PESTICIDE MONITORING IN RIBEIRA VALLEY, SOUTHEASTERN BRAZILIAN.

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Abstract

Nowadays, agriculture is an important part of the Brazilian economy. According to the Food and Agriculture Organization (FAO) there is a great consumption of pesticides in Brazil, it has occupied the eighth world place, as mentioned by the National Industries of Agriculture Defense Products Syndicate of Brazil, and São Paulo State is the greatest consumer. The Ribeira Valley is located between southern of São Paulo State and eastern of Paraná this area has 25,000 km^2 and is the major remaining Atlantic Forest of Brazil. Its economy is based on agriculture (bananas, rice and tea), mining and extraction of forest products (palm heart). The objective of this work is monitoring the level of pesticides atrazine, simazine (triazines); aldicarb, carbaryl, carbofuran (carbamate) and trifluralin (nitroaniline) in nature and treated water of the Ribeira do Iguape River Basin (Ribeira Valley). From the six pesticides studied three are established at the Brazilian guideline drinking-water standards - atrazine, simazine and trifluralin. The pesticides carbaryl and carbofuran have been among the most used in regional agriculture. At this moment, it was carried out four collecting samples in ten catchments areas of the Ribeira do Iguape River watershed, in a seasonal cycle. The analyses detected traces of aldicarb, atrazine, carbofuran, simazine and trifluralin in some these samples. This work can serve as a baseline both to management proposes and environmental management of the Ribeira do Iguape River watershed.

Key words*: pesticide monitoring; water surface; water supply; control water pollution*

1 INTRODUTION

Human activity is affecting the global environmental in a profound way. When sources of water pollution are enumerated, agriculture is, with increasing frequency, listed as a major contributor environmental pollution.

Existing knowledge indicates the agriculture operations can contribute to water quality deterioration through the release of several materials onto water: sediments, pesticides, animal manures, fertilizers and other sources of inorganic and organic matter. Many of these pollutants reach surface and groundwater resources though widespread runoff and percolation, hence, are called “non-point” source of pollution. Indication, quantification and control of non-point pollution remain relatively difficult task as compared to those of “point” sources of pollution (Ongley, 1996).

It is well know that agriculture is the single largest user of freshwater resources, using a global average of 70% of all surface water supplies. Except for water lost through evapotranspiration,

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agriculture water is recycled back to surface and/or groundwater. However, agriculture is both cause and victim of water pollution.

The agricultural impacts on water quality are diverse. Runoff of pesticides leads of contamination of surface water and biota; dysfunction of ecological system in surface waters by loss of top predators due to growth inhibition and reproductive failure; public health impact from eating contaminating fish. Pesticides are carried as dust by wind over very long distances and contaminate aquatic system 1000s of miles away.

While agriculture use of chemical is restricted to limited number of compounds, agriculture is one the few activities where chemicals are intentionally released into the environmental because they kill things.

World wide pesticide consumption breaks down as follows: Asia (25%), Western Europe (25%), North and South America (40%), with the rest of world sharing the remaining 10% (Sabik, 2000).The Brazilian Environmental Ministers database indicates that Brazil has been between ten main productions and consumption of chemical products and pesticides (Brazil, 2003). Although the number of pesticides in use is very large, the largest usage tends to be associated with a small number of pesticides products.

Data on water pollution in developing countries are limited. Monitoring data for pesticides are generally poor in much of word and especially in developing countries. Pesticide monitoring requires highly flexible field and laboratory programmers that can respond to periods of pesticide application, which can sample the most appropriate medium (water, sediment, biota), are able to apply detection level that have meaning for human health and ecosystem protection, and which can discriminate between those pesticides which appear as artifacts of historical use versus that are in current use.

The use of pesticide in developing countries is extremely variable. It is extremely heavy dosage in intensive agricultural areas of Brazil. The **Figure 1** indicates pesticides dosage for state of Brazil. The Brazilian State of Sao Paulo is typical of developing countries undergoing rapid expansion of agriculture (SINDAG, 2002).

In November 1997, the Brazilian media showed a serial of documentary TV-programs and articles in newspapers regarding a high frequency of pesticide intoxication among agricultural works (133 cases per 100 000 inhabitants), some them leading to death. In Apiaí, a municipality located in Ribeira Valley, south-east border of São Paulo State and the east border of Paraná State, Brazil, around one third of the case were children and teenagers that had started working in tomato cultivation very early. In November 1998, another documentary program, about the same subject, showed that one year later nothing had changed and agricultural workers were still dying in the region due to back the lack of information, equipment and training (Molander, Moraes, 1999).

Ribeira Valley hold the greatest continuous formation of Atlantic Rain Forest on Brazil, with more than 1 200 hectares of well preserved florest. Together with environmental and cultural elements of great interest, Ribeira Valley presents the lowest values of some social indicators of São Paulo State and Paraná, including the highest rates of child mortality and illiteracy.

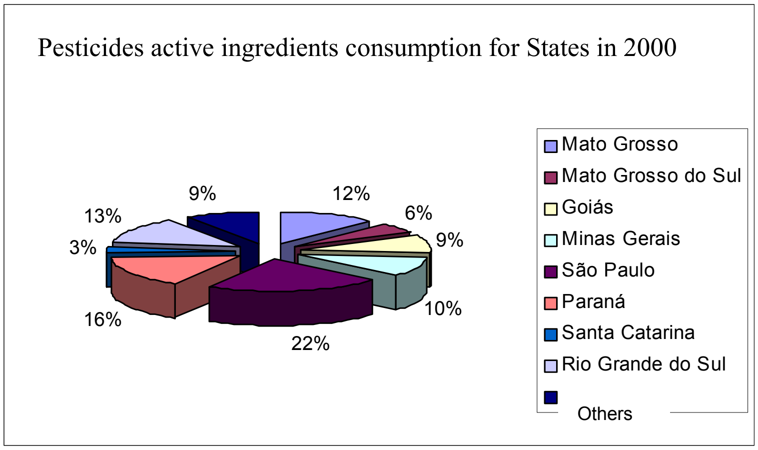

Figure 1: Brazil pesticides consumption for States in 2000 (SINDAG, 2002)

The population of about 350 000 inhabitants, does not have economical alternatives for sustainable development that could permit the rational usage of huge existing environmental and cultural heritage (Hogan, et al, 2001). The economy in the Ribeira Valley is based on agriculture (bananas, tea), mining and extraction of florest products (palm heart). According to the Agricultural Secretary of State of São Paulo, a many different fungicides, insecticides and herbicides are applied in the plantations in the region. The substances belong to different chemical group. The Table 1 shows the list of pesticides used in the region and their activity ingredients toxicological properties (Alves, 2001).

The objective of this study is to investigate the seasonal and spatial variability in pesticides concentration in water surface in River Ribeira de Iguape – Basin and in supply water. Several river water parameters were measured during the study.

2 MATERIAL AND METHODS

2.1 Sampling Campaigns

The work aimed to evaluate the environmental water quality in the localities of water supply intake for the 10 cities on the Ribeira Basin. The sampling was carried out at in a hydrologic period, were sampled bimonthly for 12 months (march 2002/ fev/2003). At study started with 18 sites were surveyed. The number of sites was reduced to 10 during the second trip. Sites were selected according to proximity agriculture fields and urbanization.

2.2 General characterization of the study area

The Ribeira do Iguape River Basin, an area of 25,000 km2, (23^0 30′ S - 25^0 30'S and 46^0 50'' W - 50^0 00' W) is home to mayor intact remnants of Brazil's Atlantic Florest, with more than a million hectares of nactive vegetation, occupying no les than 64% of region's territory in 1998. Seven state parks, two ecological station and tree environmental protected areas have been create. More than a half million hectares are protected, restricting economic activities. Its is the least urbanized region of the state of São Paulo. The watershed is 17.180,09 km2. The hydrographic basin from Ribeira River have a large agriculture influence on limnologic, physic and chemical characteristics. The surface water is used for agriculture, public as well as far other uses.

The climate is classified as subtropical humid (Cfs), 50% of basin mesotermic humid (Cfd), 45% of basin and tropical humid (Af), 5%, according to Kopper. Two air masses affect the region during a year. The Atlantic Tropical air mass is the most prevalent, and influences the rain distribution. The influence of the Atlantic Polar air mass just last for sort period during the winter season, the dry period occurs between April to September (Hogan et al, 2001).

Table 1: The main active ingredients of the pesticide products used in Ribeira Valley .

PESTICIDES COMERCIAL NAME	ACTIVE INGREDIENTS	TOXICOLOGICAL CLASSES	CONSUMPTION IN 2000	TYPE
Mineral oil	Hidrocarbonetos	IV	1800000 L.ano^{-1}	Fungicides
Tilt	Propiconazole	III	20000 L.ano^{-1}	Fungicides
Folicur	Terconazole	III	4000 L.ano^{-1}	Fungicides
Juno	Propiconazole	III	4000 L.ano^{-1}	Fungicides
Cercobin	Benzimidazoles	IV	4000 L.ano^{-1}	Fungicides
Priori	Azokystrobin	III	1000 L.ano^{-1}	Fungicides
Furadan líquido	Carbofuran	I	4000 L.ano^{-1}	Insect/Nemat
Furadan granulado	Carbofuran	III	60000 Kg.ano^{-1}	Insect/Nemat
Servin	Carbaryl	II	5000 L.ano^{-1}	Insect/Nemat
Counter 50G	Terbufós	I	2000 L.ano^{-1}	Insect/Nemat
Gramoxone	Paraquat	II	20000 L.ano^{-1}	Herbicides
Gramocil	Paraquat + Diuron	II	60000 L.ano^{-1}	Herbicides
Roundup	Glifosato	IV	30000 L.ano^{-1}	Herbicides
Finale	Glufosinato	IV	25000 L.ano^{-1}	Herbicides
Zapp	Sulfosate	IV	8000 L.ano^{-1}	Herbicides

(Alves, 2001).

The main tributaries to basin are: Juquiá river, Ribeira river, Ribeira de Iguape river; São Lourenço river; Jacupiranga river, Pardo river, Uma da Adeia river and Itariri river. The reservoirs are: Alecrim, Barra, França, Porto Raso, Salto de Iporanga and Serraria.

2.3 Sampling Sites

The description of sample sites is present in Table 2. Latitude and longitude of each site was determined using a GPS receiver (GPS 45 – Garmin). All sites were selected according to land use activities. Figure 2 is a schematic representation of sample sites location relatively to the main sources of pollution. The classifications of these points are described following: Site $\mathbf{I_I}$ (Iporanga) were selected as controls (absence of known sources of contamination upstream). Sites $\mathbf{R_E}$ (Eldorado), $\mathbf{J_C}$ (Cajati), $\mathbf{R_S}$ (Sete Barras) $\mathbf{J_T}$ (Juquitiba) and $\mathbf{J_A}$ (Juquiá) are in streams located near agriculture areas and mining. Site $\mathbf{R_R}$ (Registro) is also in streams located near agriculture areas and urbanization. Site $\mathbf{R_I}$ (Iguape) and $\mathbf{I_C}$ (Cananéia) were selected as estuarine and environmental protected areas.

2.4 Selected parameters

Anthropogenic organic compounds present the main hazard to life and health of humans and the flora and fauna. The number of known organic compounds is now estimated to be about 16 million. Presently, about 70,000 organic compounds are commercially available with an annual global production of 100-200 million tons. Approximately one-third of all organic compounds produced ends up in the environment, including water and many of which are biologically active. Pesticides are particularly important pollutants among organic compounds as a result of their common use, persistence in the environment and toxicity. They are predominantly anthropogenic. Pesticides are a group of organic compounds hazardous to human health and life. They are used in agriculture, industry and households to kill weeds, insects, fungi, rodents, mollusks, mites, round worms, aphis and eggs then they are necessarily toxic. The present global annual production of pesticides is estimated at several hundred thousand tons (Biziuk, 1996).

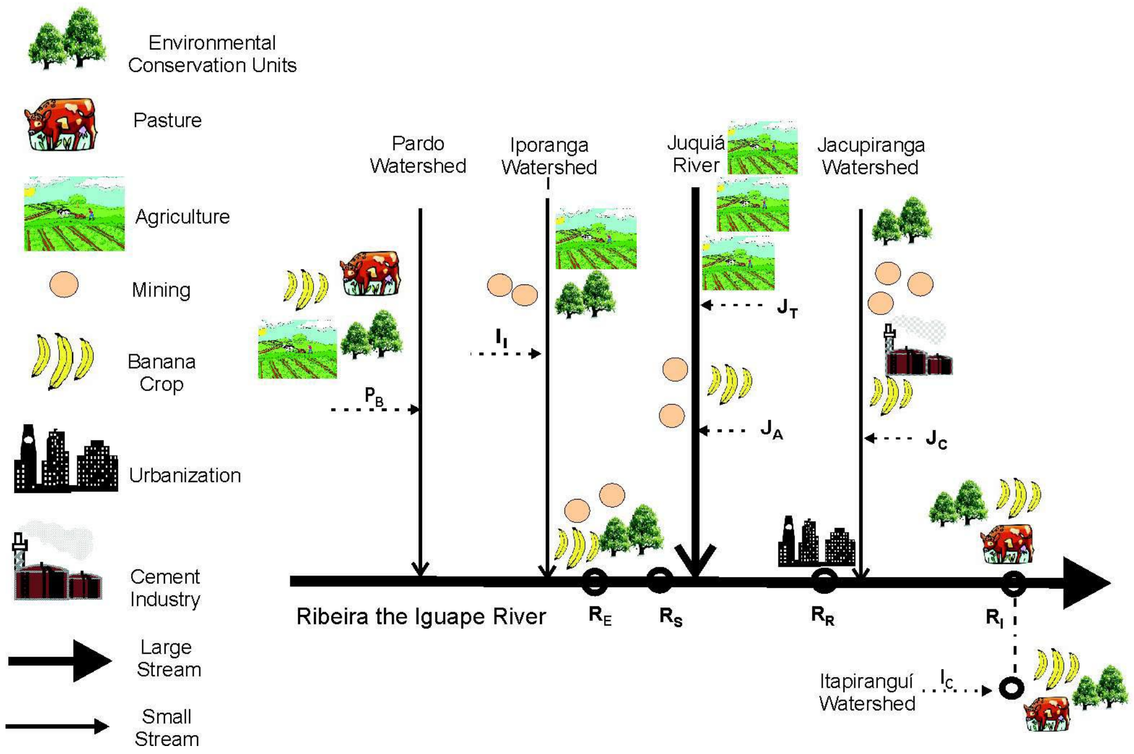

Figure 2: Schematic representation of sample sites and locations of main sources of pollution- Ribeira de Iguape Basin.

In this work the concentration of atrazine, simazine (triazines); aldicarb, carbaryl, carbofuran (carbamate) and trifluralin (nitroaniline) were measured in superficial and supply water of the Ribeira do Iguape River Basin (Ribeira Valley). From the six pesticides studied three of them are controlled at the Brazilian guideline drinking-water standards - atrazine, simazine and trifluralin and have been indicated in the Dangerous Substance Directive - 76/464/EEC - (the so-called black list) (Barceló, 1993). Pesticides carbaryl and carbofuran have been among the most used in regional agriculture (see Table 1). The abiotic factors also were measured, included temperature, pH, toxic metals and total phosphorus (Pires et al, 2002; Pires et al 2000).

Table 2: Localization and description of the sampling sites. (SABESP, September 2002 date).

City	Catchments	Type of Treatment	Code	Date started operation	Flow (L/s)	Latitude and longitude
Registro	Ribeira de Iguape River	ETA	R_R	1994	188	**Catchment** S: 24^0 28’ 24,5” WO: 47^0 50’ 36,2” **ETA** S: 24^0 29’ 05,5” WO: 47^0 50’ 58,9
Sete Barras	Ribeira River	ETA	R_s	1994	25	Catchment S: 24^0 23’ 32,0” WO: 47^0 55’ 41,7”/ ETA S: 24^0 23’ 28,7” WO: 47^0 55’ 42,7”
Cajati	Jacupiranguinha River	ETA	J_C	1998	80	Catchment S 24° 43’ 48,9” WO: 48° 07’ 55,0” ETA: S 24° 43’ 39,8” WO 48° 07’ 59,2”
Barra do Turvo	Pardo River	ETA	P_B	1994	16	Catchment S 24° 45’ 38” WO 48° 30’ 26,2” ETA S 24° 45’ 33,7” WO 48° 30’ 14,3”
Cananéia	Itapirangui River	ETA	I_C	1990	80	Catchment S: 24° 55’ 55,0” WO: 47° 53’ 39,3” ETA S: 24° 55’ 55,0” WO: 47° 53’ 39,3”
Eldorado	Ribeira River	ETA	R_E	1986	33	Catchment S: 24^0 31’ 09,0” WO: 48^0 06’ 52,1/ ETA S: 24^0 31’ 12” WO: 48^0 06’ 51,2”
Juquiá	Juquiá River	ETA	J_A	1986	27	Catchment S: 24^0 19’ 09,6” WO: 47^0 37’ 31,4” ETA S: 24^0 18’ 46,0” WO: 47^0 38’ 25,3”
Iguape	Ribeira de Iguape River	ETA	R_I	1978	78	Catchment S: 24^0 40’ 52,5” WO: 47^0 35’ 49,7” ETA S: 24^0 42’ 28,2” WO: 47^0 33’ 58,8”
Juquitiba	Godinhos` stream	ETA	J_T	1996	50	Catchment S 23° 55’ 29,6” WO 47° 03’ 36,3” ETA: S 23° 55’ 49,9” WO 47° 03’ 54,3
Iporanga	Iporanga	ETA	I_I	1987	10	Catchment: S: 24^0 34’ 47,9” WO: 48^0 35’ 29,6”/ ETA S: 24^0 35’ 03,7” WO: 48^0 35’ 45,2”

Water treatment plant = ETA

3 METHODOLOGY

The Pesticides were extracted by using solid-phase extraction (SPE) cartridges from SPE ENVI C_{18} 500mg 3mL (polipropilene) Supelco and compounds were separated and quantifield by reverse phase using Liquid Chromatographic – HPLC with UV detection at 220ηm (Lebre, 2000; Pires et al, 2002). Water samples (02 glass bottles, 1.000 mL from each sampling site) were buffered with monochloroacetic acid and potassium acetate in pH =3. Samples stored at 4^0C, transported to laboratories in São Paulo City and analyzed within 15 days of sampling. The analysis were measured at the Laboratory of Environmental Chemistry of the IPEN (Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil).

4 RESULTS AND DISCUSSION

Obtaining reliable data the determination of species in drinking water and surface water samples the use of analytical method that has been validated as to their accuracy, and these analytical methods must be continuously monitored to verify that they remain in control.

The mean and range distribution of the pesticides in the public water supplies and groundwater samples together with EPA and Resolution Conama 20 and Portaria 1469, Brazilian regulations for surface water and drinking waters, limits are shown in Table 3 (Brazil, 1986, 2000).

Tables 3 present average results of pesticides analyses in superficial and drinking water at seasonal cycle. In both samples the concentrations of pesticides are relatively low. One hundred samples were analyzed, fifty superficial water sample and fifty drinking water sample, and were found traces of pesticides in only twenty samples. The Figures 3 and 4 showed the pesticides residues distributions in superficial and drinking water samples, respectively.

In all samples analyzed, the means concentrations of all the pesticides for which WHO and Brazilian regulations limits exist were below the recommended values. Carbofuran was detected in 50% of the surface water samples, with a range distribution of 0.12–0.56 μgL^{-1}. The distribution of carbofuran in drinking water was 0.12–2.2 $\mu g\ L^{-1}$. Traces of albicarb were found in site J_a (Juquiá River). In surface water of Stream Godinhos' in Juquitiba Municipes (J_t) traces of simazine, carbofuran and trifluralin have been detected. It has been more information about use of pesticides in streams.

5 CONCLUSIONS

The choice of stressors pesticides in this study have been guides by an analysis of the possible way in which human activities (agriculture and human settlements) can influence the ecosystems. Because agricultural water pollution is of a non-point source nature, the quantitication of pollutants and their impact is more difficult than for point source.This study has shown that the trace pesticides quality of water in Ribeira de Iguape Basin is generally good, most of elements satisfying the Brazilian and WHO regulation for drinking waters. However, the agricultural water pollution is a reality, and prevent pollution of source is necessary.These is the first detailed study of trace pesticides aldicarb, simazine, carbofuran, carbaryl, atrazine and trifluralin in surface and drinking water in Ribeira Valley

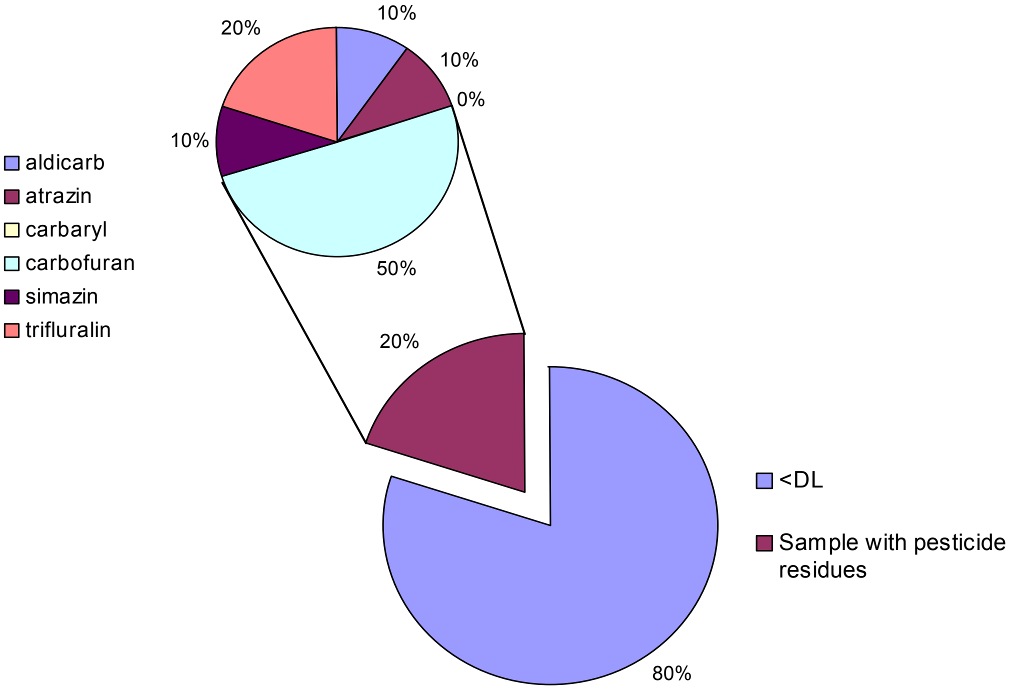

Figure 3: Pesticides residues distributions in superficial water sample

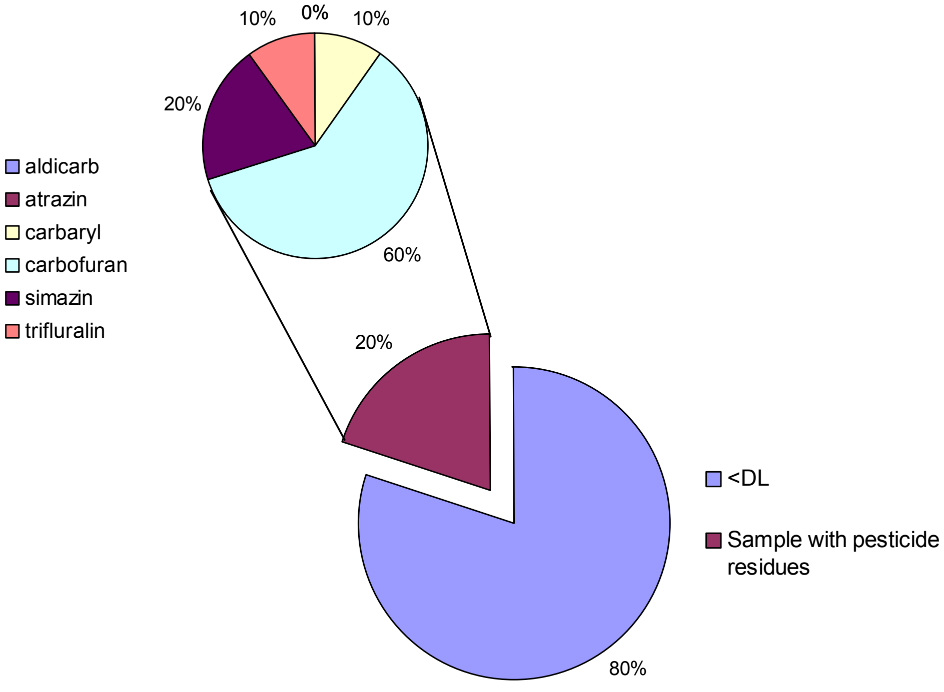

Figure 4: Pesticides residues distributions in drinking water sample

Table3: Results [a] of Ribeira Valley Basin monitoring in a seasonal cycle from march/2002 until February/2003.

City/ Catchments/ Code		Registro / Ribeira de Iguape river / (R_r)	Sete Barras / Ribeira de Iguape river / (R_s)	Cajati / Jacupiranginha river / (J_c)	Barra do turvo/ Pardo river / (P_B)	Cananéia / Itapitangui river / (I_c)	Elorado / Ribeira Iguape river / (R_e)	Juquiá / Juquiá river / (J_a)	Iguape / Ribeira de Iguape river / (R_i)	Juquitiba / Godinhos' stream / (J_t)	Iporanga / Iporanga river / (I_r)	Regulation in Brazil / EPA
Aldicarb (μGl^{-1})	**Sw**	<0,17	<0,17	<0,17	<0,17	<0,17	<0,17	<0,17 - 2,15	<0,17	<0,17	<0,17	Nr/-
	Dw	<0,17	<0,17	<0,17	<0,17	<0,17	<0,17	<0,17	<0,17	<0,17	<0,17	Nr/7,0
Simazine (μgL^{-1})	**Sw**	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01 – 0,03	<0.01	Nr//-
	Dw	<0.01	<0.01 – 0,26	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01 – 0,03	<0.01	2,0/4,0
Carbofuran (μgL^{-1})	**Sw**	<0,12	<0,12 – 0,24	<0,12 – 0,12	<0,12	<0,12 – 0,52	<0,12 – 0,56	<0,12	<0,12 – 0,03	<0,12 – 0,31	<0,12 – 0,54	Nr/-
	Dw	<0,12	<0,12	<0,12	<0,12 – 0,60	<0,12 – 2,20	<0,12	<0,12	<0,12 – 0,65	<0,12 – 0,65	<0,12 – 0,23	Nr/40,0
Carbaryl (μgL^{-1})	**Sw**	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	20,0/Nr
	Dw	<0,01	<0,01 – 0,92	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01	Nr/-
Atrazine (μgL^{-1})	**Sw**	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	Nr/-
	Dw	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	<0,02	2,0/3,0
Trifluralin (μgL^{-1})	**Sw**	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10 – 0,59	<0,10	Nr/-
	Dw	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10	<0,10 – 2,06	<0,10	20,0/Nr

Obs: Sw = superficial water; Dw = drinking water

a = results are avarege for five samples; Nr- Non regulatory EPA= maximum contaminant level goal

São Paulo, Brazil. Although this study identifies the relative importance of antropogenic inputs of trace pesticides to the freshwater reaches of the Ribeira de Iguape River, further work is required to quantify, the contribution of an elements from the various key components with each input (e.g. agricultural and urban runoff). Quantification of these components is consistent with a revised framework for the regulation and management of water resources in Brazil (BRASIL, 2000), one which adopts a more holistic and integrated pollution prevention approach. It is now clear that current regulatory approach is not as appropriate tool for resolving the problems of diffuse source of pollution, such as urban and agriculture runoff, which have just as great, if not great, affect on water quality.

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REFERENCES

ALVES, G.G. Agrotóxicos no Vale do Ribeira Coordenadoria de defesa agropecuária (CDA) – Escritório de defesa agropecuária de Registro, 2001.

BARCELÓ, D.; Journal of Cromatography, 643(1993) 117-143.

BIZIUK, M.; et al Journal of Chromatography A, 754(1996) 103-123.

BRASIL. MINISTÉRIO DO DESENVOLVIMENTO URBANO E MEIO AMBIENTE. CONSELHO NACIONAL DO MEIO AMBIENTE (CONAMA). Resolução n^o 20 de 18/06/86, D.O.U., de 30/07/86, Brasília. BRAZIL.

BRASIL. MINISTÉRIO DA SAÚDE. Portaria n^0 1469 de 30/12/2000, D.O.U., Brasília.

EPA Drinking Water Standars and Health Advisories 822-B-00-001, SUMMER 2000, Office of Water 4304

HOGAN, D. J.; CARMO, R. L.; ALVES, H. P. F.; RODRIGUES, I. A. Desenvolvimento sustentável no Vale do Ribeira (SP): conservação ambiental e melhoria das condições de vida população. www.unicamp.br/nepo/staff/roberto/valeribeira.htm – 16/12/01.

LEBRE, D.T. Desenvolvimento de metodologia para a determinação de herbicidas e inseticidas em águas superficiais utilizando extração líquido - sólido e cromatografia líquida de alta eficiência. Dissertação de mestrado, IPEN, 140p. Maio 2000.

MOLANDER, S. , MORAES, R. 1998. Ecological Risck Assessment of human impact on Ecosystems in Parque estadual Turistico do Alto Ribeira (PETAR), State of São Paulo, Brazil.Status Report from an ERA Project. August 1998. technical Environmental Planning CTH. Report 1998:3.43p.

ONGLEY, E.D. *Control of water pollution from agriculture, Food and agriculture Organization of the United Nations* -FAO, Paper 55; 1996

PIRES, M.^{a}F; MARQUES, M.N.; COTRIN, M.E.B. Avaliação de novos herbicidas no controle de qualidade da água dos mananciais**.** In**:** Anais do II Congresso Brasileiro de Pesquisas Ambientais , Santos, Brazil, 03-04 junho 2002, CD ROM, 5p 2002.

PIRES, M.A.F.; et al. Revista Brasileira de Pesquisa e Desenvolvimento, vol 3, fascículo 2, novembro, 2001, p 127-138.

PIRES ET AL. Análise Critica da legislação sobre padrão de Potabilidade. Projeto Fapesp n 00/020140-4, São Paulo, Brazil.

SABIK,H.; ET AL. Journal of Chromatography A, 885(2000) 217-236.

SIDAG, http:// www.sindag.com.br. Banco de dados do Sindicato Naciona da Indústria de Produtos para Defensivos Agrícolas – SINDAG , consultado, agosto, 2002.