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Pesticide Leaching and Run-off Hazard in the Ribeira de Iguape River Basin in São Paulo State, Brazil

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ABSTRACT

The aim of this study is to provide technical information concerning water resource protection to enhance environmentally sound public policy and planning for compatible regional development. We investigated the potential threat linked to agricultural development, which is the major economic activity directly associated with surface and underground water contamination. A preliminary analysis was carried out on the potential contamination of surface and underground water by the most commonly used chemical ingredients in the Ribeira de Iguape agricultural basin. In-depth evaluations of several active ingredients related to the use of pesticides were appraised by the United States Environmental Protection Agency – USEPA screening criteria combined with the Groundwater Ubiquity Score (GUS) and a method proposed by Gos (1992). Almost all the pesticides evaluated contained some environmental mobility, with the exception of terbufos and carbaryl.

Key words: pesticides, leaching, run-off, Ribeira de Iguape.

RESUMO

Risco de contaminação de agrotóxicos por lixiviação e aluvião na bacia do rio Ribeira de Iguape, SP, Brasil

Este trabalho tem por objetivo contribuir com informações técnicas relativas à proteção dos recursos hídricos para auxiliar na elaboração de políticas públicas e de planejamento para o desenvolvimento regional compatível com o meio ambiente. Neste estudo, investigou-se o risco potencial do desenvolvimento da agricultura, principal atividade econômica da região, a qual está diretamente associada com a contaminação da água de superfície e subterrânea. Realizou-se uma análise preliminar do potencial de contaminação da água de superfície e subterrânea pelos ingredientes químicos mais usados na agricultura da bacia do rio Ribeira de Iguape. Avaliaram-se diversos ingredientes ativos dos agrotóxicos mais usados na região, utilizando-se os critérios de “screening” proposto pela Agência de Proteção Ambiental dos Estados Unidos (USEPA) combinados com o índice de vulnerabilidade – Groundwater do Ubiquity do Groundwater (GUS) – e um método proposto por Gos (1992). Quase todos os agrotóxicos avaliados apresentaram alguma mobilidade ambiental, à exceção dos terbufos e do carbaril.

Palavra-chave: agrotóxicos, lixiviação, aluvião, Ribeira de Iguape.

INTRODUCTION

Brazil has approximately 10% of the world's fresh water, with an annual average river flow of 182,600 m³ s⁻¹. When all areas of the Amazon region are considered, including the territory in neighboring countries, the outflow is around 272,000 m³ s⁻¹

(Projeto Água, 2003). Although Brazil is considered rich in water due to its extensive landmass, there is a high disparity in distribution of this resource among its regions. The Amazon River Basin, for instance, has only 5% of the total population and about 80% of the available water. Conversely, the Northeast region has only 3.3% of the country's resources and 30% of the population.

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Several other factors may contribute to water shortage relating to the availability of water. This is the case of São Paulo State, located in the Southeast region of Brazil. In fact, its environmental problems are serious due to high population density in many areas associated with deficient sanitary infrastructure, high impact of industrial areas and diffuse water contamination caused by agricultural development. Moreover, the rapid process of urban development and increases in agricultural productivity in the last few decades has been affecting the quality and availability of water. Consequently, conflicts in different sectors and among users have generated more concern and attention from the federal government, which has established new policies to aid management and planning of water resources.

According to the Brazilian Constitution of 1988 (Article 21, section XIX), the government has the power to institute the national water resource management system and the responsibility to establish conditions for the corresponding legislation. In 1997, Federal Law 9,433 was enacted, which established the National Water Resource Policy (PNRH in the Portuguese initials). This law regulates section XIX of Article 21, to allow the implementation and operation of the PNRH.

This study intends to contribute to the database required by government agencies regulating water management. We based our approach on research by Gustafson (1989), Goss (1992), Dores & Freire (2001), Ferracini *et al.* (2001) and Primel *et al.* (2005) to develop a preliminary analysis of potential contamination threats caused by pesticides on surface and underground water, by investigating the physical characteristics of the pesticides applied in the Ribeira de Iguape River Basin (São Paulo State). We expect that this information will help to improve environmental protection measures and make them more sustainable.

MATERIAL AND METHODS

Ribeira de Iguape River Basin

Situated along the southern coast of Brazil (23°30'S – 25°30'S and 46°50'W – 50°00'W), the Ribeira River originates in the state of Paraná, with its name downstream known as the Ribeira de Iguape River after the confluence, its main tributary being the Juquiá River in São Paulo, where it is the most important river from the hinterland flowing into the Atlantic Ocean. Various elements are associated with its tropical landscape formation and a special climate characterized by the mountains of the Serra do Mar and the Parapanema plateau and lowlands linked to flood plains (Associação Ecojureia, 2003). Although classified as being in a tropical climate (average temperature of 23.2°C, ranging between 18°C and 28°C, with average monthly rainfall between 97 mm and 160 mm), the river is located in an area with broad climatic variation due to local factors and conditions determined by

specific areas such as mountains, vegetation and ocean (CIIAGRO, 2003; Marques, 2005).

The main agricultural activity in the basin, banana cultivation, is responsible for approximately 90% of pesticide consumption. Thus, fungicides represent the main product of the pesticides applied in the region. Approximately 4,000 rural properties are involved (Marques, 2005).

Consumption records of the region were compiled and assessed to verify the type of pesticides commonly used. Based on the records collected from EDA/RE (Farming Defense Office of Registro-SP) (Table 1), Farming Defense Coordinating (CDA), Agriculture and Food Supply Secretariat of the São Paulo State, responsible for management, use, supervision, commercialization, storage, installation service and appropriate destination of pesticide packages of 40 EDA distributed on São Paulo State (Marques *et al.*, 2003). Table 2 presents the physical-chemical properties of the active ingredients.

Potential assessment criteria of surface and groundwater contamination in Ribeira de Iguape River Basin

In order to treat the issue of groundwater contamination, the following criteria were applied: the screening criteria recommended by the U.S. Environmental Protection Agency (USEPA) and the Groundwater Ubiquity Score (GUS) developed by Gustafson (1989). To evaluate the possibilities of surface water contamination by pesticides, a method suggested by Goss (1992) was applied (Cohen, 1995; Dores & Freire, 2001; Ferracini *et al.*, 2001; Primel *et al.*, 2005).

USEPA Criteria

For underground water contamination by pesticides, a preliminary potential assessment through the USEPA screening criteria was based on the following: water solubility > 30 mg L⁻¹; organic carbon adsorption coefficient – K_{oc} < 300-500; Henry's Law constant – K_H < 10⁻² Pa.m³ mol⁻¹; speciation – negatively charged (either fully or partially) at room temperature pH (5-8); soil half-life > 2-3 weeks; hydrolysis half-life > 25 weeks; vulnerable field conditions (annual precipitation > 250 mm, aquifer not confined, porous soil).

The Gustafson (1989) GUS was based on the values of half-life and on the soil organic carbon adsorption coefficient (K_{oc}), with no additional properties such as water solubility taken into consideration. However, based on a scale of GUS rankings, four categories of pesticide leaching can be considered.

Large:	If $\log(\text{half-life}) \times (4 - \log(K_{oc})) \geq 2.8$
Small:	If $\log(\text{half-life}) \times (4 - \log(K_{oc})) \leq 1.8$
Very small:	If $\log(\text{half-life}) \times (4 - \log(K_{oc})) < 0.0$ or solubility < 1 and half-life ≤ 1.0
Medium:	Everything else between the presented range

Table 1 – The main active ingredients of pesticides applied in Ribeira de Iguape River Basin.

Pesticide commercial name	Active ingredient	Chemical class	Amount marketed in 2000 (L year ⁻¹)	Toxicological class	Class
Mineral oil	Hydrocarbons	Hydrocarbons	1.8×10^6	IV	Fungicide
Tilt	Propiconazole	Azole	2×10^4	III	
Folicur	Tebuconazole	Triazóis	4×10^3	III	
Juno	Propiconazole	Azole	4×10^3	III	
Cercobin	Thiophanate-methyl	Benzimidazoles	4×10^3	IV	
Priori	Azoxystrobin	Estrobilurinas	1×10^3	III	
Furadan líquido	Carbofuran	Carbamatos	1×10^3	I	Insecticide and nematicide
Furadan granulado	Carbofuran	Carbamates	4×10^3	III	
Sevin	Carbaryl	Carbamates	6×10^4 kg year ⁻¹	II	
Counter 50G	Terbufos	Organophosphorus	5×10^3	I	
Gramoxone	Paraquat	Bipiridílios	2×10^3	II	Herbicide
Gramocil	Paraquat + Diuron	Bipiridílios + Urea	6×10^4	II	
Roundup	Glyphosate	Glicines	3×10^4	IV	
Finale	Glufosinate	Aminoacid	2.5×10^4	IV	
Zapp	Sulfosate	Glicines	8×10^3	IV	

Table 2 – The active components of pesticides used in Ribeira de Iguape River Basin: physical-chemical properties at 20-25°C.

Class	Active ingredients	Vapor pressure, mmHg	Water solubility, mg L ⁻¹	Log K _{ow} ⁽¹⁾	K _{oc} ⁽²⁾ , cm ³ g ⁻¹	DT ₅₀ ⁽³⁾ in soil, days	DT ₅₀ a hydrolyses, days	K _H ⁽⁴⁾ , atm m ³ mol ⁻¹	GUS ⁽⁵⁾
Fungicide	Propiconazole	1×10^{-6}	100-110	3.5	1.900	40-70	25-85	4.1×10^{-9}	1.33
	Tebuconazole	1.3×10^{-11}	36 (20°C)	3.7	–	–	–	1.45×10^{-10}	–
	Thiophanate-methyl	7.6×10^{-5}	2.01×10^3 (30°C)	1.32	110	–	–	3.7×10^{-7}	–
	Azoxystrobin	8.3×10^{-13}	6	2.5	550	4015	–	6.91×10^{-14}	4.54
Insecticide and nematicide	Carbofuran	0.031-0.072 mPa	320	2.32	22	30-60	>>365 (pH 4) 121 (pH 7) e 31 (pH 9)	4.4×10^{-9}	4.52
	Carbaryl	4.1×10^{-5}	120	2.36	300	10	12 (pH 7) 3.2h (pH 9)	8.8×10^{-8}	1.52
	Terbufos	3.2×10^{-4}	15 (ppm)	3.68	2400	5	3.5	2.4×10^{-5}	0.43
Herbicide	Paraquat	$< 1 \times 10^{-5}$	soluble	4,22	15473-1000000	1,000	–	1×10^{-9}	0.57
	Diuron	6.9×10^{-8}	36.4	2.68	224-879	330	–	5.8×10^{-10}	2.66-4.15
	Glyphosate	Low	12,000	0.17×10^{-2}	24000	45-60	–	–	-0.64
	Glufosinate	9.1×10^{-12}	1370	< 0.1 (pH 7)	9.6-1.229	6-20	> 300	4.4×10^{-14}	2.35-5.09
	Sulfosate	–	–	–	–	–	–	–	–

⁽¹⁾K_{ow} = octanol/water partition coefficient; ⁽²⁾K_{oc} = organic carbon adsorption coefficient; ⁽³⁾DT₅₀ = half-life; ⁽⁴⁾K_H = Henry's Law constant; ⁽⁵⁾GUS calculated.

Note: The data were obtained from Dores & Freire (2001); Exttoxnet (2003); Rodrigues & Almeida (1998); and Tomlin (1994).

Table 3 – Surface water criteria for evaluating contamination potential (Goss, 1992).

Pesticide run-off potential for sediment transport	Pesticide run-off potential for solution-phase transport	Half-life in soil (days)	K _{oc}	Solubility in water (mg L ⁻¹)
Large	–	≥ 40	1000	–
Large	–	≥ 40	≥ 500	≤ 0.5
Small	–	< 1	–	–
Small	–	≤ 2	≤ 500	–
Small	–	≤ 4	≤ 900	≥ 0.5
Small	–	≤ 40	≤ 500	≥ 0.5
Small	–	≤ 40	≤ 900	≥ 2
–	Large	> 35	<100,000	≥ 1
–	Large	< 35	≤ 700	≥ 10 and ≤ 100
–	Small	–	≥ 100,000	–
–	Small	≤ 1	≥ 1,000	–
–	Small	< 35	–	< 0.5
Medium: Everything else				

Goss method

For surface water contamination threat, the proposed criteria are shown in Table 3. In this table, unclassified substances among these criteria are considered as the average level (potential) for contaminating surface waters.

RESULTS AND DISCUSSION

The Ribeira de Iguape River Basin is one of eleven Water Management Units in São Paulo State. According to the Natural Water Quality Index for Public Supply (IPA) and the São Paulo State Sanitation Company (CETESB, the water and sanitation utility owned by the state government), several rivers in the basin are moderately preserved with good quality water for public supply (CETESB, 2005). The basin is known for its high availability of water resources, while surface and ground water demands are low, respectively 1.0% and 0.6%. Thus, in such circumstances with low demand and a favorable environmental situation, the quality and quantity called for in the water development plan should aim at maintaining environmental features in harmony with future regional development, by providing guidelines for sustainable protection of its natural resources and, human interventions compatible with land and water features, principally the water catchments and the remaining native forest cover.

Compared with the other regions of the state of São Paulo, figures on socioeconomic and demographic parameters have distinguished this area as the least developed region of São Paulo (Hogan *et al.*, 2001). However, it is immediately apparent that sustainable development is compromised, considering the

limited areas of subsistence agricultural activities, current urban pressures from internal expansion of each town and from external encroachment by larger metropolitan regions, in particular that of the city of São Paulo (Meyer *et al.*, 2004).

The use of pesticides in Brazilian agriculture has been increasing above rate of expansion of planted areas. Regarding the quality of pesticides sold in 2002, herbicides rank first (29.1%), followed by insecticides (approximately 28.4%) and fungicides (25.9%), while other products such as acaricides, nematicides etc. (16.6%) round out demand (SINDAG, 2006). This profile is similar to global tendencies because worldwide consumption of herbicides has significantly increased in the last 30 years above the amount of both fungicides and insecticides (Lara & Batista, 1992; Marques, 2005).

Thus, this evaluation was carried out only on the physical-chemical properties of active compounds of the pesticides commonly applied in Ribeira de Iguape River Basin. The physical-chemical properties of active components in pesticides as shown in Table 2 are related to several crops to which they were applied. Subsequently, the physical-chemical properties presented here were used in both evaluation involving potential criteria for water contamination, considering: Henry's Law constant (K_H), water solubility, octanol/water partition coefficient (K_{ow}), organic carbon adsorption coefficient (K_{oc}) with soil and water half-life (DT₅₀).

The results of Table 2 were obtained by observing the differences among the properties of several compounds with the same or other chemical class. A broad survey of environmental impacts was not possible specifically related to pesticides.

Although there are few studies on pesticides in tropical environments and pesticide behavior on land and water are expected to vary between temperate and tropical conditions, data for temperate environments were used in order to enable comparison between recognized conditions (Castilho *et al.*, 1997).

Considering toxic sensitivity, a significant portion of the pesticides are classified as having low toxicity. Sevin, Gramoxone and Gramoxil are considered highly toxic, while Furadan liquid and Counter 50G insecticides are considered extremely toxic.

Potential underground water contamination

Based on the screening criteria proposed by the USEPA, Table 4 presents the potential for underground water contamination. The properties analyzed in Table 2 were considered for the possibility of their effect upon reaching the water table. Some of the data in Table 4 were not established in the literature.

A number of the active components can be classified as compounds that present a greater probability of traveling to the water table due to high water solubility, low organic soil adsorption and a relatively long half-life in the soil. Potential pollutants are considered as those active substances indicated by physical chemical properties, characterized by the possibility of contaminating underground water for the following reasons:

- Although water solubility and organic carbon adsorption coefficient (K_{oc}) of azoxystrobin do not comply with the screening established by the USEPA,

the long half-life of nearly 11 years indicates the possibility of groundwater contamination.

- The solubility and the coefficient K_{oc} of diuron are in the specified limit, demonstrating the capacity of being highly absorbed by the soil, but based on other characteristics and literature data, contamination by this substance indicates it poses a considerable threat of water contamination.
- Though glyphosate is strongly absorbed by the soil, it can contaminate groundwater only when the characteristics of the soil do not favor adsorption or when it is associated with dissolved organic matter.

The aim of this study was to evaluate the potential of active chemical components to contaminate water sources. We preferred a conservative approach in order to consider other cases with suspicious characteristics as well. In the case of tebuconazole and sulfosate, for which no information was found in the literature, the results of their chemical compounds are therefore inconclusive.

According to Cohen *et al.* (1995), compounds on the leach or transition range (1.8-2.8) would require further investigation by a more sophisticated method. Compounds classified as improbable of leaching may certainly be considered as non-pollutants of groundwater. Considering this detail with criteria from the EPA (see Table 4), only terbufos presents no risk of water contamination. Propiconazole, carbaryl, paraquat and glyphosate are identified as probable intermediate contaminants; nevertheless, they require more assessment to substantiate their probability of water contamination.

Table 4 – Summary of groundwater contamination Analysis (Ribeira de Iguape River Basin, SP, 2002): based on the screening criterion (USEPA) and on the GUS index.

Class	Active ingredients	Solub.	K_{oc}	$^1DT_{50}$ soil	DT_{50} hydr.	2K_H	GUS	Result
Fungicide	Propiconazole	✓	⊗	✓	⊗	✓	⊗	IN
	Tebuconazole	✓				✓		I
	Thiophanate-methyl	✓	✓			✓		CP
	Azoxystrobin	⊗	⊗	✓		✓	✓	CP
Insecticide and nematicide	Carbofuran	✓	✓	✓	⊗	✓	✓	CP
	Carbaryl	✓	⊗	⊗	⊗	✓	⊗	IN
	Terbufos	⊗	⊗	⊗		✓	⊗	NC
Herbicide	Paraquat	✓	⊗	✓		✓	⊗	IN
	Diuron	✓	✓	✓		✓	✓	CP
	Glyphosate	✓	⊗	✓			⊗	IN
	Glufosinate	✓	✓	✓	✓	✓	✓	CP
	Sulfosate							I

⊗ – out of criterion; ✓ – criterion as dangerous potential; CP – potential contaminant; NC – non contaminant; IN – middleman; I – no conclusion possible; $^1DT_{50}$ – half-life; 2K_H – Henry's Law constant.

The potential of surface water contamination

Although the criteria suggested by Goss (1992) were used to verify whether pesticides used in the region could reach surface waters when being applied in local agriculture, research is divided into two areas: one pertaining to materials that can be transported when dissolved in water and the other to those transported along with sediments in suspension (see Table 5). In this case, the classification of pesticides according to this criterion is presented below. Among those with high transport potential associated with sediments are propiconazole, paraquat and glyphosate.

Dispersed in water, the pesticides that have presented high mobility are propiconazole, thiophanate-methyl, azoxystrobin, carbofuran, paraquat, diuron and glyphosate, some of which were also identified as potential pollutants of groundwater (thiophanate-methyl, azoxystrobin, carbofuran and diuron). Of all the pesticides studied, carbofuran stands out, due to its long half-life in water, which was detected and

later confirmed among the samples investigated in the surface waters of Ribeira de Iguape River Basin (Marques, 2005; Marques *et al.*, 2003).

CONCLUSION

The evaluation of the data presented in the list of compounds reveals that among the pesticides most commonly used in agriculture in the Ribeira de Iguape River Basin, all of those investigated presented mobility in the environment, with the exception of terbufos and carbaryl. Although a significant portion of the study region currently lies within environmental protection areas, indicating moderate influence and human activity, the disturbing probability of surface and ground water contamination by agriculture is still an important issue not to be ignored. The flood-prone character of this region is a significant factor in determining field conditions raising the risk of surface and ground water contamination.

Table 5 – Classification of the active components in pesticides used in the region of Ribeira de Iguape River Basin (2002): capacity for contaminating surface waters.

Active ingredients	Propiconazole	Tebuconazole	Thiophanate-methyl	Azoxystrobin	Carbofuran	Carbaryl	Terbufos	Paraquat	Diuron	Glyphosate	Glufosinate	Sulfosate
Pesticide run-off potential for sediment transport	L	I	S	M	S	S	M	L	M	L	S	I
Pesticide run-off potential for solution-phase transport	L	I	L	L	L	M	M	L	L	L	M	I

L – large; S – small; M – medium; I – no conclusion possible.

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