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Original Research Article

Pesticide use in farmland with intensive soil use in Southern Brazil

ABSTRACT

Poor soil management and intensive use of pesticides causes serious damage to soil and water quality. Two studies were conducted in an area with intensive farming in Southern Brazil with the following objectives: i) to evaluate the level of pesticides in the river adjacent to the farmland during different seasons (river study) and; ii) to analyze the potential contamination 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 sampling 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 represent the most commonly used pesticides in the study region. None of the pesticides tested were found in the riverwater or riverbed-sediment samples at any time point. The detection limit in river water samples for glyphosate and its metabolite was $5 \mu\text{g L}^{-1}$ and for the other pesticides was $1 \mu\text{g L}^{-1}$. On the other hand, the runoff study (one hour rainfall) demonstrated that all pesticides were present at high levels ($36 \mu\text{g L}^{-1}$ for tebuconazole, $3.24 \mu\text{g L}^{-1}$ for metalaxyl, and $5.74 \mu\text{g L}^{-1}$ for chlorothalonil in runoff samples) suggesting a high probability of contamination in downstream environments during intense rainfall events after pesticides application. Our data highlights the importance of good management practices to prevent pesticides contamination from agricultural runoff to downstream environments such as rivers.

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

1 INTRODUCTION

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

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Pesticides applied on farmland can reach the water body 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 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 [10].

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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] and [13] establish the maximum limits for pollutants in superficial and ground waters and [14] in soil. Also, the Brazilian Health Department, by resolution [15], establish limits for drinking water. 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 [18] should also be considered.

The Campestre catchment is located in Colombo, Paraná State, south of Brazil, occupied by family farmers who produce 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 increasing the potential for rivers, lakes, and groundwater contamination. Colombo city plays an important role for domestic water supply because of the surface drainage network and the presence of the Karst aquifer [20].

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. Second, under laboratory conditions, we simulated rainfall to analyze runoff potential contamination in events of intense precipitation after recent applications of pesticides.

2 MATERIAL AND METHODS

2.1 Physical-chemical properties and transport potential of the pesticides

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

The GUS index, created by [21], is based on the half-life in soil and the soil organic carbon sorption coefficient (K_{oc}) ($GUS = (\log \text{half-life in soil}) \times (4 - \log K_{oc})$) [22]. Values greater than 2.8 indicate a high potential for leaching, while values below 1.8 indicate that this pesticide will be lost by runoff [23]. According to the GUS criteria (Table 2), metalaxyl has a high leaching potential followed by tebuconazole. Conversely, deltamethrin, chlorothalonil and glyphosate have a very low leaching potential.

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

The GOSS method evaluates the potential transport associated with the sediment as follows: a) high potential associated with sediment transport (half-life in soil ≥ 40 days and $K_{oc} = 1,000$ or half-life in soil ≥ 40 days and $K_{oc} \geq 500$ and solubility in water $\leq 0.5 \text{ mg L}^{-1}$; b) low potential associated with sediment transport (half-life in soil < 1 day or half-life in soil ≤ 2 days and $K_{oc} \leq 500$ or half-life in soil ≤ 4 days and $K_{oc} \leq 900$ and solubility in water $\geq 0.5 \text{ mg L}^{-1}$ or half-life in soil ≤ 40 days and $K_{oc} \leq 500$ and solubility in water $\geq 0.5 \text{ mg L}^{-1}$ or half-life in soil ≤ 40 days and $K_{oc} \leq 900$ and solubility in water $\geq 2 \text{ mg L}^{-1}$; c) high potential dissolved in water transport (half-life in soil > 35 and $K_{oc} < 1,000,000$ and solubility in water $\geq 1 \text{ mg L}^{-1}$ or $K_{oc} \leq 700$ and solubility in water between 10 and 100 mg L^{-1}); d) low potential dissolved in water transport ($K_{oc} \geq 1,000,000$ or half-life in soil ≤ 1 day and $K_{oc} \leq 100$ or half-life in soil < 35 days and solubility in water $< 0.5 \text{ mg L}^{-1}$); e) substances that do not fit into any of the above criteria are considered to have an average potential to pollute surface water [25]. Following these criteria (Table 2), tebuconazole and metalaxyl have low potential associated with sediment transport and high potential dissolved in water. Chlorothalonil and deltamethrin are in a transition zone between low and high potential associated with sediment transport while glyphosate has a low potential for transport dissolved in water.

78 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. (°C)	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

79 M- Molecular mass, S- Solubility in water, V.P.-Vapor pressure, M.P. - Melting point, K_{ow}-Octanol-
80 water partition coefficient, K_{oc}-Soil organic carbon sorption coefficient, K_H -Henry's constant, DT50
81 soil - Half-life in soil, DT50 water - Half-life in water.
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84 Table 2. Leaching and runoff potential according to GUS, 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 potential)	-3.35 (no leaching potential)	-0.36 (no leaching potential)
EPA	high leaching potential	high leaching potential	no leaching 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 potential with sediment	between low and high potential with sediment	low potential dissolved in water

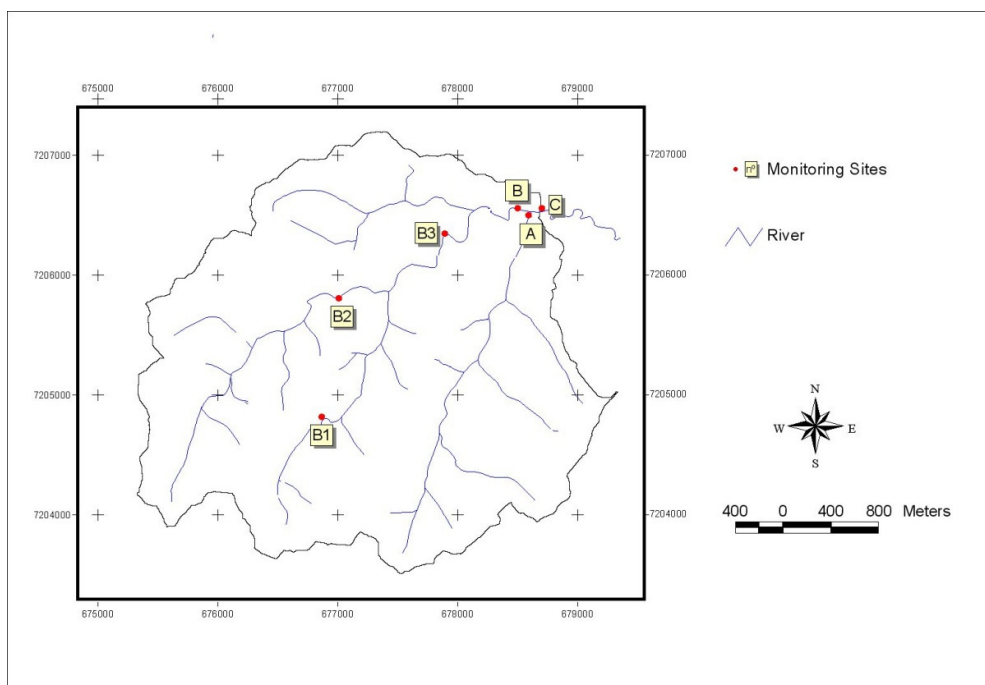
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87 2.2 Study 1 – Pesticides in the river

88 2.2.1 Area characterization

89 This study was carried out in Colombo, Metropolitan region of Curitiba, Paraná state, Southern Brazil (Figure
90 1). The Campestre catchment belongs to the Capivari river catchment. The climate is mesothermal humid
91 subtropical (Cfb) by Köppen with average annual rainfall of 1400 to 1600 mm[27]. Cambisol is the
92 predominant soil, with Leptosol mainly on the top of the hills[28].
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95 Fig.1. Drainage network and monitoring sites in the Campestre catchment, Colombo, Paraná, Brazil.

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97 Most of the land in the study area is covered by native vegetation (57%) (Table 3). However, 19% is arable
98 land and located on high slopes (Table 4) cropped by small family farmers with several kinds of vegetables
99 grown throughout the entire year (winter and summer cultivar; using the conventional system). Besides that,
100 43% of the riparian area that should be preserved by law is not covered with native forest (Table 5).
101 According to Brazilian law [29], the drainage network should have 30 m each side populated by native forest.
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103 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

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

		Slope classes (%)													
Monitoring sites		0 - 3		3-8		8-13		13 - 20		20 - 45		45 - 75		>75	
		ha	%	ha	%	ha	%	ha	%	ha	%	ha	%	ha	%
A	Agriculture	0.1	0.4	1.1	3.8	7.7	26.8	7.6	26.6	10.6	37	1.3	4.6	0.2	0.8
	Total	0.5	0.2	6.6	2.0	36.3	11.0	68.2	20.6	164.3	49.6	43.1	13.0	12.1	3.7
B	Agriculture	0.5	0.3	14.1	8.7	32.2	19.8	51.0	31.3	58	35.6	5.8	3.6	1.3	0.8
	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

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

		Land use of the riparian area											
Monitoring sites		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

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113 **2.2.2 Monitoring sites and sampling**

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

116 The river water sampling was carried out from September 2008 to September 2009 every three months. On
117 September 9th, 2008 (spring) and June 3^d, 2009 (winter) riverbed-sediment wasalso sampled. Soil (0-10 cm
118 and 10-20 cm)from field cropped with vegetable wasalso sampled on September 9th, 2008 (spring) and June
119 3^d, 2009 (winter) in a conventional management system in the experimental area conducted by [30]. On the
120 sampling of March 3th, 2008 (autumn), December 15th, 2008 (summer) and September 15th, 2009 (spring),
121 only water from the river was sampled. All river samples were collected on dry days in polyethylene bottles,
122 transported in ice boxes to the Food Processing Research Center at the Federal University of Paraná and
123 kept under refrigeration at a temperature of 5° C until further analysis.

124 **2.2.3 Pesticide analysis**

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

127 The extraction of pesticides (tebuconazole, metalaxyl, deltamethrin, chlorothalonil)from river water samples
128 was performed using decantation funnels as described inApha[31]. An aliquot of 1 literof the sample was
129 added to a 60 mL beaker containing 15% of the solvent hexane/dichloromethane (v/v) (15% analytic grade)
130 and agitated for three minutes. The sample was then drained from the solvent with a separating funnel. This
131 procedure was repeated three times. The extracted solvent (180 mL) was dried in a vaporizer and the
132 remaining (1 mL) was injected in to a gas chromatographer and mass spectrophotometer with an electron
133 detector [31]. Forthis method,the detectionlimitfor eachpesticidewas 1 µg L⁻¹.

134 Glyphosate and its metabolite (aminomethylphosphonic acid - AMPA) in the river water samples was
135 analyzed by the Chelex – 100 column[32] after filtering the acidified sample (pH 2.0 ± 0.4 with HCl 6 M)
136 through a glass filter. The detection limitforglyphosatein waterwas 5 µg L⁻¹.

137 For the analysis of the pesticides (tebuconazole, metalaxyl, deltamethrin, chlorothalonil)in riverbed-sediment
138 and soil, 30 g of the sample was added to 20 mL of the solvent ethyl acetate and agitated for six hours. The

solvent was separated and dried in the same way as the water sample. The final volume (1 mL) was injected into the gas chromatographer and mass spectrophotometer with electron detector [33]. The detection limit of these pesticides in sediment and soil was 0.04 mg kg^{-1} .

For the extraction of glyphosate and its metabolite in the riverbed-sediment and soil, 20 g of dried (40°C) and sieved sample was placed in Turrax bottles with 80 mL of NH_4OH (0.25 M) and 80 mL KH_2PO_4 (0.1 M). The mixture was agitated in a shaker for 90 minutes and centrifuged (5000 rpm) for 20 minutes. The supernatant was transferred to a fresh beaker and acidified (pH 2.0) with the addition of HCL (6 N). The extract was again centrifuged and transferred to a fresh beaker and incubated at $80 \pm 0.5^\circ\text{C}$ to evaporate until 5 mL remained. After that it was applied to the column with resin AG[®] 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°C , 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 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

This study was carried out in erosion boxes with a rainfall simulator. Runoff samples were analyzed by the Brazilian Agricultural Research Corporation – Embrapa Forestry. The top soil (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 holes 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 (30.5 g kg^{-1}); clay (280 g kg^{-1}); silt (370 g kg^{-1}) and sand (350 g kg^{-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

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; 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 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 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

Prior to pesticide extraction, samples were passed through a $0.45 \mu\text{m}$ cellulose ester membrane. The extraction of the pesticides was carried out as in Study 1. The chromatographic analysis was performed by gas chromatography (GC Focus) coupled to a mass spectrometer (Polaris Q Ion Trap). The samples were automatically injected and separated by chromatography column containing 5% polysilphenylene-siloxane (DB-5, 30 m, 0.25 mm id, film 0.25 mm thick). The analysis was done as follows: injection of 1 μL without breaking the flow with a transfer line temperature of 290°C . Helium was the carrier gas with a flow rate of 1 mL min^{-1} with a constant flow, and vacuum compensation. The oven temperature was 90°C with 5 minutes isotherm up to 160°C at a rate of $15^\circ\text{C min}^{-1}$ and 300°C at a rate of $15^\circ\text{C min}^{-1}$ with an isotherm of 8

minutes. The mass spectrometer was operated with an electron impact of 70 eV. To quantify the pesticides the following fragments: m/z 265 for chlorothalonil, m/z 205 for metalaxyl, m/z 250 for tebuconazole and the m/z 180 for deltamethrin were 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 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 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 and tebuconazole were much lower than the maximum value allowed for drinking water according to the Brazilian Ministry of Health (500 mg L⁻¹ and 180 µg 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 no maximum values defined by the Brazilian laws. USEPA [37] has a higher maximum limit for glyphosate in drinking water (700 µg L⁻¹). However, the maximum limit established by [18] is 0.1 µg L⁻¹ for any pesticide 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 use, we expected to find pesticides in river water. The [38] analyzed the water quality of the Campestre catchment area for one year and also found a very low concentration of nitrogen, phosphorus, and carbon.

Low pesticide levels in the river water can be explained by both the catchment land cover and the sampling time. Most of the catchment is covered by forest (41% of native and 24% of planted forest), buffering the effect of agriculture (arable land), which represents only 19% of the catchment. Retention of pesticides in native vegetation has been demonstrated with the 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 little contamination by runoff which normally follows intense rainfall. The sampling in days without precipitation, on the other hand, suggests that the subsurface water which supplies the river is 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 authors [41, 42]. The [43] in a study carried out in the Mediterranean Sea found contamination levels of metalaxyl and chlorothalonil in the River Rhône (France) and River Pó (Italy), 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).

In addition, values were below the detection limit (0.04 mg kg⁻¹ for metalaxyl, chlorothalonil, deltamethrin, and tebuconazole, and 0.1 mg kg⁻¹ for glyphosate and its metabolite) in the riverbed-sediment. Conversely, we found increased levels of the glyphosate metabolite in the soil samples taken from the hillside (0 - 10 cm depth). This metabolite may represent a potential long-term hazard for water contamination. Glyphosate is classified as moderately persistent in the soil with an estimated half-life of 47 days with a variation from 1 to 174 days, depending on the clay content, organic matter and microbial activity. This pesticide is highly adsorbed by most soils [44] with a low potential for leaching and high potential for superficial drainage (as estimated by GUS, EPA and GOSS models, Table 2). The high adsorption and persistence of glyphosate in the soil makes the presence of its metabolite in the sediment highly likely.

3.2 Study 2 – Pesticides in simulated runoff

The highest concentrations in runoff for all pesticides were detected in the first 30 minutes, decreasing with rainfall duration (Figure 2). These results confirmed the hypotheses that intense precipitation may increase

river contamination. In this study, only the dissolved fraction of the pesticides (which passed through a 0.45 μm cellulose membrane) was analyzed and so chemicals trapped in the particulate fraction were not extracted. Very high concentrations of pesticides in the dissolved fraction ($3.24 \mu\text{g L}^{-1}$ for metalaxyl, $36 \mu\text{g L}^{-1}$ for tebuconazole, and $5.74 \mu\text{g L}^{-1}$ for chlorothalonil) were obtained after one hour of rainfall (Figure 2). Deltamethrin was not detected during the last 30 minutes of rain, showing the low potential for being transported in a dissolved fraction (in the surface runoff).

Even with a greater runoff volume in the final 30 minutes of rainfall ($\sim 2.52 \text{ L}$ against 1.69 L in the first 30 minutes), pesticides loss was greater in the first 30 minutes (Table 6). However, the total amount of pesticides lost by runoff were very low compared with the total amount applied (Table 6). We saw greater losses in the pesticide tebuconazole (0.71 % of the total applied was lost in the one hour runoff).

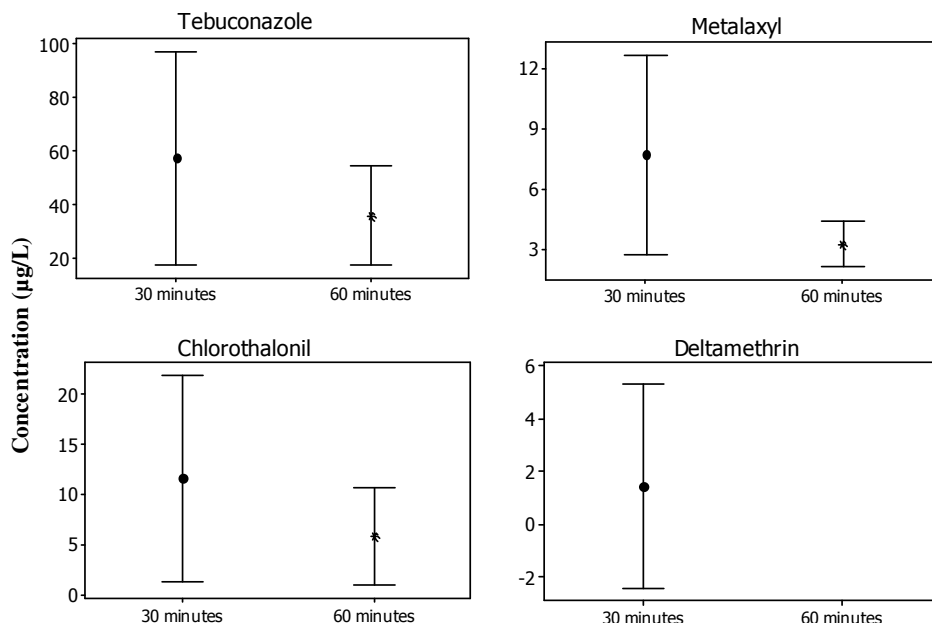


Fig.2. Mean concentration ($\pm$ standard deviation) of chlorothalonil, metalaxyl, tebuconazole and deltamethrin dissolved in surface runoff (30 and 60 minutes) under simulated rainfall at 60 mm h^{-1} .

Table 6. Losses of pesticides by surface runoff under rainfall simulation.

	Tebuconazole	Metalaxyl	Chlorothalonil	Deltamethrin
Total amount applied(mg)	24	13.5	135	1.2
Losses in the first 30 minutes of rain (mg)	0.0803	0.0170	0.0256	0.0021
Losses in the last 30 minutes of rain (mg)	0.0888	0.0087	0.0154	0.0000
Total losses(mg)	0.1691	0.0257	0.0410	0.0021
Total losses(%)	0.71	0.19	0.03	0.18

Following the GUS method (Table 2), we expected loss of tebuconazole and metalaxyl in the dissolved fraction of the runoff. This was observed with tebuconazole, but not with metalaxyl (Table 6). The [45] also observed high levels of dissolved tebuconazole in surface water. 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 was expressed at low levels in runoff (dissolved fraction), which is in agreement with the GUS, EPA and GOSS models (Table 2). These are expected to strongly adsorb to soil organic particles due to high Koc (Table 1) [50]. Chlorothalonil was applied at a higher concentration (Table

6) and was detected at lower levels. The [51] observed small losses of chlorothalonil by leaching, concluding that this agrochemical 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 estuarines [52] suggesting persistence in sediment.

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. The [54] analyzed contamination of waters in the Pantanal and found no deltamethrin in the environment, attributing this to physical-chemical properties and low use.

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

4 CONCLUSION

The pesticides tebuconazole, metalaxyl, chlorothalonil, deltamethrin, glyphosate and its metabolite were not found in any of the riverwater 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 water.

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