



Effects on Water Quality of Pesticide use in Farmland Under Intensive Soil Management in Southern Brazil

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Authors' contributions

This work was carried out in collaboration of all authors. Author LFL designed the study, managed the field work, performed the laboratory analyses, interpreted the data and wrote the first draft of the manuscript as part of the master dissertation at Soil Science Graduate Program of Federal University of Paraná State, Brazil. Author NF advisor professor, helped on the study design, field work, laboratory analyses, interpretation of data and final manuscript. Authors FAH, LFLJ, LCPL, JD and ACB, helped on the study design, field work, laboratory analyses, and interpretation of data. All authors read and approved the final manuscript.

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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 objectives to evaluate the level of pesticides in the river adjacent to the

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farmland during different seasons (river study) and to know the potential contamination resulting from surface runoff (runoff study). The river study was performed with samples from river water and riverbed sediment obtained over one year period with three months sampling period intervals (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 river water or riverbed sediment samples at any sampling period. The detection limit in river water samples for Glyphosate and its metabolite was $5\mu\text{g L}^{-1}$ while it was $1\mu\text{g L}^{-1}$ for the other pesticides. The runoff study (one hour rainfall) demonstrated that all the pesticides were present at high levels. It was $36\mu\text{g L}^{-1}$ 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 recent pesticides application. The results highlight the importance of good management practices to prevent pesticides contamination of downstream environments due to runoff from agricultural lands.

Keywords: Agrochemical; catchment; land use; riverbed sediment; runoff; water quality.

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 toxicity level, time of exposure, quantity applied and persistence [2,3].

Pesticides applied on farmland can reach water bodies 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 biotastes 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 by surface runoff along with the sediments [10].

Water quality standard is set according to risk assessments for environment, 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 Conama 357/2005, Conama 396/2008 and Cetesb [11,12,13] establish the

maximum limits for pollutants in superficial and ground waters and in soils Conama 460/2013 [14]. Also, the Brazilian Health Department established limits for drinking water by Resolution 2914/2011 [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 Campestre catchment is located in Colombo, Paraná State, south of Brazil, occupied by family farmers that 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 thereby increasing the potential for rivers, lakes, and groundwater contamination. Colombo city plays an important role in domestic water supply because of the surface drainage network and the presence of the Karst aquifer [20].

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

2. MATERIALS AND METHODS

2.1 Physico-Chemical Properties and Transport Potential of the Studied Pesticides

The physical and chemical properties of the studied pesticides are described in Table 1 [21], and the potential for leaching or runoff transport estimated by three methods, which includes GUS, EPA and GOSS (Table 2).

The GUS method [22] is based on the half-life in soil and the soil organic carbon sorption coefficient (K_{oc}) ($GUS = (\log \text{ half-life in soil}) \times (4 - \log K_{oc})$) [22,23]. 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 [24]. 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 [25] 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 $> 30 \text{ mg L}^{-1}$, $K_{oc} < 300-500 \text{ g mL}^{-1}$, $K_H < 10^{-2} \text{ Pa m}^3 \text{ mol}^{-1}$, half-life in soil > 14 to 21 days, half-life in water > 175 days and annual rainfall $> 250 \text{ mm}$ [25]. 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 [26] 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 the 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 [26]. 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 had a low potential for transport dissolved in water.

2.2 Study 1 – Pesticides in the River

2.2.1 Area characterization

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

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

2.2.2 Monitoring sites and sampling

Six monitoring sites were selected for water analysis (Fig. 1). Site C represents the entire study area 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 [September 9th, 2008 (spring); December 15th, 2008 (summer); March 3th, 2009 (autumn); June 3rd, 2009 (winter)]. The average temperature of the river site was 17.2°C. On September 9th, 2008 (spring) and June 3rd, 2009 (winter) riverbed-sediment was also sampled. Soil (0-10 cm and 10-20 cm) from field cropped

with vegetable was also sampled on September 9th, 2008 (spring) and June 3rd, 2009 (winter) in a conventional management system in the experimental area [30]. 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°C 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 river water samples was performed using decantation funnels with hexane/dichloromethane solvent [31]. For this method the detection limit for each pesticide was

1 µg L⁻¹. For the analysis of the same pesticides in riverbed-sediment and soil, 30 g of the sample was added to 20 mL of the solvent ethyl acetate [32]. The detection limit in sediment and soil was 0.04 mg kg⁻¹.

Glyphosate and its metabolite (aminomethylphosphonic acid - AMPA) in the river water samples was analyzed by applying the filtered acidified sample to the Chelex – 100 column [33]. The detection limit for Glyphosate in water was 5 µg L⁻¹. For the extraction of Glyphosate and its metabolite in the riverbed-sediment and soil, 20 g of the sample was placed in Turrax bottles with 80 mL of NH₄OH (0.25 M) and 80 mL KH₂PO₄ (0.1M). The extracted solution was applied to the column with resin AG[®] 50W-X2 [34]. The detection limit in riverbed-sediment and soil was 0.1 mg kg⁻¹.

The detection procedure of pesticides was performed using a gas chromatographer and mass spectrophotometer.

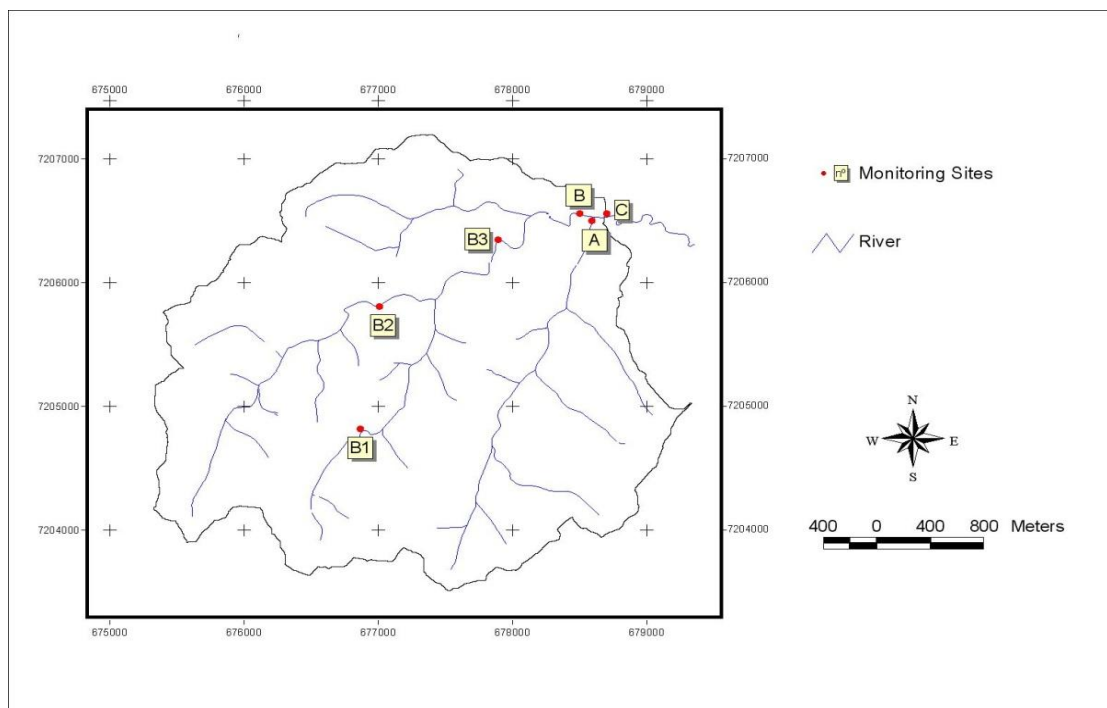


Fig. 1. Drainage network and monitoring sites in the Campestre catchment, Colombo, Paraná, Brazil

Table 1. Physical-chemical properties of the pesticides

	Pesticides				
	Tebuconazole	Metalaxyl	Chlorothalonil	Deltamethrin	Glyphosate
M (g mol ⁻¹)	307.8	279.3	265.91	505.2	169.1
S (mg L ⁻¹)	36	7100	0.81	0.0002	10500
VP (mPa)	0.0013	0.75	0.076	0.0000124	0.0131
MP (°C)	105.0	67.9	252.1	101.0	189.5
K _{ow}	5010	47	871	3.98 10 ⁴	6.31 10 ⁻⁴
K _{oc}	769	162	3032	10240000	28700
K _H (Pa m ³ mol ⁻¹)	1.00 10 ⁻⁵	1.60 10 ⁻⁵	2.50 10 ⁻²	3.10 10 ⁻²	2.10 10 ⁻⁷
DT ₅₀ soil (days)	63	42	22	13	12
DT ₅₀ water-sediment (days)	365	56	0.1	65	87

M- Molecular mass, S- Solubility in water, VP- Vapor pressure, MP- Melting point, K_{ow}- Octanol-water partition coefficient, K_{oc}- Soil organic carbon sorption coefficient, K_H- Henry's constant, DT₅₀ soil (typical)- Half-life in soil, DT₅₀ water - Half-life in water-sediment

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)	2.91 (high leaching potential)	0.70 (no leaching potential)	-3.35 (no leaching potential)	-0.49 (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

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	%
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 the Campestre catchment, Colombo, Paraná, Brazil

Monitoring sites	Slope classes (%)													
	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
A 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
B 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
C 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 the Campestre 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

2.3 Study 2 – Pesticides in the Runoff

2.3.1 Preparation of erosion boxes

This study was carried out in erosion boxes with 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, Colombo, Paraná 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

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 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 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

Prior to pesticide extraction, samples were passed through a 0.45 μm cellulose ester membrane. The extraction of the pesticides was carried out as in Study 1. The chromatographic analysis was performed by gas chromatography coupled to a mass spectrometer.

To validate this method, the amount of agrochemical recovered from 1 liter of ultrapure water with 0.8 $\mu\text{g L}^{-1}$ 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 [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 the river water samples above the detection limits (1 $\mu\text{g L}^{-1}$ for Metalaxyl, Chlorothalonil, Deltamethrin and Tebuconazole and 5 $\mu\text{g L}^{-1}$ 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 $\mu\text{g L}^{-1}$, respectively) [15]. This was also lower than the limit for Glyphosate (65 $\mu\text{g L}^{-1}$) in fresh water established by the Brazilian Environmental Council [12]. For the other pesticides there were no maximum values defined by the Brazilian laws. Usepa [17,37] has a higher maximum limit for Glyphosate in drinking water (700 $\mu\text{g L}^{-1}$).

However, the maximum limit established by the European Union [18] is 0.1 $\mu\text{g L}^{-1}$ for any pesticide and the sum of the pesticides should not be higher than 0.5 $\mu\text{g L}^{-1}$.

Due to the soil type (low depth), steep slopes, intensive soil and agrochemicals used, pesticides were expected to be found in the river water. 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 the fact that most of the catchment area is covered by forest (41% of native and 24% of planted forest), resulting in buffering effect on pesticides due to major adsorption by soil organic matter [39,40].

In addition, all samples collected during dry days there was little contamination by runoff which was against the normal trend that should follow intense rainfall. The sampling in days without precipitation, on the other hand, showed that the subsurface water was not contaminated. However, the detection limits in the present study (1 $\mu\text{g L}^{-1}$) were above the concentration obtained in rivers by some authors [41,42]. 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 [43]. Therefore, in the Campestre catchment, the pesticides might be present in the samples analyzed, but with a concentration below the detection limit 1 $\mu\text{g L}^{-1}$.

In addition, values were below the detection limit of 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 a typical half-life of 12 days [21] varying from 1 to 174 days [44], which depends on the clay content, organic matter and microbial activity. This pesticide is highly adsorbed by most soils with low potential for leaching and high potential for superficial drainage (as estimated by GUS, EPA and GOSS models, Table 2). The high adsorption and moderate persistence of Glyphosate in the soil makes the presence of its metabolite highly likely.

3.2 Study 2 – Pesticides in Simulated Runoff

For all pesticides, the highest concentrations in runoff water were detected in the first 30 minutes and it decreased with rainfall duration (Fig. 2). These results confirmed the hypotheses that intense precipitation may increase river contamination [45]. 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 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 (Fig. 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. With 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, pesticides loss was greater in the first 30 minutes. This was however very low compared with the total amount applied (Table 6). However, there was greater losses in the pesticide Tebuconazole with 0.71 % of the total applied lost in the one hour runoff.

Following the GOSS method (Table 2), 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 high level of Tebuconazole in surface water (streams and lakes) has been reported [46-50], indicating that his fungicide poses a risk of runoff transport (dissolved in water).

Chlorothalonil and Deltamethrin were expressed at low levels in runoff (dissolved fraction), which is in agreement with the GUS, EPA and GOSS methods (Table 2). These have low solubility in water and are expected to strongly adsorb to soil organic particles (Table 1) [21,51]. Chlorothalonil was applied at a higher concentration (Table 6) and was detected at lower levels. Some authors have observed small losses of Chlorothalonil by leaching [52], supporting the fact that this agrochemical has no leaching potential and medium potential for loss by sediment (Table 2). The Chlorothalonil was developed to degrade in less than four weeks [21], however, it was found in most of the Greek estuarines [53] suggesting its persistence in the river bed-sediments. Deltamethrin is degraded in one to two weeks [21,54], which may explain the fact that it was not find in the Pantanal river [55].

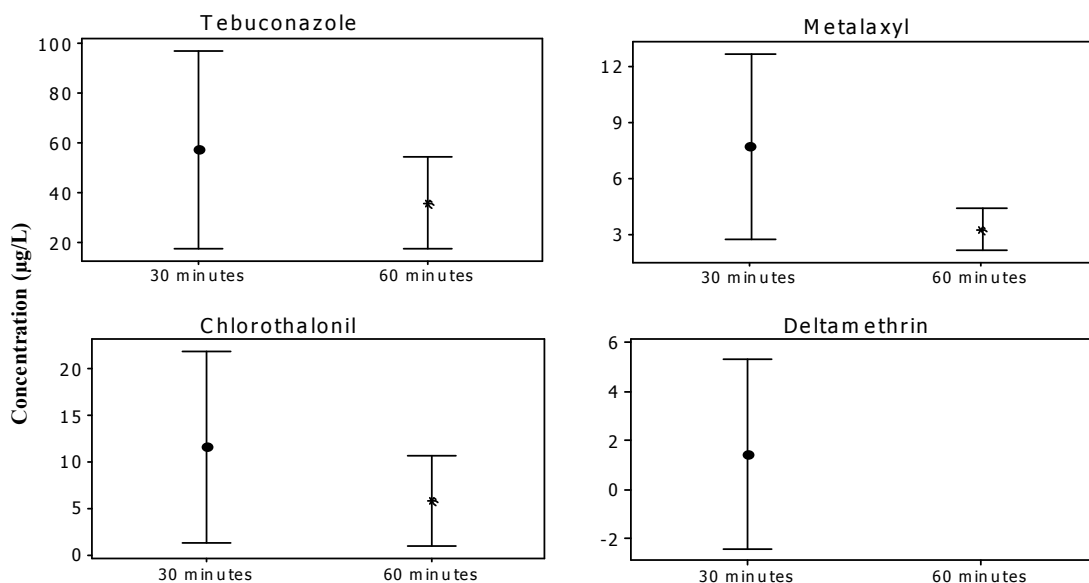


Fig. 2. Mean concentration (± standard deviation) of Chlorothalonil, Metalaxyl, Tebuconazole and Deltamethrin dissolved in surface runoff (30 and 60 minutes) under simulated rainfall at 60 mm h⁻¹

Table 6. Pesticide losses through surface runoff (dissolved fraction) under rainfall simulation

Properties	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

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

4. CONCLUSION

The pesticides Tebuconazole, Metalaxyl, Chlorothalonil, Deltamethrin, Glyphosate and their metabolites were not found in any of the river water 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, 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.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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