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

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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, 2003; 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 Orlândia, São Paulo, Brazil, at 767 m altitude bordering on a small stream, Ribeirão do Rosário, and situated at...
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 (200–300 mm month−1) and a dry autumn and winter from April to September (0–75 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 sugar cane field. The third area was 30 m wide within the sugar cane plantation that was adjacent to the riparian forest (Fig. 1).

2.3. Experiment

Herbicides were applied by a tractor directly on the sugar cane field. It had been previously treated as recommended agricultural rates with the commercial product Velpar-K to a level of 514.0 g.a.i.ha−1 of diuron and 145.2 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 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 8h. 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 mL were injected by a SIL 10A into a Shimadzu HPLC (model LC 2010) with two LC-10AD pumps equipped with a Varian C-18 (250×4.6 mm i.d.) reverse phase column preceded by a guard column (10×3.0 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 (r2=0.999) and recoveries from 90 to 103%. All concentration values from extracts were corrected on the basis of measured recoveries.
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±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 μg g\(^{-1}\) at 60–80 cm depth was very similar to the 34.3 μg 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.](https://example.com/fig2.jpg)
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 than diuron demonstrated a significant reduction of the herbicide levels from 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 absorb 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

Table 2

Diuron, hexazinone and tebuthiuron residues (mean μg g soil⁻¹ ± 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.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Sugar cane</th>
<th>Young riparian forest</th>
<th>Old riparian forest</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2003</td>
<td>2004</td>
<td>2003</td>
</tr>
<tr>
<td></td>
<td>2004</td>
<td></td>
<td>2004</td>
</tr>
<tr>
<td><strong>Diuron</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–20</td>
<td>0.19 ± 0.01</td>
<td>5.41 ± 0.24</td>
<td>0.39 ± 0.04</td>
</tr>
<tr>
<td>20–40</td>
<td>0.06 ± 0.04</td>
<td>0.53 ± 0.14</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>40–60</td>
<td>&lt;LD</td>
<td>0.06 ± 0.06c</td>
<td>0.05 ± 0.02a</td>
</tr>
<tr>
<td>60–80</td>
<td>0.14 ± 0.05</td>
<td>0.06 ± 0.04c</td>
<td>0.08 ± 0.02a</td>
</tr>
<tr>
<td>80–100</td>
<td>N.D.</td>
<td>0.07 ± 0.05c</td>
<td>0.08 ± 0.00b</td>
</tr>
<tr>
<td>100–120</td>
<td>N.D.</td>
<td>&lt;LD</td>
<td>3.95 ± 1.00a</td>
</tr>
<tr>
<td>Total</td>
<td>0.25</td>
<td>6.07</td>
<td>0.60</td>
</tr>
<tr>
<td><strong>Hexazinone</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–20</td>
<td>0.14 ± 0.14</td>
<td>5.45 ± 1.24</td>
<td>0.27 ± 0.05a</td>
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<td>20–40</td>
<td>0.05 ± 0.03</td>
<td>2.22 ± 1.78</td>
<td>0.43 ± 0.16a</td>
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<td>40–60</td>
<td>0.47 ± 0.10</td>
<td>0.61 ± 0.38c</td>
<td>0.53 ± 0.26a</td>
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<tr>
<td>60–80</td>
<td>0.66 ± 0.12</td>
<td>2.36 ± 0.97b</td>
<td>0.79 ± 0.27a</td>
</tr>
<tr>
<td>80–100</td>
<td>N.D.</td>
<td>0.86 ± 0.34c</td>
<td>0.89 ± 0.17b</td>
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<tr>
<td>100–120</td>
<td>N.D.</td>
<td>3.15 ± 1.38a</td>
<td>4.22 ± 1.23a</td>
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<tr>
<td>Total</td>
<td>1.32</td>
<td>14.47</td>
<td>2.02</td>
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<td><strong>Tebuthiuron</strong></td>
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<td></td>
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<tr>
<td>0–20</td>
<td>11.65 ± 2.82</td>
<td>5.47 ± 0.60a</td>
<td>24.57 ± 8.00a</td>
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<td>20–40</td>
<td>6.21 ± 1.70b</td>
<td>1.92 ± 1.86ab</td>
<td>5.98 ± 4.27b</td>
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<td>40–60</td>
<td>4.09 ± 0.70b</td>
<td>0.74 ± 0.67c</td>
<td>1.31 ± 0.29b</td>
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<td>60–80</td>
<td>6.18 ± 1.46b</td>
<td>3.43 ± 1.57a</td>
<td>3.96 ± 1.37a</td>
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<tr>
<td>80–100</td>
<td>N.D.</td>
<td>1.18 ± 0.58b</td>
<td>3.72 ± 0.30b</td>
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<tr>
<td>100–120</td>
<td>N.D.</td>
<td>3.65 ± 1.63a</td>
<td>5.73 ± 0.64b</td>
</tr>
<tr>
<td>Total</td>
<td>28.13</td>
<td>17.39</td>
<td>35.72</td>
</tr>
</tbody>
</table>

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.
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 tebuthiuron 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 tebuthiuron (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 tebuthiuron 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 reached 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 tebuthiuron with $2.7 \times 10^{-6}$ mbar at 20 °C compared to hexazinone with $2.7 \times 10^{-7}$ mbar at 25 °C and for hexazinone with diuron with $1.1 \times 10^{-6}$ 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 tebuthiuron 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 tebuthiuron 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; Glotefelt et al., 1989; Langenbach et al., 2000; Correia et al., 2007).

Volatile tebuthiuron residues may be moved by wind to higher above ground level and then could have remained in part by the higher riparian forest canopy. The highly soluble tebuthiuron 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 tebuthiuron 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.

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References


