***Original Research Article***

# Effects of pesticide use in farmland under with intensive soil management use in Southern Brazil

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## ABSTRACT


Poor soil management and intensive use of pesticides causes serious damage to soil and water quality in Brazil. To confirm this, two studies were conducted in an area with intensive farming in Southern Brazil with the following objectives: i) objectives to evaluate the level of pesticides in the river adjacent to the farmland during different seasons (river study) and to know; ii) to analyze the potential contamination resulting from surface runoff (runoff study). The river study was performed with samples from river water and riverbed sediment obtained over a one year period with three months sampling period intervals every three months (different seasons) on dry days (base flow effect).The runoff study was performed in the laboratory with simulated rainfall after recent pesticide application. The pesticides analyzed were Tebuconazole, Metalaxyl, Deltamethrin, Chlorothalonil, Glyphosate and its Metabolite-aminomethylphosphonic acid. They represented the most commonly used pesticides in the studied region. None of the pesticides tested were found in the riverwater river water or riverbed-sediment riverbed sediment samples at any sampling period time point. The detection limit in river water samples for Glyphosate and its metabolite was5 μg $L^{-1}$while it was 1 μg $L^{-1}$ and for the other pesticides was 1 μg $L^{-1}$. On The other hand, The runoff study (one hour rainfall) demonstrated that all the pesticides were present at high levels. (It was 36 μg $L^{-1}$ for Tebuconazole, 3.24 μg $L^{-1}$ for Metalaxyl, and 5.74 μg $L^{-1}$ for Chlorothalonil in runoff samples,) suggesting a high probability of contamination in downstream environments during intense rainfall events after pesticides application. Our data The results highlights the importance of good management practices to prevent pesticides contamination from agricultural runoff to of downstream environments due to runoff from agricultural lands such as rivers.



*Keywords: Agrochemical, catchment, land use, riverbed sediment, runoff, water quality, land use, catchment, runoff, water quality, riverbed-sediment*


## 1 INTRODUCTION

Increased in intensive agricultural production has led to a rise in the use of pesticides worldwide. Brazil is now the second largest consumer of pesticides in the world and the eighth per cultivated area [1]. Pesticides usage can cause environmental damage as well as affects human and animal health depending on its toxicity level, time of exposure, quantity amount applied and persistence [2, 3].

Pesticides applied on farmland can reach the water bodies bodiy by surface runoff, leaching (matrix flow) and preferential flow [4]. The fate of pesticides is strongly affected by the natural affinity of the chemical with the environmental solid, liquid, gaseous and biota states compartments (solid, liquid, gaseous, biota), and this behavior is usually expressed by the soil organic carbon sorption coefficient ($K_{oc}$), water solubility, Henry's constant ($K_H$) and Octanol-water partition coefficient ($K_{ow}$)[3, 4, 5]. Movement of pesticides from soil to water depends on factors such as soil texture, soil organic matter [3, 4, 6, 7], topography, and rainfall [8, 9]..Pesticides that are highly adsorbed by soil mineral and organic particles have a lower leaching potential and consequently a high potential for being transported (along with the sediment) by surface runoff along with the sediments [10].

The Water quality standard is set according to risk assessments for environment, and animal and human health. This is encoded by environmental laws which define the maximum limits of biological, chemical and physical elements. In Brazil, normative as …….. [11; 12; 13] [11], [12] and [13] establish the maximum limits for pollutants in superficial and ground waters and in soil as ……… [14] in soil. Also, the Brazilian Health Department, by resolution ……… [15] established limits for drinking water as …… [15]. However, not all pollutant groups are described in the Brazilian legislations, so international legislations, such as the United States Environmental Protection Agency [16, 17] and European Union legislations [18] should also be considered.

The Campestrecatchment is located in Colombo, Paraná State, south of Brazil, occupied by family farmers that who produces mainly vegetables to supply Curitiba and the Metropolitan market. In this catchment, most of the arable areas are in conflict with the land use capacity, with very high slope and shallow soils [19]. The conventional system of vegetable production includes intensive soil use as well as an intensive use of pesticides and fertilizers thereby increasing the potential for rivers, lakes, and groundwater contamination. Colombo city plays an important role in for domestic water supply because of the surface drainage network and the presence of the Karst aquifer [20].

This study therefore Our study included two objectives. Firstly, we assessed the level of pesticides in the river water (base flow) and riverbed-sediment affected by land use in different seasons. It also investigated Second, under laboratory conditions, we simulated rainfall to analyze runoff potential contamination in events of intense precipitation after immediate recent applications of pesticides of pesticides.

## 2 MATERIAL AND METHODS

### 2.1 Physicoal-chemical properties and transport potential of the studied pesticides

The physical – and chemical properties of the studied pesticides are described in Table 1, and the potential for leaching or runoff transport estimated by threemethods three methods which includes GUS, EPA and GOSS (GUS, EPAand GOSS) in (Table 2).

TheGUSindex The GUS index, created by[21] by ……. [21] which is based isbased on thehalf-life the half-life in soil and the soil organic carbonsorption carbon sorption coefficient(Koc) coefficient (Koc) ([GUS=( loghalf-life log half-life in soil) X (4- log$K_{oc}$)]) [22].Valuesgreater Values greater than 2.8indicate a highpotential high potential for leaching, while valuesbelow 1.8indicate values below 1.8 indicate thatthis that this pesticide will be lost byrunoff[23] by runoff [23].According to the GUS criteria(Table 2),metalaxylhas metalaxyl has a highleaching high leaching potential followed by tebuconazole. Conversely, deltamethrin,chorotalonil deltamethrin, chorotalonil and glyphosate have a very low leaching potential.

TheEPAmethod The EPA method evaluates the pesticidesaccording pesticides according to the followingphysical-chemical following physical-chemical properties: water solubility, soilorganiccarbon soil organic carbon sorption coefficient (Koc), Henry's constant ($K_H$), half-life in soil, half-life inwaterand in water and annual rainfall. According to EPAthe EPA the pesticide leaching potential is high whenwater when water solubility > 30 mg$L^{-1}$, Koc<300-500 g$mL^{-1}$, $K_H$<$10^{-2}$ Pa $m^3 mol^{-1}$, half-life in soil >14 to 21 days,half-life inwater days, half-life in water > 175 days andannual and annual rainfall > 250 mm [24]. According to the EPA criteria (Table 2), metalaxylandtebuconazolehave metalaxyl and tebuconazole have a highleaching high leaching potential, while chlorothalonil,glyphosate chlorothalonil, glyphosate and deltamethrin have noleaching no leaching potential.

The GOSS method evaluates the potential transport associated with the sediment as follows: a) high potentialassociated potential associated withsedimenttransport(half-life with sediment ransport (half-life in soil≥ 40days 40 days and$K_{oc}$ and $K_{oc}$= 1,000orhalf-life1,000 or half-life in soil ≥40 days and $K_{oc}$≥ 500 and solubility in water≤0.5mg $L^{-1}$; b) low potentialassociated potential associated with thesediment the sediment transport (half-life in soil < 1day orhalf-life or half-life in soil ≤2 days and$K_{oc}$ and $K_{oc}$ ≤ 500 or half-life in soil ≤ 4 days and $K_{oc}$≤900and 900 and solubility in water ≥ 0.5mg $L^{-1}$ or half-life in soil ≤ 40 days and $K_{oc}$≤ 500 and solubility in water ≥ 0.5mg $L^{-1}$orhalf-life or half-life in soil ≤40 days and $K_{oc}$≤ 900 and solubility in water≥2mg $L^{-1}$); c) high potentialdissolved potential dissolve d in water transport (half-life in soil > 35 and $K_{oc}$< 1,000,000 and solubility in water≥ 1 mgL$^{-1}$ or $K_{oc}$ ≤700 andsolubility and solubility in water between 10 and100mg L$^{-1}$); d) low potentialdissolved potential dissolved in water transport ($K_{oc}$≥1,000,000orhalf-life 000 or half-life in soil ≤ 1day and $K_{oc}$≤100 orhalf-life or half-life in soil <35 days and solubility in water<0.5 mg L$^{-1}$); e) substancesthat substances that do notfit not fit into anyof any of the above criteria are considered to have an average potentialtopollutesurface potential to pollute surface water [25]. Following thesecriteria these criteria (Table 2), tebuconazoleandmetalaxylhavelow tebuconazole and metalaxyl have low potential associated with sedimenttransportandhigh potentialdissolved inwater. Chlorothalonilanddeltamethrin sediment transport and high potential dissolved in water. Chlorothalonil and deltamethrin are in a transition zone between low and high potential associated with sedimenttransportwhile sediment transport while glyphosatehada glyphosate had a low potential fortransportdissolved inwater for transport dissolved in water.

Table 1. Physical-chemical properties of the pesticides [26].

| | Pesticides | | | | |
|---|---|---|---|---|---|
| | Tebuconazole | Metalaxyl | Chlorothalonil | Deltamethrin | Glyphosate |
| M (g mol$^{-1}$) | 307.82 | 279.33 | 265.9 | 505.2 | 168.07 |
| S (mg L$^{-1}$) | 36 | 7100 | 0.81 | 0.0002 | 10500 |
| V. P. (mPa) | 0.0013 | 0.75 | 0.076 | 0.0000124 | 0.0131 |
| M.P. (ºC) | 105 | 67.9 | 256.1 | 101 | 189.5 |
| $K_{ow}$ | 5011.87 | 44.66 | 758.57 | 39810.71 | 0.001 |
| $K_{oc}$ | 769 | 500 | 850 | 10240000 | 21699 |
| $K_H$ (Pa m$^3$ mol$^{-1}$) | 1 $10^{-5}$ | 1.60 $10^{-5}$ | 2.50 $10^{-2}$ | 3.10 $10^{-2}$ | 2.10 $10^{-7}$ |
| DT50 soil (days) | 62 | 42 | 22 | 13 | 12 |
| DT50 water (days) | 356 | 56 | 22 | 65 | 87 |

M- Molecular mass, S- Solubilityin water,V.P.-Vapor pressure, M.P. - Melting point,$K_{ow}$-Octanol-water partition coefficient,$K_{oc}$-Soil organic carbon sorption coefficient,$K_H$ -Henry's constant, DT50 soil - Half-life in soil, DT50 water - Half-life in water.

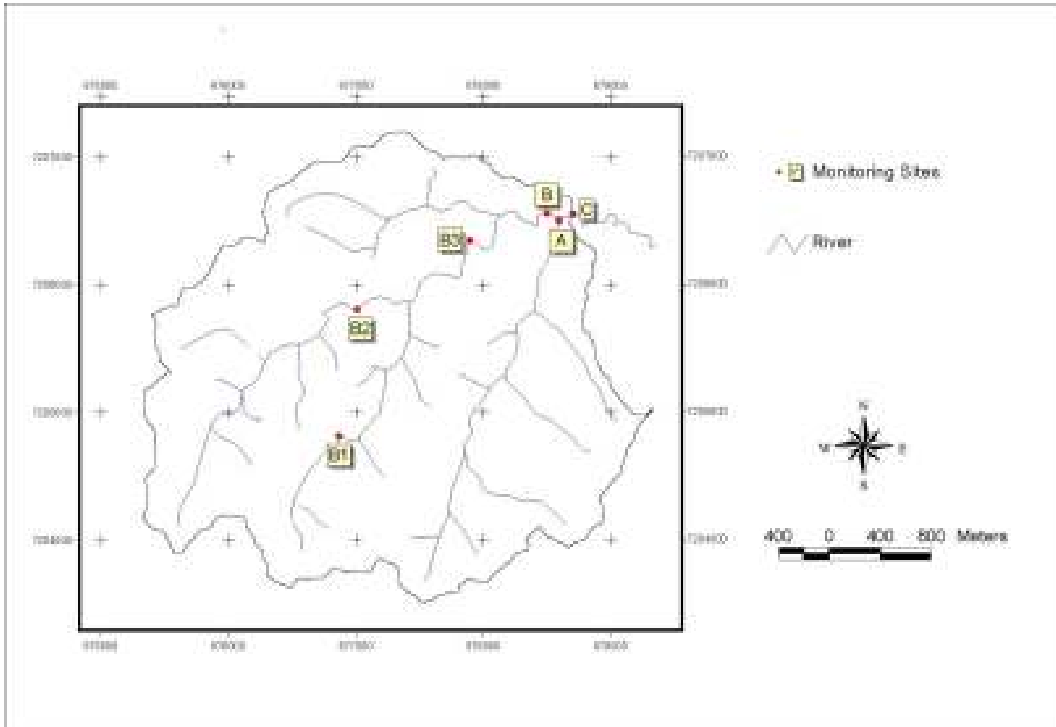
Table 2. Leaching and runoff potential according to GUS, EPAand GOSS EPA and GOSS criteria.

| | Pesticides | | | | |
|---|---|---|---|---|---|
| | Tebuconazole | Metalaxyl | Chlorothalonil | Deltamethrin | Glyphosate |
| GUS | 2.00 (high leaching potential) | 2.11 (high leaching potential) | 1.44 (no leaching potenti al) | -3.35 (no leaching potenti al) | -0.36 (no leaching pote ntial) |
| EPA | High leaching potential | High leaching potential | Nol eaching potential | No leaching potential | No leaching potential |
| GOSS | low potential with sediment and high potential dissolved in water | low potential with sediment and high potential dissolved in water | between low and high pot ential with sediment | between low and high pot ential with sediment | low potential dissolved i n water |

**y 1 – Pesticides in the river**

**a characterization**

y was carried out in Colombo, Metropolitan region of Curitiba, Paraná state, Southern Brazil (Figure 1). The Campestre catchmentbelongs c
o the Capivari river catchment. The climate is mesothermal humid subtropical (Cfb) by Köppen with average annual rainfall of 1400 to 160
Cambisol is the predominant soil, with Leptsol mainly on the top of the hills[28].




in the Campestre catchment, Colombo, Paraná, Brazil.

covered by native vegetation (57%) (Table 3). However, 19% is es (Table 4) cropped by small family farmers with several kinds hout the entire year (winter and summer cultivar; using the conv parian area that should be preserved by law is not covered with law [29], the drainage network should have 30 m each side po

Table 3. Land use (ha and %) in the Campestre catchment, Colombo, Paraná, Brazil.

| Monitoring sites | Area | Land use | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Native Forest | | Reforestation | | Agriculture | | Grassfield | | Other | |
| | ha | ha | % | ha | % | ha | % | ha | % | ha | % |
| A | 331 | 164 | 50 | 89 | 27 | 28 | 8 | 48 | 15 | 2 | 0.6 |
| B | 675 | 274 | 41 | 144 | 21 | 163 | 24 | 90 | 13 | 5 | 0.7 |
| C | 1010 | 440 | 44 | 234 | 23 | 192 | 19 | 138 | 14 | 6 | 0.6 |

Table 4. Slope classes and land use (ha and %) in theCampestre the Campe stre catchment, Colombo, Paraná, Brazil.

| Slope classes (%) |
|---|

| | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Total | 2.5 | 0.4 | 43.5 | 6.4 | 104.1 | 15.4 | 170.4 | 25.2 | 284.4 | 42.1 | 56.6 | 8.4 | 14.1 | 2.1 |
| C | Agriculture | 0.6 | 0.3 | 15.2 | 7.9 | 40.4 | 21,0 | 58.9 | 30.5 | 68.8 | 35.7 | 7.2 | 3.7 | 1.6 | 0.8 |
| | Total | 3.1 | 0.3 | 50.4 | 5.0 | 141.0 | 14.0 | 239.5 | 23.7 | 450.0 | 44.6 | 100.1 | 9.9 | 26.2 | 2.6 |

Table 5. Land use of the riparian zone in theCampestre the Campe stre catchment, Colombo,Paraná, Brazil.

| Monitoring sites | Land use of the riparian area | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Native Forest | | Reforestation | | Agriculture | | Grassfield | | Other | | Total | |
| | ha | % | ha | % | ha | % | ha | % | ha | % | ha | % |
| A | 27 | 60 | 10 | 22 | 3 | 6 | 5 | 10 | 0.4 | 0.9 | 44 | 100 |
| B | 49 | 55 | 10 | 11 | 17 | 19 | 13 | 14 | 0.4 | 0.4 | 89 | 100 |
| C | 77 | 57 | 20 | 15 | 20 | 15 | 18 | 13 | 0.8 | 0.6 | 135 | 100 |

#### 2.2.2 Monitoring sites and sampling

Six monitoring sites were selected for water analysis. Site C represents the entire study area (Figure 1) and site A and B represent the sub-basins.

The river water sampling was carried out from September 2008 to September 2009 every three months interval. On September 9th, 2008 (spring) and June 3rd, 2009 (winter) riverbed-sediment wasalso was also sampled. Soil (0-10 cm and 10-20 cm)from field cropped with vegetable wasalso was also sampled on September 9th, 2008 (spring) and June 3rd, 2009 (winter) in a conventional management system in the experimental area conducted by [30]. On the sampling of March 3th, 2008 (autumn), December 15th, 2008 (summer) and September 15th, 2009 (spring), only water from the river was sampled. All river samples were collected on dry days in polyethylene bottles, transported in ice boxes to the Food Processing Research Center at the Federal University of Paraná and kept under refrigeration at a temperature of 5$^{o}$ C (was that the temperature of the river site????) until further pending laboratory the time for analysis.

#### 2.2.3 Pesticide analysis

A survey of the most applied pesticides in the region was carried out. As a result, tebuconazole, metalaxyl, deltamethrin, chlorothalonil and glyphosate were chosen for analysis in the present study.

The extraction of pesticides (tebuconazole, metalaxyl, deltamethrin, chlorothalonil)from chlorothalonil) from river water samples was performed using decantation funnels as described inApha[31]. An aliquot of 1 literof liter of the sample was added to a 60 mL beaker containing 15% of the solvent hexane/dichloromethane (v/v) (15% analytic grade) and agitated for three minutes. The sample was then drained from the solvent with a separating funnel. This procedure was repeated three times. The extracted solvent (180 mL) was dried in a vaporizer and the remaining (1 mL) was injected in to a gas chromatographer and mass spectrophotometer with an electron detector [31]. Forthis method,the detectionlimitfor eachpesticidewas For this method,the detection limit for each pesticide was 1 $\mu g\ L^{-1}$.

Glyphosate and its metabolite (aminomethylphosphonic acid - AMPA) in the river water samples was analyzed by the Chelex – 100 column[32] after filtering the acidified sample (pH 2.0 ± 0.4 with HCl 6 M) through a glass filter. The detection limitforglyphosatein waterwas limit for glyphosatein water was 5 $\mu g\ L^{-1}$.

For the analysis of the pesticides (tebuconazole, metalaxyl, deltamethrin, chlorothalonil)in chlorothalonil) in riverbed -sediment and soil, 30 g of the sample was added to 20 mL of the solvent ethyl acetate and agitated f remained. After that it was applied to the column with resin AG[a] 50W-X2. The chromatographic column (4 x 150 mm) Glyphosate (Pickering) with guard Glyphosate (Pickering) column (3 x 20 mm) was used with 0.4 mL $min^{-1}$ flow of mobile phase, oven temperature of 55 ºC, and post column oven. A fluorescence detector was used with emission 430 nm and excitation of 340 nm. The injection volume was 50 µL and the retention time for the glyphosate was 13.60 and 26.49 minutes for its metabolite[34]. The detectionlimitof glyphosateinriverbed-sedimentand soilwas detection limit of glyphosate in riverbed-sediment and soil was 0.1 mg $kg^{-1}$.

## 2.3 Study 2 – Pesticides in the runoff

### 2.3.1 Preparation of erosion boxes

### 2.3.1 Preparation of erosion boxes

This study was carried out in erosion boxes with a rainfall simulator. Runoff samples were analyzed by the Brazilian Agricultural Research Corporation – EmbrapaForestry. Embrapa Forestry. The top soil (0-5 cm)was (0-5 cm) was collected from the Campestre catchment area, Colombo, Parana State, at the same field of the river study. Before filling the erosion box (30 cm wide, 40 cm long and 10 cm deep, with small roles on the bottom for drainage) the soil was sieved through a 5 mm mesh and dried. The boxes were filled with 7.5 cm of dried fine sand (washed with HCl 3% and deionized water to eliminate any contamination).The upper 2.5 cm was filled with soil using a field bulk density of 0.92 g $cm^{-3}$ [30].Some physical and chemical attributes of the soil (0-20 cm) [30]: organic carbon (30.5gkg$^{-1}$); clay (280gkg$^{-1}$), silt (370 gkg$^{-1}$) and sand (350 gkg$^{-1}$). Six boxes were used per pesticide. The erosion boxes were protected with a 5 cm high galvanized plate to avoid lateral losses and the runoff was collected in a bucket by a covered funnel placed at the end of the erosion boxes.

### 2.3.2 Pesticide application and rainfall simulation

### 2.3.2 Pesticide application and rainfall simulation

Three commercial products were used for the experiment. For Tebuconazole the Folicur® 200 EC (Bayer; 200 g $L^{-1}$of Tebuconazole) was used following the recommendation for beetroot (1 L of the commercial product per hectare). For chlorothalonil and metalaxyl the Folia Gold®(Syngenta Gold® (Syngenta; 675 g $kg^{-1}$ of Chlorothalonil and 67.5 g $kg^{-1}$ of Metalaxyl) was used following the recommendation for tomatoes (1.5 kg $ha^{-1}$). For Deltamethrin the K-Othrine® SC 25 (Bayer; 25 g $L^{-1}$ of Deltamethrin) was used following the recommendation for ground insects (8 mL of the commercial product per liter with application of 500 L per hectare).

To simulate rainfall, a programmable simulator equipped with a nozzle (Veejet 80-100) was used with deionized de-ionized water. The simulator was placed 2.4 m from the ground and the erosion boxes inclined 12%, simulating the field hillside slope. To obtain moisture uniformity, a rainfall of 20 mm $h^{-1}$was simulated for 10 minutes. After that, a rainfall intensity of 60 mm $h^{-1}$ was applied for one hour. The runoff was collected twice (30 and 60 minutes). The runoff volumes were recorded and a representative sample was refrigerated for further analysis.

Pesticides were applied in 100 mL of deionized de-ionized water, according to recommendations per hectare and using a spray bottle for better product distribution and moisture uniformity. The pesticides were applied at night to avoid higher temperatures, thus preventing chemical breakdown. Rainfall was simulated 12 hours after pesticide application.

### 2.3.3 Pesticide analysis

### 2.3.3 Pesticide analysis

Prior to pesticide extraction, samples were passed through a 0.45 µmcellulose ester membrane. The extraction of the pesticides was carried out as in Study 1. Thechromatographic analysis was performedby performed s operatedwith spectrometer was operated with an electron impactof70eV impact of 70 eV. To quantifythe quantify the pesticides the following fragments: m/z265 for chlorothalonilm/z205 formetalaxyl,m/z250 Chlorothalonil m/z205 Formetalaxyl m/z250 for tebuconazoleand Tebuconazole and the m/z 180 Fordeltamethrin were used.Quantificationwasperformedagainst anexternal standardusingacalibration used. Quantification was performed against an external standard using a calibration curve.

To validate this method, the amount of agrochemical recovered from 1 liter of ultrapure water with 0.8 μg $L^{-1}$ of the standard pesticide was measured. The recovered value (40 to 120%) was within the values recommended by [35].

The detection limit was determined based on the standard deviation and inclination of the calibration curve with the formula: LOQ = 10 (SD / S), where LOQ is the detection limit; SD is standard deviation and S isinclination is inclination of calibration curve [36]. The detection limit obtained for Metalaxyl was the lowest, 1.92 ng $L^{-1}$, and the highest value was for Deltamethrin, 23.59 ng $L^{-1}$.

## 3 RESULTS AND DISCUSSION

### 3.1 Study 1 – Pesticides in the river

None of the analyzed pesticides (Metalaxyl, Chlorothalonil, Deltamethrin, Tebuconazole, Glyphosate and AMPA) were detected in any of our riverwater the river water samples above the detection limits (1 μg $L^{-1}$for Metalaxyl, Chlorothalonil, Deltamethrin and Tebuconazole and 5 μg $L^{-1}$for glyphosate and its metabolite). The detection limit for glyphosate andtebuconazolewere muchlower and Tebuconazole were much lower than themaximum the maximum value allowed fordrinking for drinking water according to the Brazilian Ministry of Health (500 $mgL^{-1}$ and 180μg $L^{-1}$,respectively) [15]. This was also lower than the limit for glyphosate (65 μg $L^{-1}$) in fresh water established by the Brazilian Environmental Council [12].For the other pesticides there are were no maximum values defined by the Brazilian laws. USEPA [37] has a higher maximum limit for glyphosate indrinking in drinking water (700 μg $L^{-1}$). However, the maximum limit established by [18] is 0.1 μg $L^{-1}$for any pesticideand pesticide [18] and the sum of the pesticides should not be higher than 0.5 μg $L^{-1}$.

Due to the soil type (low depth), steep slopes, intensive soil and agrochemicals used, we expected to find pesticides were expected to be found in the river water. The [38] Authors have analyzed the water quality of the Campestre catchment area for one year and also found a very low concentration of nitrogen, phosphorus, and carbon [38].

Low pesticide levels in the river water can be explained by both the catchment land cover and the sampling time. the fact that most of the catchment area is covered by forest (41% of native and 24% of planted forest), resulting in buffering the effect of agriculture (arable land), which represents only 19% of the catchment. Retention of effect on pesticides in native vegetation has been demonstrated with the due to major contributor being adsorption by soil organic matter [39, 40].

In addition, all samples were collected during dry days. At these sampling days, there would be there was little contamination by runoff which was against the normal trend that should normally follows intense rainfall. The sampling in days without precipitation, on the other hand, suggests showed that the subsurface water which supplies of the river is was not contaminated. However, it is important to note that the detection limits in the present study (1 μg $L^{-1}$) were above the concentration obtained in rivers by several some authors [41, 42]. In The [43] in a study carried out in the Mediterranean Sea, it was found that contamination levels of metalaxyl and chlorothalonil in the River Rhône (France) and River Pó (Italy) were below 2 and 1 ng $L^{-1}$, respectively. Therefore, in the Campestre catchment, the pesticides might be present in the samples analyzed, but with a concentration below the detection limit 1 μg $L^{-1}$ (1 μg $L^{-1}$).

sorption and persistence of Glyphosate in the soil makes the presence of its metabolite in the sediment highl y likely.

### 3.2 Study 2 – Pesticides in simulated runoff

For all pesticides, the highest concentrations in runoff water for all pesticides were detected in the first 30 mi nutes and it decreased decreasing with rainfall duration (Figure 2). These results confirmed the hypotheses t hat intense precipitation may increase river contamination (Authority). In this study, only the dissolved fractio n of the pesticides (which passed through a 0.45 μm cellulose membrane) was analyzed and so chemicals tr apped in the particulate fraction were not extracted. Very high concentrations of pesticides in the dissolved fr action (3.24 μg $L^{-1}$ for metalaxyl, 36 μg $L^{-1}$ for tebuconazole, and 5.74 μg $L^{-1}$ for chlorothalonil) were obtained after one hour of rainfall (Figure 2). Deltamethrin was not detected during the last 30 minutes of rain, showin g the low potential for being transported in a dissolved fraction in the surface runoff (in the surface runoff). Ev en With a greater runoff volume in the final 30 minutes of rainfall, with values of ~2.52 L against 1.69 L in the first 30 minutes (~2.52 L against 1.69 L in the first 30 minutes), pesticides loss was greater in the first 30 min utes (Table 6). This was however, the total amount of pesticides lost by runoff were very low compared with t he total amount applied (Table 6). We saw However, there was greater losses in the pesticide Tebuconazole with 0.71 % of the total applied was lost in the one hour runoff (0.71 % of the total applied was lost in the on e hour runoff).

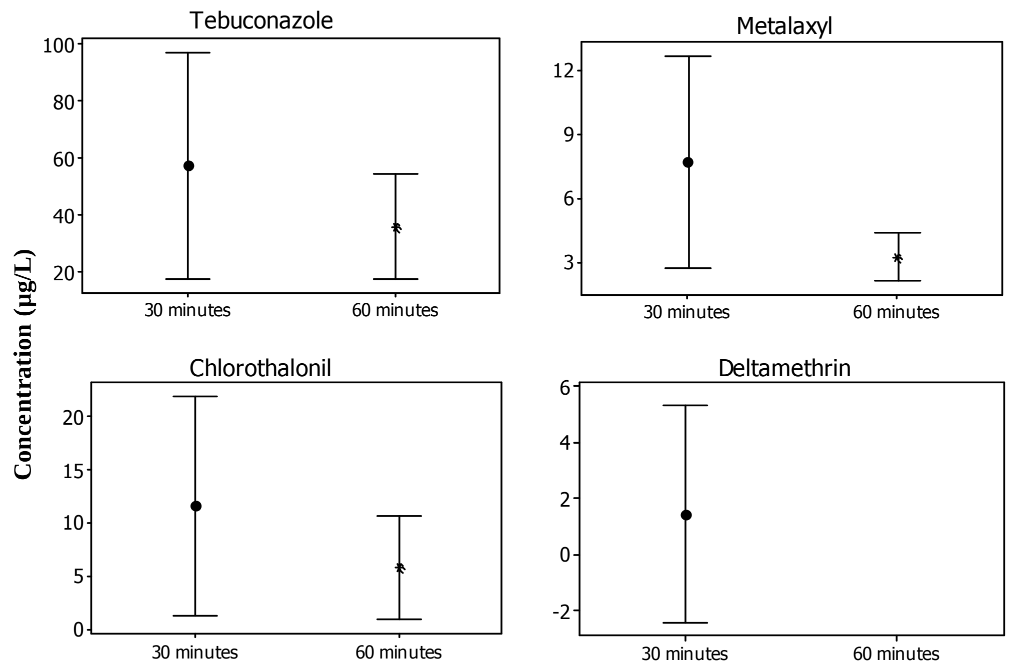



Fig.2. Mean concentration (± standard deviation) of Chlorothalonil, Metalaxyl, Tebuconazole and Deltamethri n dissolved in surface runoff (30 and 60 minutes) under simulated rainfall at 60 mm $h^{-1}$.

Table 6..Pesticide losses through surface runoff under rainfall simulation Losses of pesticides by surface run off under rainfall simulation.

Following the GUS method (Table 2), we expected loss of tebuconazole and metalaxyl in the dissolved fraction of the runoff was expected. This was observed with Tebuconazole, but not with Metalaxyl (Table 6). Similar The [45] also observed high levels of dissolved Tebuconazole in surface water has been reported [45]. Tebuconazole has also been detected in streams, wastewaters and lakes [46, 47, 48, 49], and hence this fungicide poses a risk of runoff transport.

Chlorothalonil and Deltamethrin were was expressed at low levels in runoff (dissolved fraction), which is in agreement with the GUS,EPAandGOSS GUS, EPA and GOSS models (Table 2). These are expected to strongly adsorb to soil organic particles due to its high Koc (Table 1) [50]. Chlorothalonil was applied at a higher concentration (Table 6) and was detected at lower levels. Some authors have The [51] observed small losses of chlorothalonil by leaching [51], supporting the fact concluding that this agrochemicals has a greater potential for loss by runoff in the particulate fraction. The Chlorothalonil was developed to degrade in less than four weeks in water, however, it was found in most of the Greek estuaries [52] suggesting its persistence in the riverbed sediments.

Deltamethrin is degraded in one to two weeks [53], which may explain the fact that we could not find this chemical in soil or river water (after how long?). The results of [54] analyzed contamination of waters in the Pantanal and found no Deltamethrin in the environment [54], attributing this to its physical-chemical properties and low use.

However, even with a small percentage of the applied pesticides being lost by runoff, the concentrations can could be high enough to cause serious environmental and human health problems. To avoid contamination in the river waters, pesticides use should be carefully managed.

## 4 CONCLUSION

The pesticides Tebuconazole, Metalaxyl, Chlorothalonil, Deltamethrin, Glyphosate and its their metabolites were not found in any of the riverwater river watet or riverbed-sediment samples from the Campestre catchment area. However, it must be considered that all sampling was carried out on dry days (base flow effect) with no influence of agricultural runoff from intense rainfall storms. On the other hand, our simulated rainfall study demonstrated a high potential for pesticide contamination by surface runoff (dissolved fraction< 0.45 µm). In addition to pesticide management it is also important to perform soil management to prevent pollutants contained in agricultural runoff from reaching river waters.

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