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17

Pesticides Reaching the Environment as a Consequence of Inappropriate Agricultural Practices in Argentina

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1. Introduction

Recent water quality inventories show that agricultural non-point source pollution (NPS) is the leading source of water quality impacts to surveyed rivers and lakes, and also a major contributor to groundwater contamination and wetlands degradation (Blankenberg et al. 2006; Haarstad and Braskerud 2005; Bergstrom 2004; Thiere and Schulz 2004; Schreiber et al. 2001; Huber et al. 2000; Luo and Zhang 2010).

Pest management is one of the main scopes of pesticides usage, because more than 45% of annual food production is lost due to pest infestation. In particular, at tropical climates this is enhanced due to prevailing high temperature and humidity. However, the sporadic use has been leading to significant consequences not only to public health but also to food quality resulting in an impact load on the environment and hence the development of pest resistance (Giupponi and Rosato 1999; Luo and Zhang 2010)

Through overuse, misuse and losses due to the inappropriate application of pesticides there is considerable waste contributing to the environmental burden (Li et al. 2006; Giupponi and Rosato 1999; Hu et al. 2010; Marco and Kishimba 2007; Luo and Zhang 2010). It is well known that most of the applied pesticides are subject to many transport and conversion processes. Thus, they do not remain at their target site but often enter aquatic environments via soil percolation, air drift or surface run-off, affecting abundance and diversity of non-target species, producing complex effects on the ecosystems and, altering trophic interactions (Islam and Tanaka, 2004). Pesticides overuse also destroys the healthy pool of bio-control agents that normally co-exist with the vegetation. Simultaneously, some soil biological functions such as the bioavailability of nutrients and organic matter decomposition could also be altered (Hendrix 1996; Guo et al. 2009). For instance, the herbicides can influence soil microbial biomass carbon (MBC) and metabolic quotient (qCO), variables directly related to soil quality (Reis et al. 2009). In addition, agrochemical application on soybean shoots affects the activity of soil microorganisms in the plant rhizosphere (Reis et al. 2009).

The bulk of pesticides worldwide used is herbicides and there is almost no knowledge of their impact on potential non-target plant species, especially rare or endemic species

(McLaughlin and Mineau 1995). For example, granular insecticides such as carbofuran are very efficient at killing a large proportion of the songbird population breeding on the edge of fields where they are applied (De Silva et al. 2010; Tataruch et al. 1998).

These compounds affect the whole ecosystem by entering into the food chain and polluting the soil, air, ground and surface water. As an immediate consequence, humans are exposed to pesticides found in the media. These come to human contact by different routes of exposure such as inhalation, ingestion and dermal contact. As is widely stated, recent and chronic pesticides residues are being detected in child blood, human adipose tissue and breast milk (Perez-Maldonado et al. 2010; Waliszewski et al. 2010; Waliszewski et al. 2009; Wang et al. 2009; Lopez-Espinosa et al. 2008; Ntow et al. 2008). These exposures could ultimately result in acute and chronic health problems, increasing the incidence of cancer, chronic kidney diseases, suppression of the immune system, sterility among males and females, endocrine disorders, neurological and behavioral disorders, especially among children, have been attributed to chronic pesticide poisoning (Gbaruko et al. 2009; Lin et al. 2009; Casabe et al. 2007; Bila and Dezotti 2007; Aronson et al. 2010; Panegyres et al. 2010; Rull et al. 2009; Silva and Gammon 2009).

As an agricultural country, Argentina was estimated from 26 to 30 million hm2 of farmland using pesticides in the period 2005-2008. It is stated that during pesticides application, up to 30-50% of the applied amount can be lost to the air. Assuming an average dose of a 4.3 kg.hm-1, the amount of pesticides used range between 112 to 129 million Kg with losses to the environment ranging from 33.6 to 64.5 million Kg per year (this means a minimum of about 1 Kg of pesticide in the environment per habitant). In addition, this estimate is not considering that the number of treatments has increased in the last decade, with 66% of the cropped area using two or more herbicide types, and 80% using two or more insecticides during treatment.

To sum up, the existing evidence arguments in favour of revising and restructuring the national agriculture policy and monitoring programs. As a first step, this chapter will discuss some elements of the Argentinean agricultural practices and policies, and then it will focus in reviewing pesticides' occurrence in the environment.

2. Country and agricultural practices

The Argentinean Republic is a country with a total area of 3.761.274 Km^2, including 964.000 Km^2 of islands and Antarctic lands. Its population was of 36.260.130 inhabitants in 2001 (the year of the last census), with an average density of 13 inhab/km^2. Despite this, 46% of the population is located around the country's capital city, Buenos Aires. Argentina reaches up to 89.9% of urban population. 77% of housing has access to drinking water through the national network and 59% of people have social medical insurance. The % of literacy is up to 97.8% (older than ten years) and about 34% complete a secondary education (12 years). The last census also showed 14.3% of homes below the line of poverty (Health Ministry, Argentina, 2003).

The combination of adequate temperatures, soil richness and rainfalls provides, as a consequence, top quality lands for agricultural use. The permanent population growth causes an increase on natural resources pressure that conduces to an overexploitation of them. By 2002, the country counted with 332.057 agricultural exploitations (AE), including an area of about 172.105.798 Ha. The major area was sowed with cereal and oilseeds. AE`s population reached up to 1.447.365, mainly constituted of workers.

About the pesticides regulation in Argentina, the government implemented the Rotterdam Convention by the year 2000. The Convention regulates the import and export of certain hazardous chemicals and pesticides. It is based on the fundamental principle of Prior Informed Consent (PIC), meaning that under the Convention, a chemical listed in the Convention may only be exported with the importer's prior consent. The Convention establishes a procedure to disseminate the decisions taken by the importing countries, thus implementing the PIC principle in the international trade in chemicals. It contains provisions requesting detailed information on the chemicals so that these decisions may be taken once data are available on the properties and the incidence of these products in particular on human health and the environment.

By the date of this convention, Argentina already had several pesticide regulations' laws. As a result, the Rotterdam Convention did not prohibit additional pesticides. The present existing regulation for pesticides in Argentina is summarized in Table 1.

Statistics reveals that the pesticide's usage is well regulated by different government offices, upon the destination by which they are registered in the National Phytosanitary Pesticides' Registry. In general, the province legislations agree with the national directives, however there are a few provinces and cities which run their own and independent registry. This reflects a kind of incoherence in the current legislation.

About pesticide's toxicological information, there are 21 Toxicological Assistance Centers in Argentina, offering several information services pointed to prevention, diagnosis and poisoning treatments. Since 1999, it was established a unique Registry of Toxicological Statistics, established in agreement with the INTOX Project of the International Programme Chemical Safety of the United Nations.

3. Country economy and probable agriculture evolution

The agriculture participation in the Gross Domestic Product (GDP) for 2002 was about 6 %. Inside this contribution area, the agriculture was the highest contributor (63%), followed by stockbreeding (31%). The sector's evolution estimation is of continuous growth (in magnitude of sowed surface and crops), about 16% by the end of 2010 and 9% by 2016. The estimated production for 2010 reaches 100 millions of Tons, and is expected to grow up to 150 millions in five years. These projections define a strong agriculture sector, which represents country wealth but also an environment threat.

3.1 Evolution of the pesticides' market

Pesticide use has increased dramatically over the last four decades to an estimated 2.59 x 109 kg of active ingredient used globally during1995 (Golfinopoulos et al. 2003). The gradual change in Argentina towards modern and intensive agricultural activities has led to an increase in the use of pesticides (Figure 1). Between the years 1994 and 2002 there was a 130% increase in the consumption of phytosanitary products, from 80 to almost 180 million liters (Miglioranza et al. 2003a). The physical volume commercialized during the present decade was about three times from the 90's, with a drastic increase in consumables for Glyphosate (N-(phosphonomethyl) glycine), a broad-spectrum systemic herbicide used to kill weeds, especially perennials, in particular for soybean cultivation by direct sowing.

In Argentina, the major pesticide class is Herbicides (commonly known as a weedkillers; substances used to kill unwanted plants). During 2006, 71% of the pesticides' market was

Compound	Restriction Level	Details of the restriction	Year
2,4,5-T	P	Decree-law 2.121/90	1990
ALDICARB	SR	Restrictions in soil usage: Decree-law 2.121/90	1990
ALDRIN	SR	Prohibited for bovine and pigs: Decree-law 2.143/68	1968
ALDRIN	P	Decree-law 2.121/90	1990
ALFANAFTIL-TIOUREA (ANTU)	P	Prohibited as rat poison. Law 7.292/98	1998
AMINOTRIAZOL	SR	Prohibited in Tobacco: Law 80/71	1971
ARSENIC	P	Decree-law 2.121/90	1990
ARSENIC and arsenic compounds	P	Prohibited as rat poison. Law 7.292/98	1998
LEAD ARSENATE	P	Decree-law 2.121/90	1990
AZINFOS, METIL	SR	Prohibited in horticulture and fruit trees. Resolution 10/91	1991
BARIUM compounds	P	Prohibited as rat poison. Law 7.292/98	1998
MERCURY dichloride	SR	Prohibited in Tobacco: Law 80/71	1971
METHYL BROMIDE	SR	Prohibited in public (urban or domestic) pest control. Res. 280/98	1998
CANFECLOR	SR	Prohibited for bovine and pigs: Decree-law 2.143/68	1968
CANFECLOR	SR	Prohibited as weevil insecticide. Law 47/72 and in the entire life cycle of cereals and leguminous plants. Law 79/72.	1972
CAPTAFOL	P	Decree-law 2.121/90	1990
CARBOFURAN	SR	Prohibited for pear tree and apple tree . Res. 10/91	1991
CLORDANE	P	Decree-Law 2.143/68. Law 18.073/69. Decree-Law 2.678/69	1969
CLORDANE	SR	Prohibited in Tobacco: Law 80/71	1971
CLORDANE	SR	Prohibited as weevil insecticide. Law 47/72	1972
CLORDANE	SR	Prohibited in grassland and fodder. Law 18.073/69. Decree-Law 2.678/69	1969
CLORDANE	SR	Prohibited in the entire life cycle of cereals and leguminous plants. Law 79/72	
CLORDANE	SR	Legal usage: ants insecticide and soil treatment.	
CLORDANE	P	Prohibited for domestic insecticides. Disposition 7.292/98	1998
CLOROBENCILATHE	P	Decree-law 2.121/90	1990
DAMINOZIDE	S	Decree-law 2.121/90	1990
		Allowed for chrysanthemum controlled production. Resolution:175/91.	1991
D.D.T.	SR	Prohibited for bovine and pigs: Decree-law 2.143/68	1968
D.D.T.	P	Decree-law 2.121/90	1990
D.D.T.	P	Resolution 133/91	1991
D.D.T.	P	Prohibited for domestic insecticides. Disposition 7.292/98	1998
ETHYLENE DIBROMIDE	P	Decree-law 2.121/90	1990
DICLORVOS	R	Prohibited for domestic insecticides. Disposition 7.292/98	
DIELDRIN	P	Law 22.289/80	1980
DINOCAP	S	Decree-law 2.121/90	1990
DISULFOTON	SR	Prohibited for apple tree and peach tree. Resolution:10/91	1991
ENDRIN	SR	Prohibited for bovine and pigs: Decree-law 2.143/68	1968
ENDRIN	P	Decree-law 2.121/90	1990
STRYCHNINE SULFATE	P	Decree-law 2.121/90	1990
STRYCHNINE	P	Prohibited as rat poison. Law 7.292/98	1998
ETHYL AZINFOS	SR	Prohibited in horticulture and fruit trees. Resolution 10/91	1991
ETION	SR	Prohibited for apple tree and pear tree. Resolution:10/91	1991
PHENYLMERCURY ACETATE	SR	Prohibited in Tobacco: Law 80/71	1971
METALLIC PHOSPHYTES	P	Prohibited as rat poison. Law 7.292/98	1998
WHITE PHOSPHOROUS	P	Prohibited as rat poison. Law 7.292/98	1998
H.C.B.	SR	Prohibited for bovine and pigs: Decree-law 2.143/68	1968
H.C.B.	SR	Prohibited as weevil insecticide. Law 47/72	1972
		Allowed for seed treatment. Res. 10/91.	1991
H.C.H.	P	Law 22.289/80.	1980
H.C.H.	P	Prohibited for domestic insecticides. Disposition 7.292/98	1998
HEPTACHLORO	P	Decree-Law 647/68. Law 18.073/69. Decre-Law 2.678/69.	1969
HEPTACHLORO	P	All usages prohibited. Res. IASCAV 27/93 -	1993
HEPTACHLORO	P	Prohibited for domestic insecticides. Disposition 7.292/98	1998
LINDANE	SR	Prohibited for bovine and pigs: Decree-law 2.143/68	1968
LINDANE	SR	Prohibited in Tobacco: Law 80/71. Prohibited as weevil insecticide. Law 47/72. Allowed for: ants and grasshooper insectice/soil and seeds treatment	1971 1972
LINDANE	SR	Allowed for louse treatment. Res. 133/91	1991
LINDANE	P	Prohibited for domestic insecticides. Disposition 7.292/98	1998
METOXICHLOR	P	Prohibited for domestic insecticides. Disposition 7.292/98	1998
METOXICHLOR	SR	Prohibited as weevil insecticide. Law 47/72 and in the entire life cycle of cereals and leguminous plants. Law 79/72. Prohibited for bovine and pigs: Decree-law 2.143/68.	1968 1972
MIREX	P	Prohibited for all usages. Res. 627/99	1999
MONOCROTOFOS	SR	Prohibited for alfalfa crops. Res. 396/96 . Prohibited in horticulture and fruit trees. Resolution 10/91	1991 1996
MONOCROTOFOS	P	Prohibited for all usages. Res. 627/99	1999
MONOFLUORO-ACETHAMIDE	P	Prohibited as rat poison. Law 7.292/98	1998
SODIUM MONOFLUORO ACETATE	P	Prohibited as rat poison. Law 7.292/98	1998
PARATHION	P	Res. 7/96	1996
PARATHION (ETHYL)	P	Res. SAGYP 606/93	1993
PARATION (METHYL)	P	Res. SAGYP 606/93	1993
PCP	P	Res. 356/94	1994
THALLIUM compounds	P	Prohibited as rat poison. Law 7.292/98	1998

P: Prohibited; SR: Severely Restricted; S: Suspended

Table1. Restricted Pesticides in Argentina (adapted from information provided by the Health Ministry of Argentina, García et al., 2003).

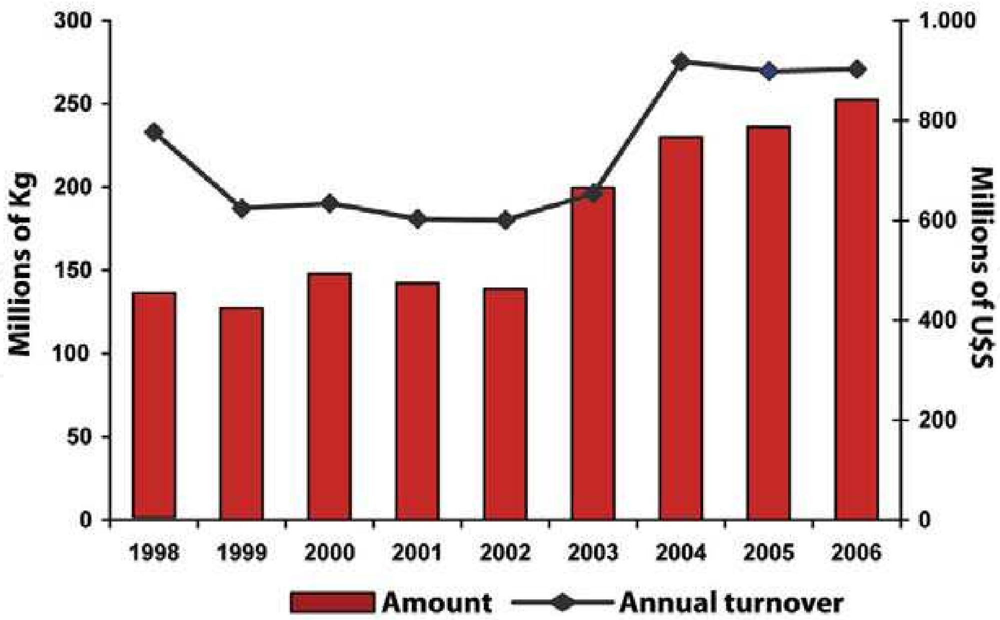

Fig. 1. Evolution of the Argentinean pesticides market (data from the Argentinean House of Agricultural and Livestock Health and Fertilizers)

dominated by herbicides, in particular by Glyphosate (46%), the principal herbicide used in the soybean cultivation (Figure 2).

Apart from these, there is another item hard to document: the illegal commercialization of pesticides. One of the documents delivered by the National Program of Chemical risks (Health Ministry, Argentina) identified the following compounds as the main products of this commerce: Pentachlorophenol, Parathión, DDTs, HCHs and Daminozide (Alar, Kylar, B-NINE, DMASA, SADH, B 995), a plant growth regulator usually sprayed on fruits (in Argentina for apples and pears) to regulate their growth, make their harvest easier, and enhance their color.

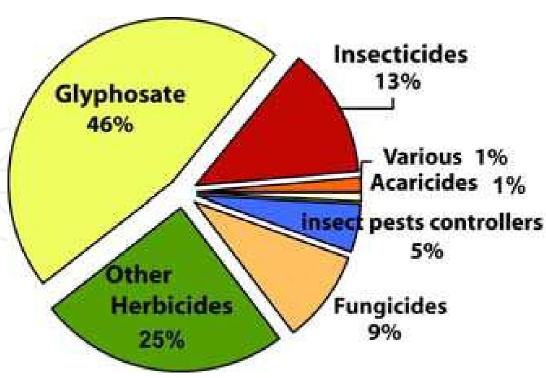

Fig. 2. Distribution of the Argentinean pesticides market for the year 2006 (data from the Argentinean House of Agricultural and Livestock Health and Fertilizers)

4. Factors affecting the application of pesticides

The technology used for their application is a critical factor when considering waste of pesticides and unnecessary environmental contamination. The design of nozzles is one of the major variables that could save up to 70% of pesticides compared to usual farmer's practice (Mathews, 1998). Although the Argentinean pesticide spraying systems do not use droplet size < 200 um -avoiding much of the airborne drifting-, pesticide application management usually relies on farmers personal decisions, with scarce regulatory control. Farmers and sprayers equipment operators still have wrong notion that high volumes, high pressure and high doses being perceived as the most appropriate ways for pesticide application (Abilash & Singh, 2009). In the pest's chemical control, the traditional method use nozzles of high volume rates, which require great volume of water to reach to the dripping point. Nozzles are normally not replaced and are even enlarged on purpose to achieve higher flow rates. The distribution patterns under these conditions are uneven; leaving sections with no pesticide coverage and others receiving overdoses (Mathews, 1998).

The common factors which alter pesticides efficiency, in particular in non industrialized producers are:

- Nozzles' poor calibration. Usually the equipment is inappropriate or obsolete.
- Inappropriate tractor speed which is reflected in unsatisfactory turbine's air volumes and pulverized water.
- Late or inadequate fruit pruning which facilitates infestation (in fruit production).
- Inadequate choice of the treatment opportunity time. This reflects ignorance of the pest's biology.
- Poor weather conditions: weather plays a major factor in affecting timing decisions; these conditions also play a significant role in the occurrence of spray drift. This is a major concern because it diverts the pesticide from the intended target, reduces efficacy, and deposits pesticide where it is not needed or wanted. The factors influencing spray drift contamination are: operating pressure, nozzle, type, orientation, orifice size, wind speed, wind direction, temperature, relative humidity and atmospheric stability. When a pesticide drifts, it may cause both environmental and economic damage through injury to susceptible vegetation, harm to wildlife, deposition of illegal residues on crops, and contamination of water supplies.
- Inadequate choice of the pesticide product in order to the target pest or absence of new pesticides application after precipitations events

Advanced producers are less affected by the abovementioned factors. Many of them use control techniques based on sanitary, environmental and economic criteria; in e.g., the sexual confusion of the *Carpocapsa* pest technique. These producers have integrative corporations that include many steps of the production process or are close-related to export agents. These conditions put them in the center of the commercial scenario, in a way that pesticides control and regulations must be thoroughly observed.

However, recent projections of several agriculture and livestock trend researchers for one of the most important agriculture regions (Alto Valle, Argentina, Huerga & San Juan, 2004) point that about 5% of crops are performed under "organic" practices (no pesticides usage), 10% under EUREGAP25 practices (=EURE Good Agricultural Practics), 45% under direct responsibility of the exporting corporation -with own protocols- and 40% with no particular system.

5. Potential risks of inappropriate pesticides' usage

There are at least three potentially dangerous items to consider about pest control:

1. Farm worker and rural population intoxications

2. Food contamination
3. Environment and natural resources contamination.

At present, is feasible to avoid these negative effects of pest controlling by regulation, control, education and technological assistance of the producer, executed by both, particular producers and government agents. However, in Argentina, this is hardly achieved and serious risk situations for producers, farms and food consumers are widely observed. Problems are well identified, so as well solutions, then, key questions arise: Why solutions are not applied? Who should be the main funding agent for these secure practices?

The last Agriculture and livestock census in 2002 showed that only 40% of farms were doing pest monitoring and only 10% accurately protecting their workers (Table 2). A key factor for the inclusion of good agricultural practices is the socioeconomic condition of the farm. For example, in the Alto Valle is clearly observed the two scenarios: worked land and abandoned scrubland. The last one usually belongs to low socioeconomic producers stroked by the 2002 crisis. Scrublands are then normal pest reservoirs, which diminish the results of the pest control efforts. A second commonly found scenario is traditionally hand-worked farms, which result inappropriate for pesticides' modern application techniques (Huerga & San Juan, 2004). As a result, the low socioeconomic condition of many farms affects the whole group of producers, including the ones who adopted good agricultural practices (GAPs).

Good Agricultural Practices (GAPs) adoption for pest control

Provinces and cities	Farms (Nº)	Area (ha)		Use agrochemicals according to pre-harvest intervals		Assessment of the balance status between pests and diseases		Adopt organic control practices		Promote integrated pest management (IPM)		Application by specially trained and knowledge-able persons		Empty containers management	
		Total	Sowed	Nº	%	Nº	%	Nº	%	Nº	%	Nº	%	Nº	%
Buenos Aires															
Colón	402	79.560	63.305	5	1,2	129	32,1	8	2,0	18	4,5	18	4,5	113	28,1
Pergamino	1.117	285.991	231.580	249	22,3	395	35,4	21	1,9	172	15,4	124	11,1	121	10,8
Rojas	584	183.273	149.897	129	22,1	277	47,4	13	2,2	94	16,1	61	10,4	104	17,8
Salto	516	139.423	121.261	83	16,1	149	28,9	33	6,4	31	6,0	58	11,2	76	14,7
San Nicolás	293	53.104	43.475	4	1,4	79	27,0	4	1,4	8	2,7	37	12,6	61	20,8
Córdoba															
Marcos Juárez	2.077	833.774	708.470	588	28,3	553	26,6	44	2,1	279	13,4	498	24,0	511	24,6
Gral. San Martín	786	343.195	297.971	43	5,5	54	6,9	7	0,9	165	21,0	137	17,4	117	14,9
Río Segundo	1.420	495.255	437.263	362	25,5	372	26,2	8	0,6	205	14,4	606	42,7	417	29,4
Mendoza															
Junín	1.589	20.322	13.932	424	26,7	53	3,3	4	0,3	7	0,4	303	19,1	172	10,8
Santa Fe															
Constitución	1.641	869.216	224.498	54	3,3	458	27,9	32	2,0	263	16,0	200	12,2	269	16,4
Iriondo	1.435	297.495	261.657	341	23,8	765	53,3	43	3,0	258	18,0	424	29,5	387	27,0
Tucumán															
La Cocha	660	47.325	33.758	164	24,8	90	13,6	9	1,4	57	8,6	283	42,9	400	60,6
Lules	159	12.230	9.230	31	19,5	17	10,7	2	1,3	3	1,9	29	18,2	31	19,5

Table 2. Good Agricultural Practices for Pest Control. Data from the Agriculture and Livestock breeding National Census (2002), adapted from the Agriculture Zonal Study, Huerga & San Juan, 2004.

Farm worker, rural population intoxications and pesticide food contamination are away of the scope of this chapter. However these risks are close linked to the environment pollution. There are two major pathways for pesticides reaching the environment:

1. Accidental spills, as punctual sources, generally registered in farm lands but can also occur away from rural environments (acute incidents, generally characterized as point source pollutions).

2. Continuous spills in lower concentrations due to pesticides applications to sowed land etc (chronic releases to the environment, generally characterized as non-point source pollution).

The following section deals with scientifically documented occurrence of pesticides in environmental compartments of Argentina, as a result of the abovementioned sources.

6. Pesticides reaching Argentinean environments

6.1 Water

Most of the Earth's living resources are found in specific geographical locations such as the global coastal environment and the catchment basins of large river systems. Furthermore, more than 3 billion people live in close proximity to these regions and are dependent upon it for either part or much of their food supply and industrial raw materials (Moore et al. 2004). The consequence of this situation is that much of the industrial, domestic and agricultural wastes are ultimately transported into aquatic environments, generating ecosystem changes and habitat destruction. These environments are of the greatest biological and economic significance and are quite likely to impact on human life's quality. In Argentina, the POPs environmental monitoring data is usually related to densely populated areas along the major rivers such as the Río de la Plata, Paraná and Reconquista. The bulk of this information relates to freshwater environments, in detriment of coastal marine areas, which have historically received less attention. There is a general lack of large-scale regional water monitoring programs in the country. Further, only potentially contaminated ecosystems are usually monitored. Scarce multidisciplinary approaches considering simultaneous evaluation of a number of factors and processes are found in the country; in fact, the historic freshwater quality monitoring has been developed on water chemistry and bacteriology, with measurements of only the main variables required for the determination of quality indexes (Salibián, 2006).

6.1.1 De la Plata River

De la Plata river is an international river (Buenos Aires province), which is part of the second largest hydro geographic system of South America, after the Amazon, and the fifth largest in the world. It covers an area of about 38,800 km^2 and drain a 3,170,000 km^2 basin. It is situated on the East coast of the country, delimited by Argentina and Uruguay. The tidal river is used for commercial fishing, angling, shipping to and from several mayor ports, recreation and tourism, especially along the sandy north shore. The waters of the river are a depository for many raw wastes and effluents from industries, cites and towns, and from the disposal of dredging spoils. Extensive chemical and physical pressures occur on this river, the same as other estuarial systems surrounded by cities and industries (Kurucz et al. 1998). In 1991, Janiot et al. observed the presence of six chlorinated pesticides (alpha, gamma and delta hexachlorociclohexane (HCH), heptachlor-epoxide, p,p'DDE and p,p'DDD) in sixteen water samples (water and suspended material) from the South shore and along a transect in the outer boundary of the river. Levels were higher near the coast, indicating the HCHs as the most frequent isomers. As levels decreased with increasing shoreline's distance, the observed distribution supported the hypothesis of a dilution effect in the river as a whole. More recent studies at the South coastal shoreline, showed that high concentrations of chlorinated pesticides (Mirex, Lindane (γHCH), Dieldrin, Aldrin, etc.; 6,8-80 ng/L) in the water column were limited to the mix areas of discharge and tributaries

(FREPLATA. 2004). A similar behavior was previously observed in the discharge area of *Río Santiago* River (a highly industrialized -8 km long- tributary of D*e La Plata* River); however, this spot was influenced by the discharge of other tributary, which receives chronic inputs from one of the major petrochemical complexes of the area. Relatively high organochlorine levels were also detected at coastal sampling stations from *La Plata* Harbor. The release of hydrophobic organochlorines from sediments disturbed by dredging and ship transit could have contributed to the high values of this place. As well as Janiot et al., this study pointed γHCH as dominant in the dissolved phase which was widely detected, in concentrations ranging between 0.9 and 61 ng/L (Colombo et al., 1990). In the same work, an hexachloro component of technical Chlordane was also detected at several stations in relatively high levels (0.4-28 ng/L). On the contrary, other chlorinated pesticides showed lower levels or were under the detection limit at several stations.

Geographically moving to the south, at the outer zone of *de la Plata* River*'s* Estuary is located the *Samborombón* Bay and the maritime front (Atlantic Ocean). The available information at these sites showed that, unless some punctual exceptions, pesticides in the water column were moderate to low (1.8±2.7 ng/L), away from the maximum limits suggested for the protection of the biota. Again, γHCH was the most frequent compound; however it was under the guide value in all cases (FREPLATA. 2004).

More than the 97% of the total water in *De La Plata River* comes from *Paraná* and *Uruguay* rivers. 2004 monitoring surveys showed that the contribution of organochlorinated and organophosphorous pesticides, PCBs and PAHs from these rivers were of little significance, as their concentrations in water were under the detection limits of the used techniques. Only PCBs were detected in a station near *Paraná de las Palmas* (46 ng/L, FREPLATA. 2004). In general, chlorinated pesticides occurred at very low concentration in water samples collected along the *Uruguay* River. As in *De La Plata* River, HCH isomers were the most commonly detected compounds, with concentrations ranging from the detection limits to 10 ng/L. Heptachlor, Heptachlor-epoxide, Aldrin, Dieldrin, p-p´DDE and p-p´DDT were occasionally encountered while o-p´DDE, p-p´DDD, o-p´DDD and o-p´DDT were never detected (Janiot et al. 1994).

In the lower *Paraná* River's Delta the concentrations of chlorinated pesticides in water were low and similar between sites (3.9±5.1 ng/L), as informed by Cataldo el al. in 2001. In this survey, γHCH accounted for 45-63% of total chlorinated pesticides, reflecting the relatively high water solubility of this chemical (7 ppm). Pollutant concentrations followed a clear geographic pattern with the highest values in the densely populated area of the *Reconquista* and *Luján* Rivers, lower levels in the *San Antonio*, and lowest loadings in the remote *Paraná de las Palmas* River. This gradient adequately matched the pattern of mortality rates of the mollusk *Corbícula flumínea*, which were highest in the *Reconquista-Luján* Rivers (40 ± 93%) and lowest (and not significantly different from the control) in the *Paraná* River (3.3 ± 23%).

6.1.2 *Reconquista* River

The Reconquista River is a typical lowland watercourse located at the Buenos Aires Province. More than 3 million people (10% of the population of the country) are settled on its basin. It is located in a temperate subtropical region, crossing what is known as the Pampa Region, sedimentary, flat in topography, with a total surface of 167,000 Ha and 50 km in length. It flows into the *Luján* River. For over a century, complex mixtures of domestic, agricultural, industrial solids and liquid wastes (mostly untreated) have been dumped in the river, which has thus become a typical example of the adverse impact of human activities on the health of aquatic environments (Salibián, 2006). For instance, Rovedatti et al. indicated that over 60 samples analyzed 35% presented organochlorine pesticides in a concentration greater than 0.1µg/L (2001). On the opposite, in the same study organophosphates were found in no case, possibly due to their low persistence because of their short half-lives in aquatic environments. Some of the detected compounds were DDT and its metabolite DDE, γ-Chlordane, Heptachlor and HCH isomers. They did not find temporal or spatial trends and there was not a relationship between the time of samplings and the fumigation season for farming purposes. At all locations, pesticides levels were found to be between 40 and 400 times higher than the legal limits established for protection of aquatic life. Recently, new studies demonstrated the effects of poor water quality and environmental deterioration on biomarkers of native fishes species, however in that paper, organochlorine compounds were not found in the water samples (de la Torre, 2007). This fact could be explained due to the low water solubility of organo-halogenated compounds, however, it was clearly documented the occurrence of the "*hit and run*" effect: although the xenobiotic is not present, it is possible to measure its effects in biota.

6.1.3 *Pergamino-Arrecifes* system

Soybean production in Argentina has increased over the last decade, currently with 10,000,000 hectares of sowed land. A total of 95% of this area corresponds to a transgenic variety of glyphosate tolerant soybean, which is cultivated by direct sowing (Pengue, 2005). Recent monitoring surveys showed that the levels of glyphosate in water, from a transgenic soybean cultivation area located near to tributaries streams of the *Pergamino-Arrecifes* system in the north of the province of Buenos Aires, ranged from 0.10 to 0.70 mg/L (Peruzzo et al. 2008). The authors concluded that temporal variation of glyphosate levels depended directly on the time of application and the rain events. This emerges as a documented example of pesticides reaching the environment as a consequence of inappropriate agriculture practices.
There is scarce available information about pesticides pollution for other regions of Argentina. In the Central and Midwest region of the country (i.e.; San Juan and San Luis provinces), on account of the intense agricultural activity near the rivers that drain the region, the presence of high pesticides' concentrations is likely to occur.
In 2003, Baudino et al. performed a survey at San Juan and after analyzing the overall mean value for the concentration of OCs in water sources, only βHCH (6.556 µg/L) and Dieldrin (5.354 µg/L) were above the maximum permissible value recommended by international organizations (E. C. Council Directive 1980). The authors concluded that the San Juan River basin was the most contaminated area, possibly due to the higher population density, larger cultivated area and industrial complexes.
In San Luis province, water samples coming from agricultural-livestock areas principally indicated an homogeneous distribution of the pesticides found in the area with a clear predominance of HCH isomers and DDT analogs over chlorodines. A prevalence of 4, 4-DDE was observed, suggesting old DDT inputs. Further, this was corroborated by local farmers (Luco et al. 1992), as DDT was a common pesticide in the past.
At the South region of the country (i.e.; *Río Negro* province), organochlorinated and organophosphorous pesticides have also been detected. Monitoring stations located at Negro River basin's origin, confluence of *Limay* and *Neuquén* Rivers, detected the presence of α-HCH, γ-HCH and Parathion, but in non toxic concentrations for aquatic biota. DDT and metabolites have also been detected but in much less quantity (Natale et al., 1995). Added to this, near this region, ground water samples from fruit production farms belonging to the

Valley of *Neuquen* River frequently showed organophosphorus pesticides levels that exceeded the acute toxicity risk ratios for aquatic life protection (Loewy et al. 2003). It was found that some pesticides, as Azinphos methyl, had a high detection frequency - 66% of the samples- with concentrations varying from non detectable to 48.9 ppb. Dimethoate, Metidathion and Phosmet were also detected but in less frequency and values. Finally, these authors found that pesticides in ground water samples followed seasonal variations and temporal trends.

6.2 Sediments

Regional POP information for sediments is also dominated by chlorinated pesticides. Overall, as observed for waters, sediment data indicates a complex situation in densely populated areas affected by urban-industrial inputs. The applied pesticides can be transported through surface runoff, leaching, and vapor phase and generally, estuarine and marine sediments are the temporary or long-term ultimate sinks for most of OCs. Consequently, these sediments act later as secondary sources of these substances reaching the ocean and biota. The most frequently reported POPs are DDTs, HCHs, PCBs, and heptachlors, however, concentrations show a large variability.

The FREPLATA 2004 program showed the occurrence of pesticides in sediments from the discharge of *De la Plata* River basin. The organochlorines' levels were around 1.9±3.84 ng/g. In the middle and external area of the river, the concentration was under the detection limit of the method. Contrarily, on the South coast of this river, the values of toxic compounds were higher than the levels suggested for the protection of aquatic biota. It was found that pesticide levels diminished by distance from coast line and from tributaries discharge's sites. Similarly, littoral affluents between *De La Plata* River and Necochea City showed concentratios of 3.1±6.5 ng/g, with maximum values of 12-31 ng/g in *Atalaya* and *Mar del Plata* harbor. In general Chlordane, DDT and its derivates predominated among OCs.

In 2001, pesticides monitoring in the *Reconquista* and *Luján* Rivers showed levels around 2.8±3.9 ng/g, being the trans-Chlordane the most abundant (Cataldo el a., 2001). As previously shown in sediments sampled from *De la Plata* River (Colombo et al., 1990), the abundance of DDD and DDE, relative to the parent compound, indicated that DDT was being readily metabolized in the sediments.

As expected by anthropogenic pressure, the highest loadings of pollutants occurred in areas located closer to the urbanized area, decreasing toward the more remote sites. The same behavior -as abovementioned for water- was observed in *Corbicula fluminea* mortality. As expected for hydrophobic substances, all sediment samples were enriched in organic contaminants relative to water, then, in agreement with their highest pollution levels the strongest toxicity responses were obtained with them (Cataldo et al., 2001).

In relation with organophosphorus pesticides, levels of Glyphosate in sediment and soils from a transgenic soybean cultivation area located near to tributaries streams of the Pergamino-Arrecifes system in the north of the Buenos Aires' province were between 0.5 and 5.0 mg/Kg (Peruzzo et al. 2008).

Results from two creeks of the Southeast Argentina region showed similar total OCs concentrations in sediments, in the range from 6 to 25 ng/g (dry wt.), being below the sediment quality criteria demanded for wildlife protection. ΣEndosulfans, ΣDDTs and ΣChlordanes were the main OCs' group, with Endosulfan sulfate being the most frequent and abundant compound. The predominance of metabolites with respect to parent

compounds suggested a contamination mainly by runoff from aged and weathered agricultural soils (Miglioranza et al. 2004). The latter shows another clue about pesticides inputs to the environment due to inappropriate application practices.
Moving toward the south, the Southwest coastal area of Buenos Aires province presented total OCs levels from non-detectable to 166.5 ng/g (d.w.) (Menone et al. 2001; Arias et al. 2010). In example, in terms of average concentration, the major pesticides detected in sediments from *Bahía Blanca* Estuary were Mirex > Heptachlor-epoxide > Metoxychlor > δ-HCH > Endosulfan I > α-HCH > Heptachlor > DDE > DDD (Arias et al. 2010).
Macroinvertebrate bioturbation affects the fate and partitioning of sediment-bound contaminants in sediment profiles, pore water and the water column. These factors increase the rate of important physicochemical processes that occur at the sediment-water interface such as diffusion, desorption, degradation, and resuspension of organic and inorganic compounds (Ciarelli et al. 2000). The burrowing crab, *Neohelice granulata*, is a bioturbator widely distributed in SW Atlantic estuaries. These crabs inhabit almost all the zones of the intertidal, the soft bare sediment flats and the lower salt marsh zones (Iribarne et al. 1997). Crab beds act as sinks for OC pesticides in SW Atlantic coastal environments. Sediments from these sites from the northeastern of the country exhibited total OC pesticide concentrations in the order of other Argentinean coastal environments (Menone et al. 2000; Menone et al. 2004). β- and γ-isomers of Hexachlorocyclohexane, γ-Chlordane, Dieldrin and p,p-DDE were the dominant OC pesticides detected in all sediment samples, while Aldrin, Metoxichlor and p,p´-DDD were below the detection limits (Menone et al. 2006).

6.3 Soils

Extensive agricultural practices can cause soils’ degradation by means of hydric and wind erosion, structure deterioration, salinization, fertility diminution and desertification. Moreover, soils are natural sinks for persistent and lipophilic compounds that strongly adsorb to organic carbon and remain relatively immobile in this reservoir. Pollutants enter the soil either by deposition from air, drift or by washing-off from plant surface during rainfall or irrigation. The proportion of applied pesticide reaching the target pest has been found to be less than 0.3%, thus leaving over 99% elsewhere in the environment (Pimentel 1995). POP monitoring in soils is also limited within the region. There are no regional monitoring programs, and most data refer to agricultural areas.
Agricultural soils in the Southeastern region of Argentina could be an important source (if not the major) for OC pesticides. In 2003, the highest values for OCs (656.1 ng/g d.w.) were found in the most superficial layers of soil, even though at sites which have never received direct OCs application (Miglioranza et al., 2003). At sowing lands, OCs levels were of 30.19 ng/g dry wt in the surface horizon. The pattern of OCs distribution was similar at all sampled soils, with DDT and metabolites > HCHs > Heptachlor > Chlordanes. In this work the authors concluded that volatilization could have been one of the major causes of pesticide loss from the sowing target area, due to inappropriate management practices (Miglioranza et al. 2003b).
In the same geographical area, other researchers found that total OCs levels in soil from conventional farm were greater than those from organic farm, but with the same distribution pattern - DDT and derivatives as the major compounds- (Gonzalez et al. 2005).
In 2005 Andrade et al. studied the concentrations of organochlorine and organophosphorus pesticides in soils from the South of Buenos Aires province. Results showed that the

horticulture dedicated soils contained higher pesticide levels than the wheat, soybean and sunflower dedicated ones. This fact probably reflected the differences in soil management according to the different crops. The studied soils contained DDT and their metabolites, Heptachlor-epoxide, Dieldrin, Endrin, Lindane, Malathion and Parathion. In the same study the authors concluded that the soil pesticide accumulation was principally due to the age and persistence in the application of these products (Andrade et al. 2005).

Concentrations of OCs in the Patagonia region are of importance on account of their massive past and/or present use in fruits and vegetable production. Recent studies showed that levels in *Río Negro* Valley reached up to 492 ng/g and 3.43 ng/g for DDTs and Endosulphanes, respectively (Mitton et al., 2010). The authors found that in different vegetables and fruit plants of this region, OCs were more abundant in the roots than in the aerial parts. In this way, they demonstrated the translocation of toxic compounds from the soils and the capacity of plants for bioaccumulating highly hydrophobic compounds.

6.4 Air

POPs monitoring in air as well as studies about volatilization of persistent pollutant from the sowed land are scarce in Argentina. Stronger efforts have to be made in this research discipline in order to test the volatilization/air drift and atmospheric transport from other matrices.

6.5 Biota

Available data on POPs in Argentina for both aquatic and terrestrial animals is poor when comparing to other regions of the world. Among this information, aquatic organisms are by far the most studied organisms; in special bivalves and fish are the preferred ones. In Argentina, the most comprehensive program of POP monitoring in coastal organisms was the global Mussel Watch (Farrington and Tripp 1995). In this monitoring, the highest levels of POPs were obtained in mussels from the coastal Hudson City (southern Buenos Aires province). On the one hand, among the reported POPs, PCBs dominated, followed by Chlordanes and DDTs. On the other hand, in 2006, Endosulfan sulfate, Chlordanes, HCH isomers and DDT compounds dominated in tissues and ingested food of fish (*Cynoscion guatucupa*), from *Bahía Blanca* Estuary (Lanfranchi et al., 2006). These authors also identified α-Chlordane, Heptachlor and p,p´-DDE as the major bioaccumulated and biomagnified OCs.

Recent studies in birds from the arid-semiarid Midwest region of Argentina showed the presence of several OCs in fat tissue [ΣHCH range: ND to 3168.41 ng/g fat, ΣCHL range: ND to 4961.66 ng/g fat, ΣALD range: 287.07 to 9161.70 ng/g fat, ΣDDT range: 1068.98 to 6479.84 ng/g fat] with the exception of p,p'-DDT. Total OCs concentration in all bird species ranged from 2684.91 to 19231.91 ng/g fat (Cid et al. 2007). This point to an immediate threat, since in a previous study, Gil et al. indicated concentration of pesticides under the detection limit of the method at Patagonia coasts, corresponding the higher value for pp´-DDE. In the same study, the concentration in mammals did not exceed 0.1 mg/L (Gil et al., 1997).

7. Conclusions

About the regulatory point of view, Argentina's government implemented the Rotterdam Convention by the year 2000. Despite this, by the date of this convention, Argentina already had several pesticide regulations' laws. This reflects a strong national regulatory framework, however, there are a few provinces and cities which run their own and independent registry and regulations. This reflects a kind of incoherence in the current legislation. Added to this, some of the more severely regulated pesticides have been identified as main compounds in the illegal trade-market (Pentachlorophenol, Parathión, DDTs, HCHs and Daminozide) and in environmental samples.

About *Good Agricultural Practices*'s adoption, although many steps have been taken, Argentina still has a long way to cover. As a matter of fact, recent projections of several agriculture and livestock trend researchers for one of the most industrialized agriculture regions showed up to 40% of the producers with no particular system of Agricultural practices.

According to the environmental point of view, the most relevant problems with pesticides arise from the improper use, disposal, and maintenance of the available stock. The discharge of untreated effluents throughout the whole region is recognized as a major input pathway of POPs into the environment. There is enough scientific information to conclude that pesticides are extensively reaching the environment, with levels in some compartments exceeding the permitted values to protect wildlife. These levels include several already banned pesticides.

It came clear that POP's survey, inventory and monitoring are still poorly developed in the country. Argentina lacks of routine monitoring programs and most of the available data were generated by punctual studies in urbanized areas. The bulk of the information corresponded to aquatic animals, waters and sediments, with scarce information regarding soils and atmosphere. Finally, it is recommended the consideration of the actual relevance of atmospheric transport of pesticides, since they were usually identified in pristine regions or geographically distant areas from the pesticides application points.

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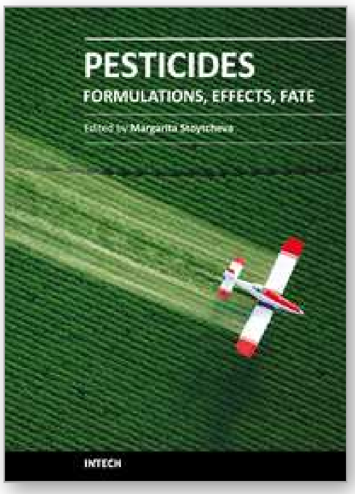

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.