



Herbicide distribution in soils of a riparian forest and neighboring sugar cane field

S.T.T. Bicalho ^{a,*}, T. Langenbach ^a, R.R. Rodrigues ^b, F.V. Correia ^c, A.N. Hagler ^a, M.B. Matallo ^d, L.C. Luchini ^d

^a Instituto de Microbiologia Prof. Paulo de Góes, Centro de Ciências da Saúde, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

^b Departamento de Ciências Biológicas, ESALQ, Universidade de São Paulo, Piracicaba, SP, Brazil

^c Fundação Oswaldo Cruz. Laboratório de Ecotoxicologia do CESTEH – ENSP, Rio de Janeiro, Brazil

^d Instituto Biológico, Agência Paulista de Tecnologia Agropecuária, São Paulo, SP, Brazil

ARTICLE INFO

Article history:

Received 6 March 2009

Received in revised form 11 May 2010

Accepted 12 June 2010

Available online 22 July 2010

Keywords:

Tebuthiuron

Diuron

Hexazinone

Phytoremediation

Riparian forest

Pesticide volatilization

ABSTRACT

Riparian forests are protected by Brazilian law to preserve rivers and their margins. A sugar cane field adjacent to a strip of young riparian forest bordering an older riparian forest along a stream was used to study the riparian forest as a buffer zone to prevent pesticides pollution. Concentrations of the herbicides diuron, hexazinone and tebuthiuron were determined in different soil layers of a Red Yellow Oxisol during 2003 and 2004. The determination was done by High Performance Liquid Chromatography with reverse phase C-18 column, through two mobile phases. Diuron and hexazinone concentration diminished between the sugar cane and riparian forest as buffer strip demonstrating a protective effect. However, tebuthiuron had about four times higher concentrations in the old riparian forest compared to the other areas. Concentrations were higher in the surface and decreased in deeper soil layers in the old riparian forest suggesting that this herbicide probably was introduced by air pollution. This pesticide concentrated in the canopy could be washed by rain to the soil adjacent to the stream. Our data suggest that climate conditions were responsible for enhanced volatilization exposing the old riparian forest to more air pollution that was captured by the higher canopy.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Sugar cane, as a sustainable source of fuel ethanol, has been intensely cultivated up to the limits of lakes, streams and rivers in Brazil. However, recently laws in some regions have demanded reforestation of riparian buffer zones (SMA, 2008). The intensive use of pesticides promotes the contamination of surface water intensively used for irrigation. This contamination is hazardous for flora and fauna in addition to having serious consequences for human health. Indeed, the gradual bioaccumulation from the daily intake of small quantities of some pesticides present in our food can reach concentrations that cause hormonal disturbance (Crisp et al., 1998; Hoekstra et al., 2006; EPA, 2007). Some examples in the literature have shown that pesticides are able to cause the feminization of reptiles and fishes, also can decrease human sperm viability (Hofmeister and Bonefeld-jorgensen, 2004; Argemi et al., 2005; EPA, 2007), and the appearance of cancer (Grisolia, 2005) and other disturbances (Laws et al., 2000).

Pesticides can be dispersed in the environment by diverse mechanisms like runoff, lixiviation, drift and volatilization (Ahuja and Lehman, 1983; Spencer, 1987; Pionke and Glotfelty, 1990; EPA, 1999; Correia et al., 2007). In general, buffer strips such as grasslands

or riparian forests are considered effective filters that result in reduction of pesticide contamination of surface water (Hubbard and Lowrance, 1994; Krutz et al., 2005). Progressive reduction of pesticide contamination has been described using grass filter strips with up to 10 m width in temperate conditions (Snoo and de Wit, 1998; Anbumozhi et al., 2005; Reichenberger et al., 2007) and in tropical conditions (Ludovice et al., 2003). The riparian forest as buffer zone for pesticide control was already described (Hubbard and Lowrance, 1994; Pinho et al., 2004), but the way that pesticides can be dispersed by ground water contamination or air pollution due to volatilization has not been described. We have studied the pesticide distribution in a riparian forest bordering a sugar cane plantation in the recharge area of Guarany Aquifer.

2. Materials and methods

2.1. Pesticides

Some important chemical characteristics for the distribution of the pesticides we studied in soil are presented in Table 1.

2.2. Experimental site

Samples of Oxisol were taken from a region with low hills about 6.5 km North of Orlandia, São Paulo, Brazil, at 767 m altitude bordering on a small stream, Ribeirão do Rosário, and situated at

* Corresponding author. Universidade Federal do Rio de Janeiro, CCS, Bloco I, Instituto de Microbiologia, sala 29. Cidade Universitária, CEP 21491-590. Rio de Janeiro, RJ, Brazil. Tel.: +55 21 2562 6743; fax: +55 21 2560 8344.

E-mail address: simonetaketa@yahoo.com.br (S.T.T. Bicalho).

Table 1

Pesticide movement rating, pesticide half-life in soil (days), vapor pressure (mbar), water solubility (mg L^{-1}) and sorption coefficient (K_{oc}) of diuron, hexazinone and tebuthiuron.

Sources: Adapted from Hornsby et al. (1996), Deuber, (2003) and SRC (2007), Tomlin (2000).

Herbicide	Pesticide movement rating	Soil half-life (days)	Vapor pressure (mbar)	Water solubility (mg L^{-1})	Sorption coefficient (soil K_{oc})
Diuron	Moderate	90	1.1×10^{-8} at 25 °C	42 at 25 °C	480
Hexazinone	Very high	90	2.7×10^{-7} at 25 °C	33,000 at 26 °C	54
Tebuthiuron	Very high	360	2.7×10^{-6} at 20 °C	2500 at 25 °C	80

coordinates 20°39'26.89" S latitude and 47°53'05.68" W longitude. The region is characterized by frequent and intense rains during spring and summer ($200\text{--}300 \text{ mm month}^{-1}$) and a dry autumn and winter from April to September ($0\text{--}75 \text{ mm month}^{-1}$). The samples were taken along 175 m of the stream in three sample areas. Next to the stream was a 30 m wide patch of old riparian forest that was up to 20 m high, and adjacent to it another 20 m wide area of young riparian forest about 2 years old and up to 5 m high on a former portion of the sugarcane field. The third area was 30 m wide within the sugarcane plantation that was adjacent to the riparian forest (Fig. 1).

2.3. Experiment

Herbicides were applied by a tractor directly on the sugarcane field. It had been treated previously as recommended agricultural rates with the commercial product Velpar-K to a level of $514.0 \text{ g a.i. ha}^{-1}$ of diuron and $145.2 \text{ g a.i. ha}^{-1}$ of hexazinone on March 8, 2001 before the young riparian forest existed. Velpar-K was reapplied on March 16, 2004 to a level of 1174.7 g of diuron and 331.3 g of

hexazinone a.i. ha^{-1} . The commercial product Combine was applied only on January 20, 2003 to a level of $1620.0 \text{ g tebuthiuron ha}^{-1}$.

Five soil samples were collected in holes about 35 m apart within each of the 3 areas during the period of March 17–19 of 2003 at depths of 0–20 cm, 20–40 cm, 40–60 cm, 60–80 cm. In May 18–20 of 2004, another set of soil samples were collected at the same depths and positions but with additional samples from 80–100 cm to 100–120 cm. The five soil samples from separate holes of each area were mixed to make a composite sample for each depth and stored at -10 °C for residue analysis performed in triplicate. These soil samples were dried at room temperature and sieved through a 2 mm mesh. Soil physicochemical properties as texture, pH, and organic carbon were determined by EMBRAPA Agrobiologia using their standard methods (EMBRAPA, 1997).

2.4. Analytical procedure

Pesticide residues were extracted in triplicate by Soxhlet from 50 g of each composite soil sample with 150 mL methanol during 8 h. For each sample, 100 mL of extract was dried in a Büchi rotary evaporator at 40 °C, resuspended in 5 mL of HPLC grade methanol and treated for 1 in an ultrasonic bath. Aliquots of 20 μL were injected by a SIL 10A into a Shimadzu HPLC (model LC 2010) with two LC-10AD pumps equipped with a Varian C-18 ($250 \times 4.6 \text{ mm i.d.}$) reverse phase column preceded by a guard column ($10 \times 3.0 \text{ mm i.d.}$), and UV detector operating at 254 nm. The flow speed was 1 mL min^{-1} and column temperature was 30 °C. The mobile phases used were acetonitrile:water (40:60 v/v) and as a control methanol:water (45:55 v/v). Standards of diuron (98.7% pure) and hexazinone (98.5% pure) were donated by DUPONT and tebuthiuron (97.7% pure) from DowAgroSciences. The extraction was conducted as described previously (Matallo et al., 2003, 2005; Negrisoli et al., 2005; Cerdeira et al., 2007). The following validation parameters were obtained: limit of quantification (LQ) 0.02 mg kg^{-1} and limit of detection (LD) of method 0.01 mg kg^{-1} ; linearity from 0.050 to 5.00 mg L^{-1} ($r^2 > 0.999$) and recoveries from 90 to 103%. All concentration values from extracts were corrected on the basis of measured recoveries.

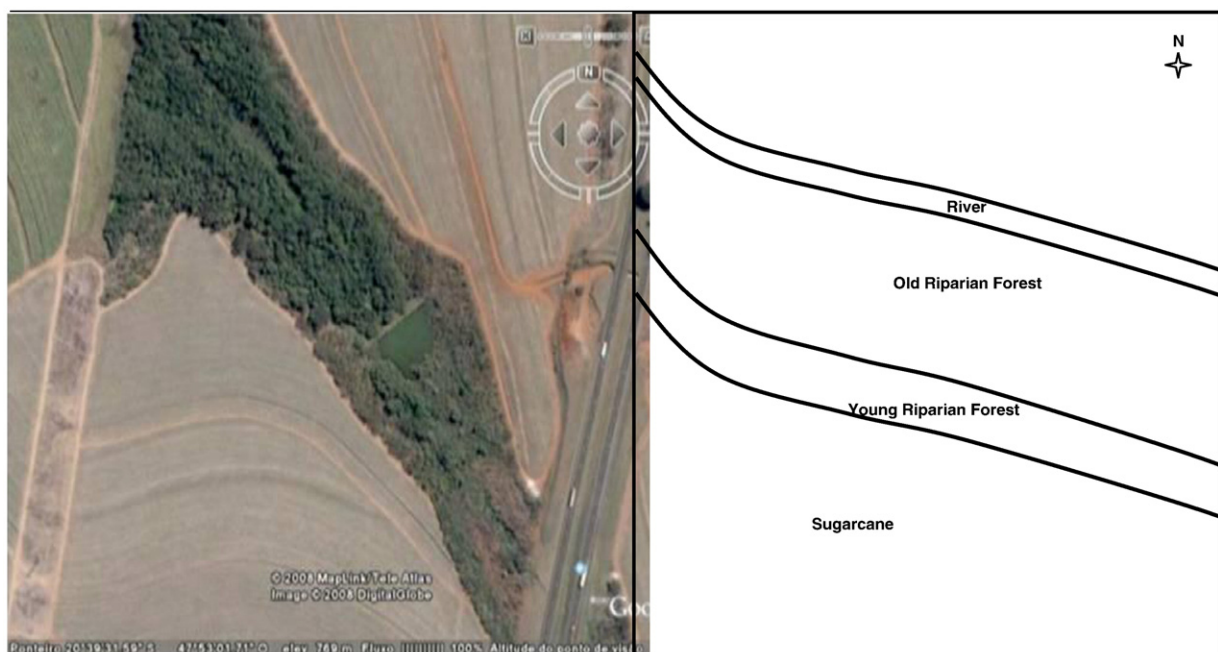


Fig. 1. Experimental site.

2.5. Statistical analysis

All the data were analyzed by ANOVA using Tukey's test for comparing the values at each depth under both areas. The results were expressed as means \pm SD (standard deviation). Results with $P < 0.05$ were considered significant.

3. Results

3.1. Soil and climate characteristics

The soil profile was predominantly sandy in all three areas with 28% clay, 6% silt, and 66% sand. The only difference was a lower pH of 4.4 in the old riparian forest soil compared pH 5.5 in the previously limed young riparian forest and sugar cane field. The organic carbon decreased between the surface layer and deep layer and was 0.66% (surface) to 0.27% (deep) in the sugar cane field soil, 0.81% to 0.33% in the young riparian forest, and 1.02% to 0.31% in the old riparian forest. Intense rain started before the tebuthiuron application and the amount of rain during the 2 month period between pesticide application on January 20, 2003 and soil sample collection on March 17, 2003 was 575.0 mm (Fig. 2). Rainfall was 244.5 mm between March 6, 2004 when diuron and hexazinone were applied and the soil collection on April 6 (Fig. 2). When tebuthiuron was applied in 2003 the mean wind was 4 m s^{-1} NW and when diuron + hexazinone were applied in 2004 it was 4 m s^{-1} S. The mean wind during the experiments varied between 0 and 5 m s^{-1} in 2003 with predominant

direction NW-N-E and was 0 to 4 m s^{-1} with predominant wind was N-E-S in 2004.

3.2. Diuron and hexazinone concentrations in soil

The residues of diuron and hexazinone applied up to 2001 were at low levels in all three areas in samples collected in 2003 (Table 2). Diuron decreased notably from the surface layer to the deeper layers in 2003 and 2004. In the young riparian forest during 2004, diuron was high only in the 60–80 cm and 100–120 cm layers. Trace amounts appeared in the old riparian forest in both years. Hexazinone distribution is quite different with higher concentrations in deeper layers. The surface layer shows high hexazinone concentration only in the sugar cane planted area soon after it was applied. No statistically significant difference was observed in different soil layers of sugar cane and young forest in 2003.

3.3. Tebuthiuron concentrations in soil

The average amount of tebuthiuron was lower in the sugar cane area than in the old riparian forest soil in 2003 and it was at high concentrations in the surface layer with gradual decrease in depth in sugar cane field and young riparian forest (Table 2). However, in the old riparian forest the residue concentration in 2003 was high in all four soil layers down to 80 cm and it was notable that the concentration of $34.1 \mu\text{g g}^{-1}$ at 60–80 cm depth was very similar to the $34.3 \mu\text{g g}^{-1}$ found in 0–20 cm surface layer. Tebuthiuron levels

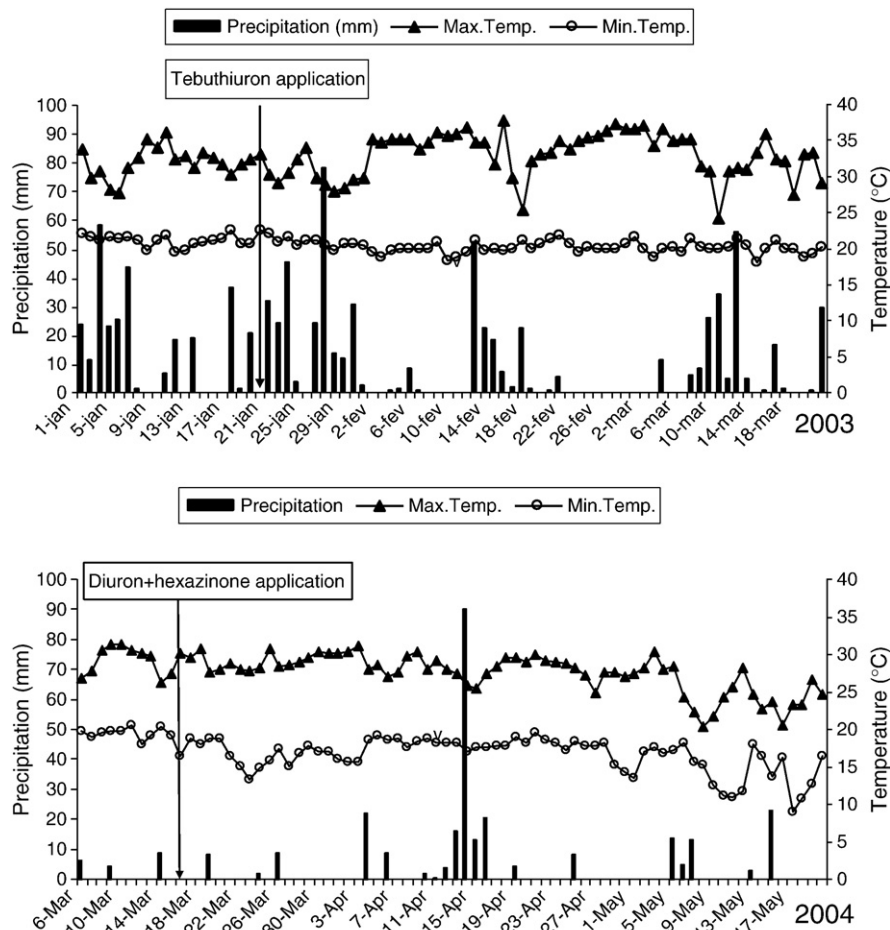


Fig. 2. Pluviometric and temperature distribution in Franca, São Paulo beginning 10 days before pesticides application to soil sampling, in 2003 and 2004.

Table 2

Diuron, hexazinone and tebuthiuron residues (mean $\mu\text{g g soil}^{-1} \pm$ standard deviation) determined at sugar cane, young riparian forest and old riparian forest, in 0–80 cm depth, at 2003, and in 0–120 cm depth, in 2004.

Depth (cm)	Sugar cane		Young riparian forest		Old riparian forest	
	2003	2004	2003	2004	2003	2004
<i>Diuron</i>						
0–20	0.19 \pm 0.01a	5.41 \pm 0.24a	0.39 \pm 0.04a	<LD	<LD	<LD
20–40	0.06 \pm 0.04a	0.53 \pm 0.14b	0.08 \pm 0.02a	0.08 \pm 0.02b	<LD	<LD
40–60	<LD	0.06 \pm 0.06c	0.05 \pm 0.02a	0.08 \pm 0.00b	<LD	<LD
60–80	0.14 \pm 0.05a	0.06 \pm 0.04c	0.08 \pm 0.02a	0.52 \pm 0.32b	<LD	<LD
80–100	N.D.	0.07 \pm 0.05c	N.D.	0.08 \pm 0.00b	N.D.	<LD
100–120	N.D.	<LD	N.D.	3.95 \pm 1.00a	N.D.	<LD
Total	0.25	6.07	0.60	4.71		
<i>Hexazinone</i>						
0–20	0.14 \pm 0.14a	5.45 \pm 1.24a	0.27 \pm 0.09a	1.32 \pm 0.96b	<LD	<LD
20–40	0.05 \pm 0.03a	2.22 \pm 1.78b	0.43 \pm 0.16a	0.89 \pm 0.38b	<LD	0.07 \pm 0.01b
40–60	0.47 \pm 0.10a	0.61 \pm 0.38c	0.53 \pm 0.26a	0.89 \pm 0.02b	<LD	0.05 \pm 0.01b
60–80	0.66 \pm 0.12a	2.36 \pm 0.97b	0.79 \pm 0.27a	3.44 \pm 0.45a	<LD	0.04 \pm 0.01b
80–100	N.D.	0.68 \pm 0.34c	N.D.	0.89 \pm 0.17b	N.D.	0.24 \pm 0.03a
100–120	N.D.	3.15 \pm 1.38ab	N.D.	4.22 \pm 1.23a	N.D.	0.44 \pm 0.23a
Total	1.32	14.47	2.02	11.65		0.84
<i>Tebuthiuron</i>						
0–20	11.65 \pm 2.82a	5.47 \pm 0.60a	24.57 \pm 8.00a	9.91 \pm 1.44a	34.34 \pm 6.10a	2.44 \pm 1.02ab
20–40	6.21 \pm 1.70b	2.92 \pm 1.86ab	5.88 \pm 4.27b	3.72 \pm 0.94b	22.84 \pm 5.58a	7.87 \pm 2.41a
40–60	4.09 \pm 0.70b	0.74 \pm 0.67b	1.31 \pm 0.29b	3.72 \pm 0.70b	24.59 \pm 1.73a	1.21 \pm 1.09b
60–80	6.18 \pm 1.46b	3.43 \pm 1.57a	3.96 \pm 1.37a	5.66 \pm 0.70b	34.13 \pm 8.75a	1.58 \pm 0.98b
80–100	N.D.	1.18 \pm 0.58b	N.D.	3.72 \pm 0.30b	N.D.	4.17 \pm 1.39a
100–120	N.D.	3.65 \pm 1.63a	N.D.	5.73 \pm 0.64b	N.D.	3.75 \pm 1.27ab
Total	28.13	17.39	35.72	32.46	115.89	21.02

N.D. = not determined.

LD = correspond to limit of detection.

Values followed by the same letter, at vertical, did not differ between layers in each year, at 5% level for Tukey's test.

Tebuthiuron reached the old riparian forest 30 m from the sugar cane field and lixiviated into soil. Diuron and hexazinone had different behaviors due to climate.

were reduced by 55%, 36% and 88% for the sugar cane area, young, and old riparian forest respectively during one year between 2003 and 2004 (Table 2). In 2004 the 80 to 120 cm layers in the old riparian forest had higher residue concentrations than the upper layers (Table 2).

4. Discussion

The background residues from previous applications of diuron and hexazinone observed in 2003 were low compared with the concentrations measured in 2004, but the distribution profiles were similar. Although the commercial product applied had four times more diuron than hexazinone the values of diuron in the soil were lower than hexazinone in all three areas (Table 2). This was probably due to more intense biodegradation of diuron in the sugar cane field since strong uptake of diuron by this plant has been noted previously (Musumeci et al., 1995). Hexazinone has a similar half life to diuron, but the much higher solubility of hexazinone should have enhanced leaching to deeper soil layers where microbial biomass is smaller and therefore biodegradation process in general should be less intense (Lavy et al., 1989). Hexazinone was found mainly in the deeper layers in the young and old riparian forest where pesticides were not applied suggesting that pollution probably occurred by residue movements in ground water from the neighboring area where the herbicides were applied. In support of this conclusion, Feng et al. (1992) reported hexazinone and its metabolite residues leached to 130 cm and were still detectable two years after applications. It has the potential to move off-site and affect non-target species up to 100m away (Allender, 1991). This was especially true of the young riparian forest where the residue concentration in deeper layers was slightly higher than in sugar cane. This may have been due to the less developed root system of the young trees resulting in reduced biodegradation

capacity. Residues could also have moved from the ground water to the upper layers driven by evapotranspiration (Cleverly et al., 2006; Bicalho et al., 2007; Fisher and Healy, 2008). It should be considered that hexazinone contamination may have occurred by subsurface displacement due to the higher solubility of hexazinone than diuron (Schneider et al., 1995). The less soluble diuron may have contaminated the young forest by horizontal transport in the ground water, but it did not reach the old forest soil.

In the superficial layer of the riparian forest, the litter and relatively high concentration of organic matter of the soil may adsorb some pesticides thus reducing them in the runoff (Gomes et al., 2001; Matallo et al., 2005; Cerdeira et al., 2007). This was observed in previous studies with atrazine (Pinho et al., 2004). Our data demonstrated a significant reduction of the herbicide levels from sugar cane through young riparian to the old riparian forest, indicating that this buffer strip was effective in reducing pesticide contamination before reaching the stream of surface water.

Pearce et al. (1997) demonstrated that the retention by the strip zone is more related to width of the strip than to the height of the vegetation. Various studies in the literature have shown that the presence of vegetation reduced pesticide concentrations of hexazinone and diuron in non-target areas (Reichenberger et al., 2007; Poletika et al., 2009; Sabbagh et al., 2009). Riparian forest plants could be able to retain or phytodegrade the pesticides using their roots in this wide strip (Hubbard and Lowrance, 1994; Reichenberger et al., 2007). However, a survey of the literature did not yield any references with evidence that tropical riparian forests can act as buffer strips for pesticide contamination.

Contrary to the buffer strip effect observed for diuron and hexazinone, tebuthiuron molecules were introduced into riparian forest area reaching significant higher concentrations than those observed in sugar cane where pesticides were applied. In order to

understand the pollution mechanism involved, possibilities of pesticide transport such as runoff, leaching, groundwater flow and air movement by drift or volatilization need to be considered.

Considering the hypothesis of runoff as the main pollution mechanism, the younger riparian forest that was closer to the sugar cane field would have been expected to have a higher amount of tebutiuron than the old forest, but our data showed the opposite. This hypothesis was also unlikely considering that in general runoff amounts do not exceed 5% of the applied pesticides (Rohde et al., 1981; Glenn and Angle, 1987; Hall et al., 1991; Correia et al., 2007), and can be less when the slope of the land is below 10% as it was in our study area. Pesticides leaching into the groundwater by horizontal flow had resulted in a distribution pattern in the neighboring riparian forest soil where the highest concentrations in the deeper soil layers were found (Table 2). In fact the low values of adsorption coefficient (K_{oc}) for hexazinone and tebutiuron (Zhu and Li, 2002) should allow high mobility by leaching (Gustafson, 1989; Spadotto, 2002; Matallo et al., 2005; Gomes et al., 2006), different than diuron with high adsorption coefficient and reduced mobility. The high amount of tebutiuron residue distributed in all layers down to 80 cm in the old riparian forest soil is a strong argument to exclude leaching as main pollution factor in this area. Leaching followed by horizontal displacement in groundwater could have occurred, but should not have enhanced total residue concentrations to more than four times higher than in the neighboring area where pesticide was applied. Air transport of drift from spray during pesticide application was another possibility for transport of these residues to non-target areas (Klöppel and Kördel, 1997; Yao et al., 2006). The wind direction on the day of pesticide application did not favor contamination of the young riparian forest by drift. The drift during pesticide application when clouds were formed and dissipated as small drops moving down by gravity could have arrived at the young riparian forest, but it was unlikely to have contaminated the old riparian forest 20 m away. The above argument makes unlikely that drift, runoff, leaching, and ground water movement increase herbicide concentrations in the old riparian forest above the values that were applied in the sugar cane field.

Volatilization seems to be the most probable pollution mechanism of the old riparian forest. For a better understanding it is necessary to analyze the parameters that influence volatilization such as sorption, vapor pressure, rain and temperature. Vapor pressure is low, but higher for tebutiuron with 2.7×10^{-6} mbar at 20 °C compared to hexazinone with 2.7×10^{-7} mbar at 25 °C and for hexazinone with diuron with 1.1×10^{-8} mbar at 25 °C. Therefore, probably the volatilization occurred in this work is not determined mainly by the physical-chemical characteristics of the molecules (Tomlin, 2000; SRC, 2007).

A striking difference of the climate was observed during and after the period of pesticides application. During tebutiuron application in 2003 there was much more rain and 3 °C higher average temperature than 2004 when diuron and hexazinone were applied (Fig. 2). The dry soil in 2004 should have adsorbed more diuron and hexazinone with stronger restriction of molecule movement for leaching as well volatilization than the wet soil in the year 2003 when tebutiuron was used. The alternation of rain and high temperatures observed as more intense in the year of 2003 compared to 2004, is a situation that should have enhanced volatilization (Spencer, 1987; Glotfelty et al., 1989; Langenbach et al., 2000; Correia et al., 2007).

Volatilized tebutiuron residues may be moved by wind to higher above ground level and then could have retained in part by the higher riparian forest canopy. The highly soluble tebutiuron could have been washed down by rain from leaves to the soil. Another possibility was of leaf fall by senescence, but this was not likely considering that the plants were in their summer growth phase. Residue distribution showed that tebutiuron maintained at high concentrations in all soil layers of the old riparian forest (Table 2) and this could be explained

by the serial input of residue by several rains that would be different from the single or few applications on the sugar cane. Further distribution of pesticide in the air should be determined by wind direction, intensity, and landscape relief. This seems to be a process combining pesticide accumulation in the canopy by filtration from the air, followed by washing it down to the soil and then uptake and translocation by plant as in phytoremediation. This climate dependent process can repeat to gradually reduce pollution through biodegradation and soil adsorption.

Acknowledgements

This work was financed by CNPq, FAPERJ, and PRONEX-CNPq. We also thank CAPES for scholarship support to STTB, and Mr. Milton Jarreta for collecting the soil samples.

References

- Ahuja, L.R., Lehman, O.R., 1983. The extent and nature of rainfall–soil interaction in the release of soluble chemicals to runoff. *Journal of Environmental Quality* 12, 34–40.
- Allender, W.J., 1991. Movement of bromacil and hexazinone in a municipal site. *Bulletin of Environmental Contamination and Toxicology* 46, 284–291.
- Anbumozhi, V., Radhakrishnan, J., Yamaji, E., 2005. Impact of riparian buffer zones on water quality and associated management considerations. *Ecological Engineering* 24, 517–523.
- Argemi, F., Cianni, N., Porta, A., 2005. Disrupción endócrina: perspectivas ambientales y salud pública. *Toxicología ambiental* 39, 291–300.
- Bicalho, S.T.T., Langenbach, T., Rodrigues, R.R., Correia, F.V., Silva, D.P., Ferreira, E.D., Martins, H.L., 2007. Dinâmica da 14C-Atrazina em *Cecropia hololeuca* Miq. *Revista Brasileira de Biociências*, Porto Alegre 5, 678–680.
- Cerdeira, A.L., Desouza, M.D., Queiroz, S.C.N., Ferracini, V.L., Bolonhezi, D., Gomes, M.A.F., Rosa, M.A., Balderrama, O., Rampazzo, P., Queiroz, R.H.C., Neto, C.F., Matallo, M.B., 2007. Leaching and half-life of the herbicide tebutiuron on a recharge area of Guarany aquifer in sugarcane fields in Brazil. *Journal of Environmental Science and Health, Part B* 42 (6), 635–639.
- Cleverly, J.R., Dahm, C.N., Allred Coonrod, J.E., 2006. Groundwater, Vegetation, and Atmosphere: Comparative Riparian Evapotranspiration, Restoration, and Water Salvage USDA Forest Service Proceedings RMRS-P-42CD. , pp. 75–80.
- Correia, F.V., Macrae, A., Guilherme, L.R.G., Langenbach, T., 2007. Atrazine sorption and fate in a Ultisol from humid tropical Brazil. *Chemosphere* 67, 847–854.
- Crisp, T.M., Clegg, E.D., Cooper, R.L., Wood, W.R., Anderson, D.G., Baetcke, K., Hoffmann, J.L., Morrow, M.S., Rodier, D.J., Schaeffer, J.E., Touart, L.W., Zeeman, M.G., Pate, Y.M., 1998. Environmental endocrine disruption: an effects assessment and analysis. *Environmental Health Perspectives* 1, 11–56.
- Deuber, R., 2003. *Ciência das plantas infestantes*. V.1: Fundamentos. Funep ed. 2ª. Edição. 452p.
- EMBRAPA – Empresa Brasileira de Pesquisa Agropecuária, 1997. *Centro Nacional de Pesquisa em Solos. Manual de métodos de análise de solo*, 2ª ed. Rio de Janeiro, 212 pp.
- EPA – Environmental Protection Agency, 1999. Spray Drift of Pesticides EPA 735F99024. Available: <http://www.epagov/pesticides/factsheets/spraydrif.htm>. 1999. Accessed 16 January 2007.
- EPA – Environmental Protection Agency, 2007. Endocrine Disruptor Screening Program (EDSP) Available: <http://www.epagov/endo/pubs/prioritysetting/draftlist.htm>. 2007. Accessed 07 May 2008.
- Feng, J.C., Sighu, S.S., Feng, C.C., 1992. Spatial distribution of hexazinone and metabolites in luvisolic soil. *Journal of Science Health* 27, 639–654.
- Fisher, L.H., Healy, R.W., 2008. Water movement within the unsaturated zone in four agricultural areas of the United States. *Journal of Environmental Quality* 37, 1051–1063.
- Glenn, S., Angle, J.S., 1987. Atrazine and simazine in runoff from conventional and no-till corn watersheds. *Agriculture, Ecosystems & Environment* 18, 273–280.
- Glotfelty, D.E., Leech, M.M., Jersey, J., Taylor, A.W., 1989. Volatilization and wind erosion of soil surface applied atrazine, simazine, alachlor and toxaphene. *Journal of Agricultural and Food Chemistry* 37, 546–551.
- Gomes, M.A.F., Spadotto, C.A., Lanchote, V.L., 2001. Ocorrência do herbicida tebutiuron na água subterrânea da microbacia do Córrego Espreado, Ribeirão Preto, SP. *Pesticidas: R.Ecotoxicologia e Meio Ambiente*, Curitiba 1, 65–76.
- Gomes, M.A., Spadotto, C.A., Pereira, A.S., Matallo, M.B., Luchini, L.C., 2006. Movimento do herbicida tebutiuron em dois solos representativos das áreas de recarga do aquífero Guarani. *Revista Brasileira Engenharia Agrícola e Ambiental*, Campina Grande 10, 479–483.
- Grisolia, C.K., 2005. *Agrotóxicos: mutações, câncer e reprodução*, Vol. 1. Editora da Universidade de Brasília, Brasília, Brazil. 392 pp.
- Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environmental Toxicology and Chemistry* 8, 339–357.
- Hall, J.K., Mumma, R.O., Watts, D.W., 1991. Leaching and runoff losses of herbicides in a tilled and untilled field. *Agricultural Ecosystems Environment* 37, 303–314.
- Hoekstra, P.F., Burnison, B.K., Garrison, A.W., Neheli, T., Muir, D.C.G., 2006. Estrogenic activity of dicofol with the human estrogen receptor: isomer- and enantiomer-specific implications. *Chemosphere* 64, 174–177.

- Hofmeister, M.V., Bonefeld-Jorgensen, E.C., 2004. Effects of the pesticides prochloraz and methiocarb on human estrogen receptor α and β mRNA levels analyzed by on-line RT-PCR. *Toxicology in Vitro* 18, 427–433.
- Hornsby, A.G., Wauchope, R.D., Herner, A.E., 1996. *Pesticide Properties in the Environment*. Springer-Verlag, New York, 227 pp.
- Hubbard, R.K., Lowrance, R.R., 1994. Riparian forest buffer system research at the coastal plain experiment station, Tifton, GA. *Water, Air & Soil Pollution* 77, 409–439.
- Klöpffel, H., Kördel, W., 1997. Pesticide volatilization and exposure of terrestrial ecosystems. *Chemosphere* 35, 1271–1289.
- Krutz, L.J., Senseman, S.A., Zablotowicz, R.M., Matocha, M.A., 2005. Reducing herbicide runoff from agricultural fields with vegetative filter strips: a review. *Weed Science* 53, 353–367.
- Langenbach, T., Schroll, R., Paim, S., 2000. Fate and distribution of ^{14}C -atrazine in a tropical oxisol. *Chemosphere* 40, 449–455.
- Lavy, T.L., Mattice, J.D., Kochendefler, J.N., 1989. Hexazinone persistence and mobility of a steep forested watershed. *Journal of Environmental Quality* 18, 507–514.
- Laws, S.C., Ferrell, J.M., Stoker, T.E., Schmid, J., Cooper, R.L., 2000. The effects of atrazine on female Wistar rats: an evaluation of the protocol for assessing pubertal development and thyroid function. *Toxicological Science* 58, 366–376.
- Ludovice, M.T.F., Roston, D.M., Teixeira Filho, J., 2003. Efeito da faixa-filtro na retenção de atrazina em escoamento superficial. *Revista Brasileira de Engenharia Agrícola e Ambiental, Campina Grande* 7, 323–328.
- Matallo, M., Luchini, L., Gomes, M., Spadotto, C., Cerdeira, A., Marin, G., 2003. Lixiviação dos herbicidas tebuthiuron e diuron em colunas de solo. *Pesticidas: Revista de Ecotoxicologia e Meio Ambiente, Curitiba* 13, 83–90.
- Matallo, M.B., Spadotto, C.A., Luchini, L.C., Gomes, M.A.F., 2005. Sorption, degradation and leaching of tebuthiuron and diuron in soil columns. *Journal of Environmental Science and Health – Part B* 40, 39–43.
- Musumeci, M.R., Nakagawa, L.E., Luchini, L.C., Matallo, M.B., Andrea, M.M., 1995. Degradação do diuron- ^{14}C em solo e em plantas de cana-de-açúcar (*Saccharum spp*) Pesquisa Agropecuária Brasileira. *Brasília* 30, 775–778.
- Negrisoni, E., Costa, E.A.D., Velini, E.D., Cavenaghi, A.L., Tofoli, G.R., 2005. Deposition and leaching of tebuthiuron on sugar cane straw applied with and without alkyl polyglycoside adjuvant. *Journal of Environmental Science and Health* 40, 207–214.
- Pearce, R.A., Trlica, M.J., Leininger, W.C., Smith, J.L., Fransier, G.W., 1997. Efficiency of grass buffer strips and vegetation height on sediment filtration in laboratory rainfall simulations. *Journal of Environmental Quality* 16, 139–144.
- Pinho, A.P., Matos, A.T., Costa, L.M., Morris, L.A., Jackson, R.C., White, W., Martinez, M.A., 2004. Retenção de atrazina, picloran e caulinita em zona ripária localizada em área de silvicultura. *Engenharia Agrícola, Viçosa* 12, 260–270.
- Pionke, H.B., Glotfelty, D.W., 1990. Contamination of groundwater by atrazine and selected metabolites. *Chemosphere* 21, 813–822.
- Poletika, N.N., Coody, P.N., Fox, G.A., Sabbagh, G.J., Dolder, S.C., White, J., 2009. Chlorpyrifos and atrazine removal from runoff by vegetated filter strips: experiments and predictive modeling. *Journal of Environmental Quality* 38, 1042–1052.
- Reichenberger, S., Bach, M., Skitschak, A., Frede, H.-G., 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness, a review. *Science of the Total Environment* 384, 1–35.
- Rohde, W.A., Asmussen, L.E., Hauser, W.W., Hester, M.L., Allison, H.D., 1981. Atrazine persistence in soil and transport in surface and subsurface runoff from plots in the coastal plain of the southern United States. *Agro-Ecosystems* 7, 225–238.
- Sabbagh, G.J., Fox, G.A., Kamanzi, A., Roepke, B., Tang, J.Z., 2009. Effectiveness of vegetative filter strips in reducing pesticide loading: quantifying pesticide trapping efficiency. *Journal of Environmental Quality* 38, 762–771.
- Schneider, J., Morin, A., Pick, F.R., 1995. The response of biota in experimental stream channels to a 24-hour exposure to the herbicide Velpar L®. *Environment Toxicology and Chemistry* 14, 1607–1613.
- SMA (Secretaria do Meio Ambiente), 2008. Resolução 08, 31 de janeiro de 2008. Fixa a orientação para o reflorestamento heterogeneo de areas degradadas e dá providencias correlatas.
- Snoo, G.R., de Wit, P.J., 1998. Buffer zones for reducing pesticide drift to dithesand risks to aquatic organisms. *Ecotoxicology and environmental safety* 41, 112–118.
- Spadotto, C.A., 2002. Screening method for assessing pesticide leaching potential. *Pesticidas: Revista de Ecotoxicologia e Meio Ambiente, Curitiba* 12, 69–78.
- Spencer, W.F., 1987. Volatilization of pesticide residues. In: Biggar, J.W., Suber, J.N. (Eds.), *Fate of Pesticides in the Environment: Proceedings of a Technical Seminar Agricultural Experiment Station. Division of Agriculture and Natural Resources, University of California, California*, p. 61.
- SRC, 2007. Syracuse Research Corporation. Interactive PhysProp Database DemoDisponível em: <http://www.syrres.com/esc/physdemo.htm>. 2007. Accessed: 20 Feb. 2007.
- Tomlin, C.D.S., 2000. *A World Compendium: The Pesticide Manual*, 12 ed. British Crop Protection Council, Farnham, UK, pp. 67–68.
- Yao, Y., Tuduri, L., Harmer, T., Blanchard, P., Waite, D., Poissant, L., Murphy, C., Belzer, W., Aulagnier, F., Li, Y.-F., Sverko, E., 2006. Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions. *Atmospheric Environment* 40, 4339–4351.
- Zhu, Y., Li, Q.X., 2002. Movement of bromacil and hexazinone in soils of Hawaiian pineapple fields. *Chemosphere* 49, 669–674.