__Original Research Article__

Effects of pesticide use in farmland under intensive soil management 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 objectives to evaluate the level of pesticides in the river adjacent to the farmland during different seasons (river study) and to knowthe 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 was5 μg L^{-1}while it was 1 μg L^{-1} for the other pesticides.The runoff study (one hour rainfall) demonstrated that all the pesticides were present at high levels.It was36 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. The results highlights the importance of good management practices to prevent pesticides contamination of downstream environments due torunofffromagricultural 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 biotastates, 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 asConama nº. 357, Conama nº. 396 and Cetesb[11, 12,13] establish the maximum limits for pollutants in superficial and ground waters and in soilsasConama nº. 460 [14]. Also, the Brazilian Health Department established limits for drinking water by Resolution MSnº 2914 [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 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 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 conditionssimulated rainfall to analyze runoff potential contamination in events of intense precipitation after immediate applications of pesticides.

2 MATERIAL 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 index[22]is based on the half-life in soil and the soil organic carbon sorptioncoefficient (Koc) ([GUS=(log half-life in soil) X (4 – logK_{oc})]) [23].Values greater than 2.8indicate a high potential for leaching, while values below1.8 indicatethat 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, Chorotaloniland 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 (Koc), 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 mgL^{-1}, Koc<300-500 gmL^{-1}, K_H<10^{-2} Pa $m^3$$mol^{-1}$, half-life in soil >14 to 21 days, half-life in water> 175 days and annual rainfall > 250 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 associatedwith sediment transport (half-life in soil≥ 40 daysand K_{oc}= 1,000 or half-life in soil ≥40 days and K_{oc}≥ 500 and solubility in water≤0.5mg L^{-1}; b) low potential associated with the sediment transport (half-life in soil < 1day or half-life in soil ≤2 days and K_{oc} ≤ 500 or half-life in soil ≤ 4 days and K_{oc}≤ 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}or half-life in soil ≤40 days and K_{oc}≤ 900 and solubility in water≥2mg L^{-1}); c) high potential dissolved 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 and solubility in water between 10 and100mg L^{-1}); d) low potentialdissolved in water transport (K_{oc}≥1,000,000 or half-life in soil ≤ 1day and K_{oc}≤100 or half-life in soil <35 days and solubility in water<0.5 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 whileGlyphosate had a low potential fortransport dissolved in water.

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 (ºC)	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- Solubilityin 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, DT_{50} soil (typical)- Half-life in soil, DT_{50} 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

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 (Figure 1). The Campestrecatchment 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 Leptsol mainly on the top of the hills[28].

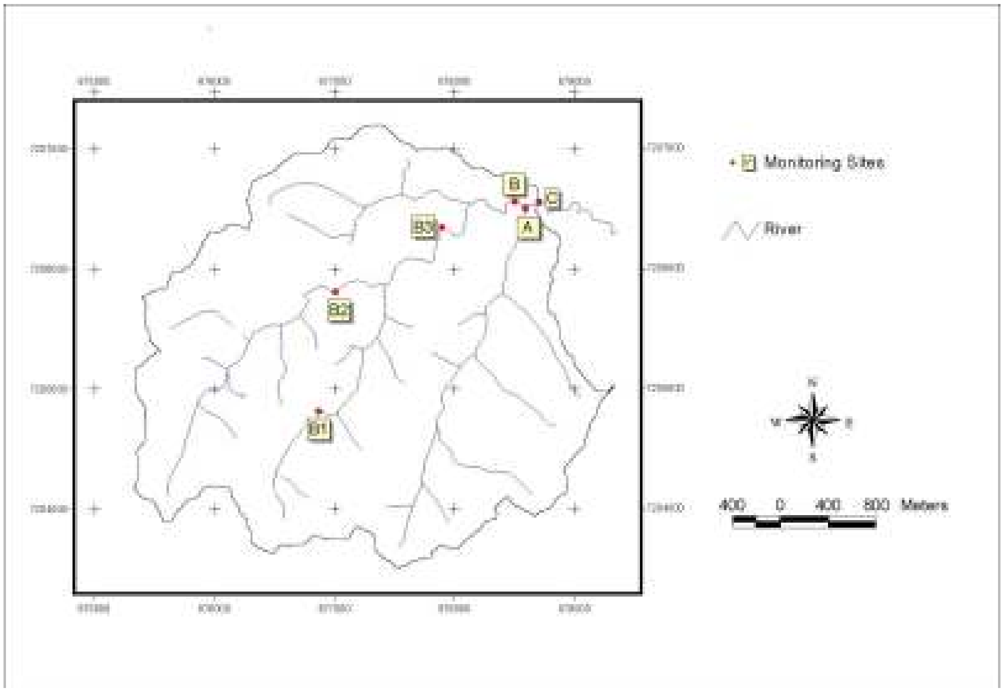

Fig.1. Drainage network and monitoring sites in the Campestre catchment, Colombo, Paraná, Brazil.

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). Accordingto Brazilian law [29], the drainage network should have 30 m each side populated by native forest.

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 the Campestre 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

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

2.2.2 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. The average temperature of the river site was 17.2ºC. 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 conducted [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°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 detection procedure was performed using a gas chromatographer and mass spectrophotometer.

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 pesticidewas 1 µg L^{-1}.For the analysis of the same pesticidesin riverbed-sediment and soil, 30 g of the sample was added to 20 mL of the solvent ethyl acetate [33]. 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[32].The detection limit for Glyphosatein water was 5 µg L^{-1}.For the extraction of Glyphosate and its metabolitein the riverbed-sediment and soil, 20 g of the sample was placed in Turrax bottles with 80 mL of NH_4OH (0.25 M)and 80 mL KH_2PO_4 (0.1M). The extracted solution wasapplied to the column with resin AG® 50W-X2 [34]. The detection limit 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 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, 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 µmcellulose ester membrane. The extraction of the pesticides was carried out as in Study 1. Thechromatographic analysis was performed by gas chromatography coupled to a massspectrometer.

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 [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 theriver 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 allowedfor 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 therewere no maximum values defined by the Brazilian laws. Usepa [17, 37] has a higher maximum limit for Glyphosate in drinking water (700 µg L^{-1}). However, the maximum limit established by the European Union[18] is 0.1 µg $L^{-1}$for any pesticide andthe 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, 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 ofthe catchment area is covered by forest (41% of native and 24% of planted forest), resulting inbuffering effect on pesticides in native vegetation 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 thenormal 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 µg L^{-1}) were above the concentration obtained in rivers by some authors [41, 42]. Ina 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 µg 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] and half-life varying from 1 to 174 days[44], whichdepends on the clay content, organic matter and microbial activity. 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 itdecreased with rainfall duration (Figure 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 t he 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 (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. 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. Thiswas however very low compared with the total amount applied (Table 6). However, there was greater losses in the pesticide Tebuconazolewith 0.71 % of the total applied lost in the one hour runoff.

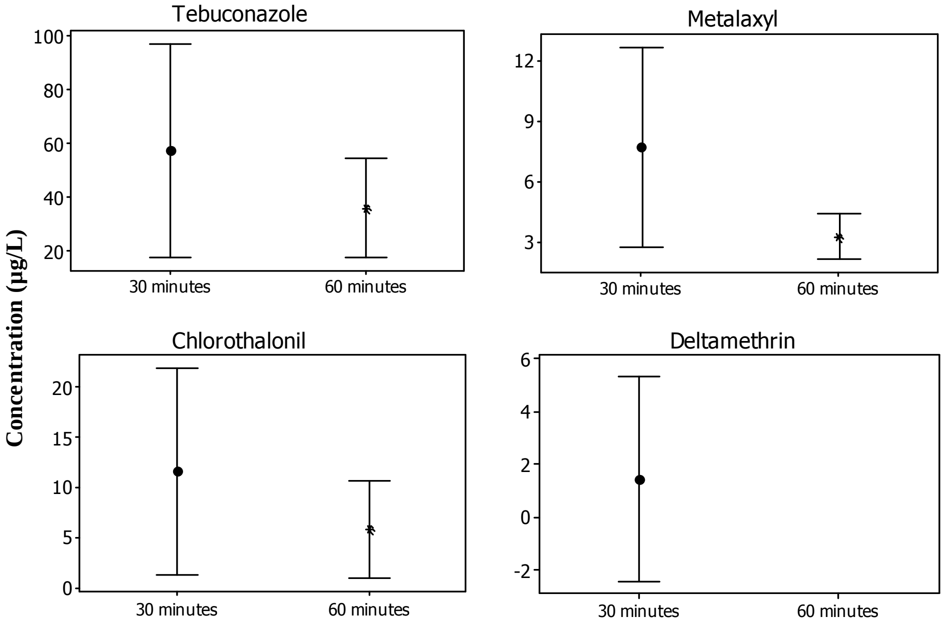

Fig.2. Mean concentration (± standard deviation) of Chlorothalonil, Metalaxyl, Tebuconazole and Deltamethrin dissolved in surface runoff (30 and 60 minutes) under simulated rainfall at 60 mm h$^{-1.}$

Table 6.Pesticide losses through surface runoff 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
Totallosses (mg)	0.1691	0.0257	0.0410	0.0021
Totallosses (%)	0.71	0.19	0.03	0.18

Following the GOSS method (Table 2), loss of Tebuconazole and Metalaxyl in the dissolved fraction of the runoff wasexpected. 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, 47, 48, 49, 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 s mall losses of Chlorothalonil by leaching [52], supporting the factthat this agrochemical has no leaching potential and mediumpotential 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 theriverbed-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].

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.

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