
Endosulfan Sulfate	Endo.Sul.	1031-07-8	EPA SW 846 M 8081	2.50E-06
Endrin	Endr.	72-20-8	EPA SW 846 M 8081	5.00E-07
Heptachlor	Hept.	76-44-8	EPA SW 846 M 8081	4.50E-06

Table 2. Pesticides present in the water bodies, their abbreviation, their CAS numbers, and the applied analytical technique and limit of detection for their determination.

Table 3 displays the average concentration, measured in mg L⁻¹. Although USEPA advises utilizing the corrected arithmetic mean as a representative parameter of a reasonably maximum level of exposure (upper confidence limit of the arithmetic mean, whose abbreviation is UCL) (USEPA, 1989, 1992b, 2002a), the arithmetic mean was used due to the extremely limited amount of data, which did not allow appropriate calculation of the UCL.

2.3 Health risk analysis model (HRA)

In this study, the exposure to pesticides through bathing was only based on accidental water intake and skin contact, given the fact that inhalation of substances that may generate vapor was considered irrelevant.

HRA estimation through these two pathways of exposure was carried out using USEPA models. Chronic exposure to a hazardous substance by accidental intake and skin contact was calculated using Eq. 1 and 2, respectively. Each variable, except for substance concentration, was treated probabilistically.

$$\text{ADDI} = [C * \text{Ir} * \text{ET} * \text{EF} * \text{ED}] / [\text{Bw} * \text{AT}] \quad (1)$$

$$\text{ADDC} = [\text{DA}_{\text{event}} * \text{SA} * \text{ET} * \text{EF} * \text{ED} * \text{FC}] / [\text{Bw} * \text{AT}] \quad (2)$$

Where

ADDI = Average Daily Dose by Accidental Intake ($\text{mg kg}^{-1} \text{ day}^{-1}$)

C = Concentration of the hazardous substance in water (mg L^{-1})

Ir = Daily water intake rate (L day^{-1})

ET = Daily duration of exposure (hour day^{-1})

EF = Annual Exposure frequency (day year^{-1})

ED = Exposure duration (year)

Bw = Weight of the exposed individual (kg)

AT = Correction factors by means of average time ($\text{ED} * 365$ days for non carcinogenic substances; Statistic life expectancy (70) $* 365$ days for carcinogenic substances)

ADDS = Average Daily Dose by means of Skin Contact ($\text{mg kg}^{-1} \text{ day}^{-1}$)

DA_{event} = Absorbed dose per event ($\text{mg cm}^{-2} \text{ event}^{-1}$)

SA = Skin contact Area with water (cm^2)

FC = Correction factor of surface and volume units ($10,000 \text{ cm}^2 \text{ m}^{-2} * 0.001 \text{ L cm}^{-3}$)

The absorbed dose per event (DA_{event}) is estimated in base to a steady state approach from USEPA (2007), applying Eq. 3.

$$\text{DA}_{\text{event}} = 2 * \text{FA} * \text{Kp} * \text{C} * (6 * \tau * t_{\text{event}}) / \pi)^{-0.5} \quad (3)$$

where

DA_{event} = Absorbed dose per event ($\text{mg cm}^{-2} \text{ event}^{-1}$)

FA = Fraction absorbed (dimensionless): is the net fraction available for absorption in the stratum corneum after exposure has ended (USEPA 2007).

Kp = Dermal permeability coefficient of the substance in water (cm hr^{-1}), estimated in base to the molecular weight (Mw, in gr) and the coefficient of octanol-water partition (Kow, dimensionless), as shown in Eq. 4 (USEPA 2007). Table 4 show the Kp used in dermal risk calculation.

$$\text{Log Kp} = -2.80 + 0.66 \log \text{Kow} - 0.0061 \text{Mw} \quad (4)$$

C = Concentration of the hazardous substance in water (mg L^{-1})

τ = Lag time per event (hr event^{-1})

t_{event} = Event duration (hr event^{-1})

Risk calculation for substances of non carcinogenic toxic effects (NCE) by pathway of exposure was conducted using the quotient of the value of ADD in contrast with a specific

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
α - HCH	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	5.00 E ⁻⁰⁶	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	1.47 E ⁻⁰⁵	5.30 E ⁻⁰⁶	9.70 E ⁻⁰⁶	1.73 E ⁻⁰⁵	1.80 E ⁻⁰⁶	2.40 E ⁻⁰⁵	2.80 E ⁻⁰⁶	5.50 E ⁻⁰⁶
γ - HCH	7.30 E ⁻⁰⁷	2.50 E ⁻⁰⁷	2.50 E ⁻⁰⁷	1.10 E ⁻⁰⁶	2.50 E ⁻⁰⁷	2.50 E ⁻⁰⁷	2.50 E ⁻⁰⁷	2.50 E ⁻⁰⁷	2.50 E ⁻⁰⁷	2.80 E ⁻⁰⁶	2.50 E ⁻⁰⁷	2.50 E ⁻⁰⁷	7.00 E ⁻⁰⁷	8.00 E ⁻⁰⁷	7.50 E ⁻⁰⁷
δ - HCH	1.50 E ⁻⁰⁹	1.50 E ⁻⁰⁹	1.50 E ⁻⁰⁶	1.50 E ⁻⁰⁹	1.50 E ⁻⁰⁹	1.50 E ⁻⁰⁹	1.50 E ⁻⁰⁹	6.00 E ⁻⁰⁷	3.00 E ⁻⁰⁷	1.50 E ⁻⁰⁹	1.25 E ⁻⁰⁵	5.20 E ⁻⁰⁶	1.50 E ⁻⁰⁹	1.50 E ⁻⁰⁹	2.00 E ⁻⁰⁹
γ - Clor.	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	5.00 E ⁻⁰⁸	2.00 E ⁻⁰⁹
Acet	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸	1.50 E ⁻⁰⁸
Aldr.	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.90 E ⁻⁰⁶	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	1.00 E ⁻⁰⁹
DDD	5.00 E ⁻⁰⁹	3.50 E ⁻⁰⁶	1.50 E ⁻⁰⁶	1.60 E ⁻⁰⁶	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹
DDT	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	1.66 E ⁻⁰⁵	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷	2.59 E ⁻⁰⁷
α - Endo	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	3.00 E ⁻⁰⁷	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	4.60 E ⁻⁰⁶	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹	1.04 E ⁻⁰⁵	5.00 E ⁻⁰⁹	5.00 E ⁻⁰⁹
β - Endo	2.30 E ⁻⁰⁶	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	8.80 E ⁻⁰⁶	2.30 E ⁻⁰⁶	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷	4.50 E ⁻⁰⁷
Endo Sul.	5.70 E ⁻⁰⁸	5.70 E ⁻⁰⁸	5.70 E ⁻⁰⁸	5.70 E ⁻⁰⁸	5.70 E ⁻⁰⁸	5.70 E ⁻⁰⁸	5.70 E ⁻⁰⁸	8.10 E ⁻⁰⁶	3.20 E ⁻⁰⁶	5.70 E ⁻⁰⁸	9.20 E ⁻⁰⁶	3.30 E ⁻⁰⁶	5.70 E ⁻⁰⁸	6.30 E ⁻⁰⁶	1.20 E ⁻⁰⁹
Endr	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	7.00 E ⁻⁰⁷	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.00 E ⁻⁰⁸	2.20 E ⁻⁰⁶	2.00 E ⁻⁰⁹
Hept	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶	2.25 E ⁻⁰⁶

Table 3. Concentrations (in mg L⁻¹) of pesticides in the studied water bodies. References for the pesticides: see Table 2. References for water bodies: 1- La Barrancosa SL, 2- La Salada SL, 3- El Chifle SL, 4- San Antonio SL, 5- Del Estado SL, 6- Quilla Lauquén SL, 7- El Paraíso SL, 8- La Brava SL , 9- De los Padres SL, 10- La Peregrina SL, 11- El Carpincho SL, 12- Blanca Chica SL, 13- La Sirena SL, 14- Monte SL, 15- 1st branch Tres Arroyos creek, 16- 2nd branch Tres Arroyos creek, 17- 3rd branch Tres Arroyos creek, 18- Claromecó creek, 19- Cristiano Muerto creek, 20- Del Azul creek, 21- Quequén Salado creek

reference dose for such route, being the value under which there are no toxicological effects on the exposed individual: risk quotient R (USEPA, 1992 a). The Reference Dose (RfD) (USEPA, 1992a) was used as threshold dose. If R exceeds the unit value, it is considered to be a potential adverse health effect over the exposed population.

For risk calculation for substances with carcinogenic toxic effects (CE), the exposure was also estimated in the light of the ADDI or ADDS, though the duration of the exposure in the AT correction factor was 70 years. Risk calculation was conducted from the product of each ADD multiplied by a referential toxicological value, utilizing for that purpose the Slope Factor SF (USEPA, 1996), also particular for each route of exposure. In fact, this methodology calculates the excess of individual risk due to cancer assuming a linear relationship between the exposure concentrations and the carcinogenic effects. Such method was applied by USEPA (1996, 2005).

Pesticides	Kp
α - HCH	2.97E-02
γ - HCH	2.97E-02
δ - HCH	2.97E-02
γ - Clor.	1.57E-01
Acet	6.10E-03
Aldr.	4.67E-01
DDD	4.00E-01
DDT	1.06E+00
α - Endo	3.29E-03
β - Endo	3.29E-03
Endo Sul.	3.29E-03
Endr	4.45E-02
Hept	2.16E-01

Table 4. Coefficients of Skin Permeability (Kp) for the different pesticides.

References for the pesticides: see Table 2.

In Argentina, the maximum accepted individual risk value due to exposure to CE substances in drinking water is 10E-5. This limit is established in the local guideline levels of water quality for human consumption (Goransky and Natale, 1996; SRHN, 2010). No criterion is available on the accepted limits for NCE, for which it is assumed the unit as reference value.

The aggregated and cumulative risks (for simultaneous exposure to the same hazardous substance through different pathways of contact and for simultaneous exposure to different substances, respectively) were calculated using an additive model into a Risk Index, which was used by USEPA for screening HRA (USEPA, 1992a; 2001a; 2003).

2.4 Model parameters

From the group of analyzed water bodies, two subgroups can be distinguished: water bodies visited throughout the year given their proximity to populated centres (the creeks),

and the less visited ones, whose main attraction is sport fishing are not normally near populated centres (the shallow lakes). Following this division, it could be distinguished:

a. An exposure scenario of a *recreational residential* type, which is defined by a larger quantity of annual contact episodes, and by a longer daily duration, given the proximity to the residence location of the exposed population. The annual usage frequency is mainly defined by temperature, and it is usually carried out in bathing resorts. As a representative user for this environment, a 10-year-old child was chosen. The parameters used to define the exposure (morphometric characteristics, frequency and duration of contact) are displayed in Table 5, along with the information source. The estimation of the body surface was conducted applying the DuBois & DuBois (1916) formula, as shown in Eq. 5, using weight and height for the age of the selected individual.

$$SC = H^{0.725} * P^{0.425} * 0.007184$$

(5)

Where:
SC: body surface (m²)
H: height (cm)
P: weight (kg)

Parameter	Det-Prob	Type of P. curve	Min	Max	AM	SD	Source
Ir (L h ⁻¹)	Det		0,05				USEPA, 1989
ET (h)	Prob	Triangular	0.5	2	1		self judgment
EF (d a ⁻¹)		Beta	0.82	45.71	20.7	11.07	Peluso et al., 2006
ED (a)		Triangular	1	30	15		self judgment
BW (kg)		Normal	24	44	32	3.33	Lejarraga & Orfila, 1987
Height (m)		Normal	1.25	1.48	1.36	0.04	Lejarraga & Orfila, 1987
SA (m ²)		Normal	0.93	1.28	1.10	0.05	Estimated in the light of DuBois & DuBois, 1916

Table 5. Parameters of exposure for the *recreational residential* scenario. References: Det-Prob. Deterministic or Probabilistic; Min: minimum; Max: maximum; AM: Arithmetic Mean; SD: Standard Deviation. Source: source of information.

Given the fact that it is assumed that the bather would have full water contact, the SC value was the one that was utilized as a replacement of SA in equation 2.

b. A *rural fishing* scenario, with a visit pattern of more sporadic annual visits, of lesser daily duration, and which requires some means of transportation to the location. In this case, although temperature is important, it is not usually a determinant of attendance to the site. Conversely, the attendance will be conditioned by the fishing opportunities that the location may offer. Sport fishing in Argentinian Pampean lakes is an activity that attracts fishermen throughout the year. In winter, the focus is set on silverside fishing (*Odontesthes bonariensis*), and in winter, on wolf fish (*Hoplias malabaricus*), silver catfish (*Rhamdia quelen*), and carps (*Cyprinus carpio*) (Grosman, 2006). The amount of sport fishermen is estimated at 1,125,000 in the Buenos Aires province alone (Lopez et al., 2001). As representative of the exposed individual in this scenario, a 60-year-old adult was chosen. In Table 6, the parameters of this exposure scenario are shown.

The frequency of exposure derives from sociological studies of a fishery in El Carpincho, where the annual attendance rates were determined (Grosman & Benito, 2004). Based on these, the frequencies of use, only for the summer (three months), were calculated, being the probabilities those presented in Table 7.

The duration of the exposure was obtained based on the amount of years in sport fishing in the location (data obtained from Grosman and Benito (2004)). Based on the group of values of this work, the best fitted curve of distribution of frequencies with Crystal Ball (Decisionnering, 2007) was tested and the descriptive parameters were obtained.

Body weight values were derived from the study of De Girolami et al., (2003) based on body mass index (BMI), extracting weight and height corresponding to the 60-year-old stratum of BMI. Subsequently, using weight and height for such age range, the body surface based on the DuBois & DuBois formula was estimated, applying Eq. 5. Following the criteria used for the other exposure scenario, SC replaces SA in Eq. 2.

Parameter	Det-Prob	Type of P. curve	Min	Max	AM	SD	Source
Ir (L h ⁻¹)	Det		0.05				USEPA, 1989
ET (h)	Prob	Triangular	0.5	1	0.75		self judgment
EF (d a ⁻¹)		Uniform	1.00	12.00	5.51	4.07	Grosman & Benito, 2004
ED (a)		Gamma	5.46	54.99	29.33	11.46	Estimated in the light of Grosman & Benito, 2004
BW (kg)		Normal	58.96	141.1	83.27	17.76	Estimated in the light of De Girolami et al., 2003
Height (m)		Normal	1.56	1.85	1.72	0.05	Estimated in the light of De Girolami et al., 2003
SA (m ²)		Normal	1.59	2.51	1.98	0.15	Estimated in the light of DuBois & DuBois, 1916

Table 6. Parameters of exposure for the rural fishing scenario. References: Det-Prob. Deterministic or Probabilistic; Min: minimum; Max: maximum; AM: Arithmetic Mean; SD: Standard Deviation. Source: information source.

FAP (events a ⁻¹)	P
1	0.09
2	0.04
3	0.49
6	0.11
12	0.26

Table 7. Probability (P) of annual frequencies of visits with sport fishing purposes for the summer in El Carpincho shallow lake (based on Grosman & Benito, 2004).

2.5 Calculation of risk level and usage of the toxicological reference value

Risk was calculated first by substance and by pathway of exposure. Secondly, risk was calculated for all substances and both routes of exposure simultaneously, applying an additive

model. The calculation, both for NCE and CE, was conducted with Crystal Ball 7.1 (Decisioneering, 2007), applying Monte Carlo for 5,000 repetitions (USEPA, 2001b) on the basis of the types of the distribution of probabilities of each variable. Table 8 shows the toxicological referentials for both NCE (RfDs) and CE (SFs) by oral intake and by skin contact, coming from the Integrated Risk Information System (IRIS) database of USEPA (2010). From the probabilistic distributions of risk values in each case, the arithmetic mean, the standard deviation, the maximum value, and the 95 percentile were calculated.

Pesticides	RfD int	RfDskin	SFint	SFskin
α - HCH	3.00E-04	2.91E-04	6.30E+00	6.49E+00
γ - HCH	3.00E-04	2.91E-04	6.30E+00	1.98E+00
δ - HCH	3.00E-04	2.91E-04	1.30E+00	1.34E+00
γ - Clor.	5.00E-04	2.50E-04	3.50E-01	7.00E-01
Acet	2.00E-02	1.00E-02	N.A.	N.A.
Aldr.	3.00E-05	1.50E-05	1.70E+01	3.40E+01
DDD	N.A.	N.A.	2.40E-01	3.43E-01
DDT	5.00E-04	3.50E-04	3.40E-01	4.86E-01
α - Endo	6.00E-03	3.00E-03	N.A.	N.A.
β - Endo	6.00E-03	3.00E-03	N.A.	N.A.
Endo Sul.	6.00E-03	3.00E-03	N.A.	N.A.
Endr	3.00E-04	6.00E-06	N.A.	N.A.
Hept	5.00E-04	3.60E-04	4.50E+00	6.25E+00

Table 8. Toxicological referential for non carcinogenic effects (RfDs) and carcinogenic ones (SFs), by oral intake (int) and by skin contact (skin). References: N.A. Not applicable. References for pesticides: see Table 2

3. Results

The results indicate there is no health risk in the two considered exposure scenarios, neither due to the pesticides present in the water bodies, nor to the non carcinogenic effects or the carcinogenic ones (see Tables 9a and 9b, 10a and 10b). The aggregated cumulative risk values of NCE for both scenarios, which is the worst condition given that the exposure is simultaneous to all substances and through both pathways of exposure at the same time, differs greatly from the value of significance ($R = 1$). As shown in Tables 9a and 9b, the highest risk for the *recreational residential* scenario is $9.06E-03$, while for the *rural fishing* scenario is around $1.83E-03$ data taken from La Peregrina shallow lake (water body 10) in both cases. The first scenario is around 5 times riskier than the second one. The second riskiest environment is the Blanca Chica shallow lake (water body 12). The aggregated cumulative risk derived from CE is also much lower than reference values ($R = 10^{-5}$), reaching values of $8.66E-07$ and $9.66E-07$ for the *recreational residential* and the

rural fishing scenarios respectively, for La Peregrina shallow lake (see Tables 10a and 10b). In this case, the rural fishing scenario generates a similar risk to the recreational residential one. The second water body with highest risk values is Del Azul creek (water body 20).

The highest cumulative risk values for both pathways of exposure for NCE and CE, can be seen in Tables 11a and 11b. In nearly all cases, the riskiest environment is La Peregrina shallow lake. However, for accidental intake exposure and NCE, for both scenarios, the riskiest compared scenario is Del Azul creek (water body 20), followed by the former mentioned shallow lake. As shown in Table 10a, for skin contact exposure and NCE, for both scenarios, the second riskiest environment is Blanca Chica shallow lake (water body 12). In the case of CE, for both pathways of exposure and both scenarios, the second riskiest environment is Del Azul creek.

Table 11c shows the percentual risk of skin contact with regard to aggregated risk, both for NCE and CE. It can clearly be seen that skin contact risk is extremely important for both scenarios and types of effects, with average values around 90%.

It is always assumed that the highest risk occurs in children, which is proven in this study by comparing the accidental intake for the recreational residential and the fishing rural scenarios. For NCE, the arithmetic mean of the maximum risks by accidental intake in the recreational residential scenario for the 21 water bodies is 14.18 times higher (SD=0.03) than in the fishing rural one; through skin contact, the mean is 4.95 times higher (SD=0.01). For CE, the relationship varies. The risks for both pathways of exposure continue being higher for the child's scenario, but the value ranges are lower. The arithmetic mean of the maximum risk values for the recreational scenario is 3.22 times (SD=0.001) higher than in the fishing rural one, while the skin contact is 0.86 times (SD=0.06) greater.

The reason why in all cases the highest risks are found in the scenarios where the child is used as representative of exposed individuals is due to the fact that in children the dose becomes higher as it is distributed in a smaller body weight. However, for both NCE and CE, the difference between accidental intake and skin contact is reduced for both children and adults.

In addition to a lower body weight, the daily volume of water intake that emerges from the multiplication of the intake rate (the same for child and adult) by the duration of the event and the frequency of exposure is higher in the child, contributing to an increase in dose. The combination of highest ET and EF, and lowest BW results in a 14 times higher average risk of accidental intake in the child compared to the adult, not compensated by the higher ED of the adult. For skin contact, the intake is negligible. Although BW continues being lower and EF higher in the child, the fisherman's body surface increases, which added to the higher ED, reduced the differences up to the point where they are minimal for EC. With a small change in the scenario, as a rise of EF that would be completely logical for some fishermen that conduct more than 12 annual fishing excursions, the risk value could match or even exceed that of the child's.

The analysis of which substances generate the highest risk values in each case is displayed in Table 12. For both NCE and CE, Aldrin is of the most importance. For accidental intake, Acetochlor (in Del Azul Creek) and the α isomer of HCH (in La Peregrina shallow lake) appear as important for NCE and CE, in both water bodies. For skin exposure, after Aldrin, Heptachlor stands out as one of the main pesticides present in all water bodies, for NCE and CE.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
AM	4.87 E ⁻⁰⁵	4.75 E ⁻⁰⁵	1.57 E ⁻⁰⁴	4.94 E ⁻⁰⁵	4.75 E ⁻⁰⁵	4.75 E ⁻⁰⁵	4.75 E ⁻⁰⁵	8.22 E ⁻⁰⁵	6.02 E ⁻⁰⁵	3.54 E ⁻⁰³	1.15 E ⁻⁰⁴	9.95 E ⁻⁰⁴	1.03 E ⁻⁰⁴	3.59 E ⁻⁰⁴	1.19 E ⁻⁰⁴
SD	2.74 E ⁻⁰⁵	2.67 E ⁻⁰⁵	8.83 E ⁻⁰⁵	2.78 E ⁻⁰⁵	2.67 E ⁻⁰⁵	2.67 E ⁻⁰⁵	2.67 E ⁻⁰⁵	4.63 E ⁻⁰⁵	3.39 E ⁻⁰⁵	1.99 E ⁻⁰³	6.48 E ⁻⁰⁵	5.60 E ⁻⁰⁴	5.80 E ⁻⁰⁵	2.02 E ⁻⁰⁴	6.68 E ⁻⁰⁵
Max	1.24 E ⁻⁰⁴	1.21 E ⁻⁰⁴	4.00 E ⁻⁰⁴	1.26 E ⁻⁰⁴	1.21 E ⁻⁰⁴	1.21 E ⁻⁰⁴	1.21 E ⁻⁰⁴	2.08 E ⁻⁰⁴	1.52 E ⁻⁰⁴	9.06 E ⁻⁰³	2.94 E ⁻⁰⁴	2.55 E ⁻⁰³	2.62 E ⁻⁰⁴	9.20 E ⁻⁰⁴	3.02 E ⁻⁰⁴
P95	9.62 E ⁻⁰⁵	9.40 E ⁻⁰⁵	3.10 E ⁻⁰⁴	9.76 E ⁻⁰⁵	9.40 E ⁻⁰⁵	9.40 E ⁻⁰⁵	9.40 E ⁻⁰⁵	1.63 E ⁻⁰⁴	1.19 E ⁻⁰⁴	6.99 E ⁻⁰³	2.27 E ⁻⁰⁴	1.97 E ⁻⁰³	2.04 E ⁻⁰⁴	7.10 E ⁻⁰⁴	2.35 E ⁻⁰⁴

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
AM	8.92 E ⁻⁰⁶	8.73 E ⁻⁰⁶	2.87 E ⁻⁰⁵	9.05 E ⁻⁰⁶	8.73 E ⁻⁰⁶	8.73 E ⁻⁰⁶	8.73 E ⁻⁰⁶	1.45 E ⁻⁰⁵	1.08 E ⁻⁰⁵	6.53 E ⁻⁰⁴	2.00 E ⁻⁰⁵	1.84 E ⁻⁰⁴	1.80 E ⁻⁰⁵	6.63 E ⁻⁰⁵	2.16 E ⁻⁰⁵
SD	6.74 E ⁻⁰⁶	6.60 E ⁻⁰⁶	2.17 E ⁻⁰⁵	6.84 E ⁻⁰⁶	6.60 E ⁻⁰⁶	6.60 E ⁻⁰⁶	6.60 E ⁻⁰⁶	1.10 E ⁻⁰⁵	8.20 E ⁻⁰⁶	4.93 E ⁻⁰⁴	1.51 E ⁻⁰⁵	1.39 E ⁻⁰⁴	1.36 E ⁻⁰⁵	5.01 E ⁻⁰⁵	1.63 E ⁻⁰⁵
Max	2.50 E ⁻⁰⁵	2.45 E ⁻⁰⁵	8.06 E ⁻⁰⁵	2.54 E ⁻⁰⁵	2.45 E ⁻⁰⁵	2.45 E ⁻⁰⁵	2.45 E ⁻⁰⁵	4.10 E ⁻⁰⁵	3.05 E ⁻⁰⁵	1.83 E ⁻⁰³	5.67 E ⁻⁰⁵	5.15 E ⁻⁰⁴	5.09 E ⁻⁰⁵	1.86 E ⁻⁰⁴	6.08 E ⁻⁰⁵
P95	2.15 E ⁻⁰⁵	2.10 E ⁻⁰⁵	6.92 E ⁻⁰⁵	2.18 E ⁻⁰⁵	2.10 E ⁻⁰⁵	2.10 E ⁻⁰⁵	2.10 E ⁻⁰⁵	3.51 E ⁻⁰⁵	2.62 E ⁻⁰⁵	1.57 E ⁻⁰³	4.83 E ⁻⁰⁵	4.42 E ⁻⁰⁴	4.34 E ⁻⁰⁵	1.60 E ⁻⁰⁴	5.21 E ⁻⁰⁵

Table 9a and 9b. NCE aggregated cumulative risk for *recreational residential and rural fishing* scenarios. References for water bodies: see Table 3. AM: Arithmetic mean; SD: Standard deviation. Max: Maximum value; P 95: 95 percentile

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
AM	6.66 E ⁻⁰⁹	7.52 E ⁻⁰⁹	9.34 E ⁻⁰⁹	7.16 E ⁻⁰⁹	6.57 E ⁻⁰⁹	6.57 E ⁻⁰⁹	6.57 E ⁻⁰⁹	1.32 E ⁻⁰⁸	8.95 E ⁻⁰⁹	1.97 E ⁻⁰⁷	1.54 E ⁻⁰⁸	2.45 E ⁻⁰⁸	1.73 E ⁻⁰⁸	7.91 E ⁻⁰⁹	1.21 E ⁻⁰⁸
SD	4.71 E ⁻⁰⁹	5.32 E ⁻⁰⁹	6.60 E ⁻⁰⁹	5.06 E ⁻⁰⁹	4.64 E ⁻⁰⁹	4.64 E ⁻⁰⁹	4.64 E ⁻⁰⁹	9.32 E ⁻⁰⁹	6.33 E ⁻⁰⁹	1.39 E ⁻⁰⁷	1.09 E ⁻⁰⁸	1.73 E ⁻⁰⁸	1.23 E ⁻⁰⁸	5.59 E ⁻⁰⁹	8.58 E ⁻⁰⁹
Max	2.95 E ⁻⁰⁸	3.33 E ⁻⁰⁸	4.19 E ⁻⁰⁸	3.18 E ⁻⁰⁸	2.91 E ⁻⁰⁸	2.91 E ⁻⁰⁸	2.91 E ⁻⁰⁸	5.99 E ⁻⁰⁸	4.02 E ⁻⁰⁸	8.66 E ⁻⁰⁷	7.05 E ⁻⁰⁸	1.08 E ⁻⁰⁷	7.95 E ⁻⁰⁸	3.54 E ⁻⁰⁸	5.43 E ⁻⁰⁸
P95	1.61 E ⁻⁰⁸	1.82 E ⁻⁰⁸	2.26 E ⁻⁰⁸	1.73 E ⁻⁰⁸	1.59 E ⁻⁰⁸	1.59 E ⁻⁰⁸	1.59 E ⁻⁰⁸	3.19 E ⁻⁰⁸	2.17 E ⁻⁰⁸	4.76 E ⁻⁰⁷	3.74 E ⁻⁰⁸	5.92 E ⁻⁰⁸	4.20 E ⁻⁰⁸	1.91 E ⁻⁰⁸	2.94 E ⁻⁰⁸

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
AM	4.91 E ⁻⁰⁹	1.33 E ⁻⁰⁸	1.61 E ⁻⁰⁸	1.26 E ⁻⁰⁸	1.16 E ⁻⁰⁸	1.16 E ⁻⁰⁸	1.16 E ⁻⁰⁸	2.20 E ⁻⁰⁸	1.54 E ⁻⁰⁸	3.50 E ⁻⁰⁷	2.55 E ⁻⁰⁸	4.34 E ⁻⁰⁸	2.85 E ⁻⁰⁸	1.37 E ⁻⁰⁸	2.10 E ⁻⁰⁸
SD	4.36 E ⁻⁰⁹	9.93 E ⁻⁰⁹	1.20 E ⁻⁰⁸	9.38 E ⁻⁰⁹	8.66 E ⁻⁰⁹	8.66 E ⁻⁰⁹	8.66 E ⁻⁰⁹	1.64 E ⁻⁰⁸	1.14 E ⁻⁰⁸	2.61 E ⁻⁰⁷	1.90 E ⁻⁰⁸	3.24 E ⁻⁰⁸	2.12 E ⁻⁰⁸	1.02 E ⁻⁰⁸	1.56 E ⁻⁰⁸
Max	2.44 E ⁻⁰⁸	3.68 E ⁻⁰⁸	4.44 E ⁻⁰⁸	3.47 E ⁻⁰⁸	3.21 E ⁻⁰⁸	3.21 E ⁻⁰⁸	3.21 E ⁻⁰⁸	6.09 E ⁻⁰⁸	4.25 E ⁻⁰⁸	9.66 E ⁻⁰⁷	7.07 E ⁻⁰⁸	1.20 E ⁻⁰⁷	7.90 E ⁻⁰⁸	3.78 E ⁻⁰⁸	5.80 E ⁻⁰⁸
P95	1.47 E ⁻⁰⁸	3.16 E ⁻⁰⁸	3.81 E ⁻⁰⁸	2.99 E ⁻⁰⁸	2.76 E ⁻⁰⁸	2.76 E ⁻⁰⁸	2.76 E ⁻⁰⁸	5.23 E ⁻⁰⁸	3.65 E ⁻⁰⁸	8.32 E ⁻⁰⁷	6.07 E ⁻⁰⁸	1.03 E ⁻⁰⁷	6.78 E ⁻⁰⁸	3.25 E ⁻⁰⁸	4.99 E ⁻⁰⁸

Table 10a and 10b. CE aggregated cumulative risk for *recreational residential* and *rural fishing* scenarios. References for water bodies see Table 3. AM: Arithmetic mean; SD: Standard deviation. Max: Maximum value; P 95: 95 percentile

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Rec. Res.	Int	3.21 E ⁻⁰⁶	2.47 E ⁻⁰⁶	1.18 E ⁻⁰⁵	3.57 E ⁻⁰⁶	2.47 E ⁻⁰⁶	2.47 E ⁻⁰⁶	2.47 E ⁻⁰⁶	2.28 E ⁻⁰⁵	9.91 E ⁻⁰⁶	9.57 E ⁻⁰⁵	4.18 E ⁻⁰⁵	2.45 E ⁻⁰⁵	3.48 E ⁻⁰⁵	1.00 E ⁻⁰⁵	1.1
	Skin	1.23 E ⁻⁰⁴	1.20 E ⁻⁰⁴	3.95 E ⁻⁰⁴	1.25 E ⁻⁰⁴	1.20 E ⁻⁰⁴	1.20 E ⁻⁰⁴	1.20 E ⁻⁰⁴	1.96 E ⁻⁰⁴	1.48 E ⁻⁰⁴	9.02 E ⁻⁰³	2.67 E ⁻⁰⁴	2.54 E ⁻⁰³	2.41 E ⁻⁰⁴	9.16 E ⁻⁰⁴	2.9
Rur.	Int	2.26 E ⁻⁰⁷	1.74 E ⁻⁰⁷	8.30 E ⁻⁰⁷	2.52 E ⁻⁰⁷	1.74 E ⁻⁰⁷	1.74 E ⁻⁰⁷	1.74 E ⁻⁰⁷	1.61 E ⁻⁰⁶	6.99 E ⁻⁰⁷	6.75 E ⁻⁰⁶	2.95 E ⁻⁰⁶	1.72 E ⁻⁰⁶	2.46 E ⁻⁰⁶	7.07 E ⁻⁰⁷	8.2
Fish.	Skin	2.48 E ⁻⁰⁵	2.43 E ⁻⁰⁵	7.99 E ⁻⁰⁵	2.52 E ⁻⁰⁵	2.43 E ⁻⁰⁵	2.43 E ⁻⁰⁵	2.43 E ⁻⁰⁵	3.96 E ⁻⁰⁵	2.99 E ⁻⁰⁵	1.82 E ⁻⁰³	5.41 E ⁻⁰⁵	5.13 E ⁻⁰⁴	4.87 E ⁻⁰⁵	1.85 E ⁻⁰⁴	6.0

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Rec. Res.	Int	9.24 E ⁻¹⁰	7.90 E ⁻¹⁰	2.81 E ⁻⁰⁹	1.09 E ⁻⁰⁹	7.39 E ⁻¹⁰	7.39 E ⁻¹⁰	7.39 E ⁻¹⁰	6.47 E ⁻⁰⁹	2.81 E ⁻⁰⁹	1.16 E ⁻⁰⁸	8.43 E ⁻⁰⁹	2.18 E ⁻⁰⁹	1.02 E ⁻⁰⁸	2.03 E ⁻⁰⁹	3.
	Skin	2.72 E ⁻⁰⁸	3.09 E ⁻⁰⁸	3.70 E ⁻⁰⁸	2.91 E ⁻⁰⁸	2.69 E ⁻⁰⁸	2.69 E ⁻⁰⁸	2.69 E ⁻⁰⁸	5.04 E ⁻⁰⁸	3.54 E ⁻⁰⁸	8.13 E ⁻⁰⁷	5.84 E ⁻⁰⁸	1.01 E ⁻⁰⁷	6.52 E ⁻⁰⁸	3.16 E ⁻⁰⁸	4.
Rur.	Int	2.87 E ⁻¹⁰	2.45 E ⁻¹⁰	8.72 E ⁻¹⁰	3.39 E ⁻¹⁰	2.29 E ⁻¹⁰	2.29 E ⁻¹⁰	2.29 E ⁻¹⁰	2.01 E ⁻⁰⁹	8.71 E ⁻¹⁰	3.61 E ⁻⁰⁹	2.62 E ⁻⁰⁹	6.78 E ⁻¹⁰	3.16 E ⁻⁰⁹	6.29 E ⁻¹⁰	9.
Fish.	Skin	2.42 E ⁻⁰⁸	3.66 E ⁻⁰⁸	4.39 E ⁻⁰⁸	3.46 E ⁻⁰⁸	3.19 E ⁻⁰⁸	3.19 E ⁻⁰⁸	3.19 E ⁻⁰⁸	5.98 E ⁻⁰⁸	4.20 E ⁻⁰⁸	9.64 E ⁻⁰⁷	6.93 E ⁻⁰⁸	1.19 E ⁻⁰⁷	7.73 E ⁻⁰⁸	3.75 E ⁻⁰⁸	5.

Table 11a and 11b. Highest NCE and CE aggregated cumulative risk for both *recreational residential* (Rec. Res.) and *rural fishing* (Rur.Fish.) scenarios, discriminating in each case, the two pathways of exposure: accidental intake (Int) and skin contact (Skin). References for water bodies: see Table 3.

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
NCE	Rec.Res.	96.24	96.81	95.39	96.01	96.81	96.81	96.81	81.17	89.08	98.86	75.02	99.11	76.88	98.84	93.84
	Rur. Fish.	98.08	98.43	97.97	98.13	98.43	98.43	98.43	92.59	95.60	98.96	90.31	99.18	90.87	99.06	97.84
CE	Rec.Res.	94.17	95.49	87.13	93.46	95.17	95.17	95.17	79.06	86.59	97.46	76.73	96.16	74.98	89.02	88.84
	Rur. Fish.	98.00	98.97	96.96	98.50	98.90	98.90	98.90	94.89	96.83	99.43	94.27	99.13	93.80	97.43	97.84

Table 11c. Percentage of the risk value through skin exposure with regard to the aggregated risk, for the *recreational residential* and the *rural fishing* scenarios differentiating NCE and CE. References for water bodies: see Table 3.

Pest.	ENC								EC							
	Int.				Skin				Int.				Skin			
	Rec. Res.		Rur. Fish.		Rec. Res.		Rur. Fish.		Rec. Res.		Rur. Fish.		Rec. Res.		Rur. Fish.	
	10	21	10	21	10	12	10	12	10	21	10	21	10	21	10	21
α – HCH	1.26 E-05	2.62 E-05	8.87 E-07	1.85 E-06	4.77 E-05	3.67 E-05	9.64 E-06	8.29 E-06	4.10 E-09	8.55 E-09	9.81 E-10	2.04 E-09	1.61 E-08	8.90 E-09	1.82 E-08	1.57 E-08
γ – HCH	3.63 E-06	3.24 E-07	2.56 E-07	2.29 E-08	1.38 E-05	1.06 E-05	2.78 E-06	2.39 E-06	1.18 E-09	1.06 E-10	2.83 E-10	2.53 E-11	1.42 E-09	7.84 E-10	1.60 E-09	1.38 E-09
δ – HCH	1.95 E-09	7.14 E-07	1.37 E-10	5.03 E-08	7.37 E-09	5.68 E-09	1.49 E-09	1.28 E-09	1.31 E-13	4.80 E-11	3.13 E-14	1.15 E-11	5.15 E-13	2.84 E-13	5.82 E-13	5.00 E-13
γ – Clor.	3.89 E-08	1.52 E-06	2.74 E-09	1.07 E-07	1.51 E-06	1.16 E-06	3.06 E-07	2.63 E-07	1.18 E-12	4.58 E-11	2.81 E-13	1.10 E-11	4.74 E-11	2.62 E-11	5.35 E-11	4.60 E-11
Acet	2.92 E-10	2.77 E-04	2.06 E-11	1.95 E-05	4.41 E-10	3.39 E-10	8.91 E-11	7.66 E-11								
Aldr.	7.66 E-05	3.63 E-06	5.40 E-06	2.56 E-07	8.85 E-03	6.81 E-03	1.79 E-03	1.54 E-03	6.74 E-09	3.20 E-10	1.61 E-09	7.64 E-11	8.08 E-07	4.46 E-07	9.13 E-07	7.84 E-07
DDD									8.06 E-14	8.06 E-14	1.93 E-14	1.93 E-14	5.92 E-12	3.27 E-12	6.68 E-12	5.74 E-12
DDT	2.02 E-07	2.02 E-07	1.42 E-08	1.42 E-08	3.78 E-05	2.91 E-05	7.64 E-06	6.57 E-06	5.91 E-12	5.91 E-12	1.41 E-12	1.41 E-12	1.15 E-09	6.35 E-10	1.30 E-09	1.12 E-09
α – Endo	2.98 E-07	8.04 E-08	2.10 E-08	5.67 E-09	2.43 E-07	1.87 E-07	4.91 E-08	4.22 E-08								
β – Endo	5.71 E-07	2.92 E-08	4.03 E-08	2.06 E-09	4.65 E-07	3.58 E-07	9.40 E-08	8.08 E-08								
Endo Sul.	3.70 E-09	4.02 E-07	2.61 E-10	2.84 E-08	3.01 E-09	2.32 E-09	6.09 E-10	5.23 E-10								
Endr	2.60 E-08	2.60 E-08	1.83 E-09	1.83 E-09	7.15 E-06	5.50 E-06	1.44 E-06	1.24 E-06								
Hept	1.75 E-06	6.35 E-06	1.24 E-07	4.47 E-07	6.50 E-05	5.01 E-05	1.32 E-05	1.13 E-05	6.80 E-10	2.46 E-09	1.62 E-10	5.88 E-10	2.62 E-08	1.45 E-08	2.96 E-08	2.54 E-08

Table 12. Highest risk values by pesticide for both pathways of exposure (accidental *intake* and *skin* contact) of each of the scenarios for the two water bodies with highest risk according to Tables 11a and 11b. References for water bodies: see Table 3. References for pesticides: see Table 2.

4. Discussion

When hazardous chemical substances are detected in waters that can be used with recreational purposes, the management procedure to evaluate whether there is risk for human populations in Argentina is to compare the concentrations found in water with Guide Levels or Highest Permitted Levels for human consumption water. Such procedure coincides with the guidelines written by WHO (1998). For such cases, the *National guidance levels for environment water quality for sources for human consumption* (SRHN, 2007b) or the Argentinian Food Code (PEN, 1969) with its Regulatory Decree 2126 (PEN, 1971), and its updates (ANMAT, 2010) are used. In the case of the analyzed water bodies in this work, because of being located in the Buenos Aires province, it is usual to resort to quality regulations for drinking water in Law 11820 (Legislature of Buenos Aires province, 1996) for comparison. This procedure, although it shares some similarities with the guidelines indicated by WHO (1998), it has some drawbacks.

The first and most evident drawback is that there are substances present in the water bodies analyzed in this work for which the regulatory framework does not have limit values (for example both Endosulfan isomers, Endosulfan Sulfate, and Endrin).

On the other hand, the comparison with regulatory levels is a management procedure that, though simple, is rigid and unrealistic in terms of the exposure. Firstly, the analysis is conducted by single substances for only one pathway of exposure. In this specific case, there are only normative regulations for water intake, not for skin contact. With regard to intake, the limit values are considering consumption intake, not recreational intake. Consumption water intake assumes intake rates much higher than the ones correspondent to accidental intake during recreational use, which causes that these values prove to be excessively conservative. The regulatory framework assumes an intake water rate of 2 L day⁻¹ (SRNH, 2007b), which is much higher than 0.1 L day⁻¹, the highest value of intake utilized in this work for the recreational residential scenario.

Conversely, this work has demonstrated that, at least for this type of chemicals, evaluating substances toxicity by ingestion alone leads to underestimation of the risk. This study proved that in the aggregated cumulative risk value by organochlorine pesticides, the risk due to skin exposure is much higher than the one produced by intake.

HRA have operational advantages over the regulatory values as management tools. These methodologies allow conducting a more exhaustive and realistic study of all exposure processes, being able to classify between routes of exposure (digestive, respiratory, skin), scenarios (recreational, residential, working), exposed individuals (children, adults), and even to consider simultaneous pathways of exposure (aggregated HRA) and substances (cumulative HRA). The regulatory framework, on the contrary, does not allow for any particular analysis with regard to the two analyzed scenarios in accordance with the technical decisions that define them.

Another advantage that the HRA offer is the possibility to operate them probabilistically. The regulatory values assume deterministic values. Therefore, a child drinks 1 liter of water every day while an adult drinks 2 liters; a child weights 30 kg and an adult 70 kg (USEPA, 1997a; USEPA, 2002b). It is obvious that this simplification, although it makes the operational aspects easier, masks the existence of variability in human populations. It has to be admitted that within the “child” category, for example, there is an extremely important

dispersion of values if different age ranges are included. Moreover, population variability for one age, between sexes and for each sex also exists. It could even be argued that similar age ranges could differ, even within a population, due to the dependency on the intake rate, or weight rate, of some socioeconomic factors (USEPA, 1997a; USEPA, 2002b). The regulatory value is a unique representative value of these distributions, which leads to estimating the danger level from a unique exposure scenario, accurate and invariant towards the hazardous substance. The probabilistic studies note that the different participating variables have, intrinsically, uncertainty and variability, which influence the risk study and, consequently, the management based on them (Thompson and Graham, 1996).

The probabilistic techniques in the HRA operate with value distributions for each variable, resulting in the estimated risk being a value distribution also, with a different level of probability. This allows the inclusion of the uncertainty and/or variability resulting from the model, which a deterministic procedure cannot. Although in this work the analysis was carried out based on the highest values obtained for each application of Monte Carlo in order to have a more simplistic model, the result of each estimation was actually a distribution from which any statistic parameter could be obtained.

Therefore, if the regulatory levels were used as the only bathing waters management tool, the question whether the presence of these pesticides could generate health conditions because of the use of these water bodies for recreational bathing, would have remained unanswered. The hereby work shows that, given the lack of another tool to control the physical and chemical quality of water for recreational use with direct skin contact, the HRA could be a possible substitute management strategy providing information which is unattainable today with the currently available management tools.

5. Conclusions

This study indicates that health risk for non carcinogenic and carcinogenic effects due to accidental intake and skin contact during bathing activity in superficial water in the Buenos Aires province would not be relevant.

The application of health risk analysis allowed identifying La Peregrina shallow lake as the riskiest environment, when considering the exposure to accidental intake and skin contact simultaneously (aggregated risk) with all substances at the same time (cumulative risk). For the recreational residential scenario (which has a child as representative exposed individual) the aggregated cumulative risk is $9.06E^{-03}$ for non carcinogenic effects (NCE) and $8.23E^{-07}$ for carcinogenic effects (CE), whereas in the fishing rural scenario (whose representative exposed individual is an adult), the risks are $1.83E^{-03}$ for NCE and $9.66E^{-07}$ for CE.

For each scenario, skin contact risks are higher than those of accidental intake (in average, skin risk reaches 90 % of the aggregated risk of the scenario, for both NCE and CE).

If the differences between scenarios are evaluated, the child's scenario always has higher risk values than the adult's, but these differences are variable. The biggest difference occurs in NCE, between accidental intakes of both scenarios, where the cumulative risk for the child is 14 times higher than the risk for the adult. When CE are analyzed, the differences between both scenarios become narrower: the recreational scenario is 3 times and less than

one time higher than the fishing rural scenario for accidental intake and skin contact, respectively.

The substance that generates the highest risk values, for both NCE and CE, is Aldrin. For accidental intake, in addition to Aldrin, Acetochlor and the α isomer of HCH appear as important for NCE and Heptachlor for CE. For skin exposure, in addition to Aldrin, Heptachlor is relevant for both NCE and CE.

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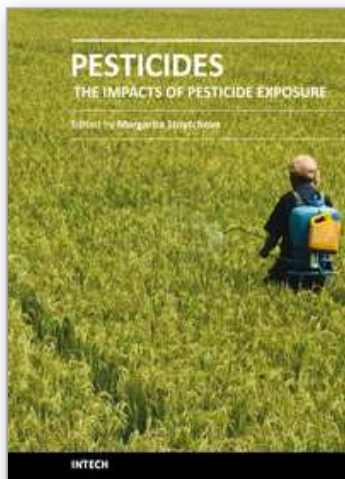
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Pesticides are supposed to complete their intended function without “any unreasonable risk to man or the environment”. Pesticides approval and registration are performed “taking into account the economic, social and environmental costs and benefits of the use of any pesticide”. The present book documents the various adverse impacts of pesticides usage: pollution, dietary intake and health effects such as birth defects, neurological disorders, cancer and hormone disruption. Risk assessment methods and the involvement of molecular modeling to the knowledge of pesticides are highlighted, too. The volume summarizes the expertise of leading specialists from all over the world.

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