La granjA:
Revista de
Ciencias de la Vida
pISSN:1390-3799; eISSN:1390-8596
http://doi.org/10.17163/lgr.n38.2023.07

Scientific paper/ Artículo científico

Environmental Pollution

Fluvial loads of pesticides in the Pisque River (Ecuador) between June 2018 and May 2019

Cálculo de la carga fluvial de plaguicidas en el río Pisque (Ecuador) entre junio de 2018 y mayo de 2019

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Article received on September 06th, 2021. Accepted, after review, on April 28th, 2022. Published on September 1st, 2023.

Abstract

The Pisque river basin in Ecuador has a high presence of the floricultural industry, hence the aim of the research is to estimate the losses of pesticides that enter the river water through sources such as surface runoff, contact with the ground, permeate of a previous runoff or by infiltration, and that can be measured in the final channel of the Pisque river before its mouth. In order to know the pesticides used, surveys have been carried out with flower producers. The measurements were made in the Granobles and Guachalá rivers, the two tributaries of the Pisque river; and at two separate points on the same river Pisque, one immediately after the conjunction between the two tributaries and a point before their mouth to the next river. The flow gauges were monthly from June 2018 to May 2019. As a sampling method, SPMD and POCIS passive devices were used during the three dry months, from June to August 2018. To obtain the retention rates of the passive devices, a calibration with the pesticides was carried out in the laboratory through a hydrodynamic channel. Twenty-four main active ingredients were identified from the surveys, mostly compounds with Type III and Type IV toxicities. According to the results of the model, the fluvial load of pesticides in surface waters was 2,982.24 Kg between the months of June 2018 to May 2019, with environmental degradation of various compounds along the stretch of the river.

Keywords: Floriculture, passive SPMD and POCIS samplers, environmental degradation of pesticides.

Resumen

La cuenca del río Pisque en el Ecuador tiene alta presencia de industria florícola, desarrollándose aquí un estudio cuyo objetivo es la estimación de la magnitud de las pérdidas de plaguicidas que ingresan al agua fluvial por fuentes como escorrentía superficial, contacto con el suelo, permeado de una escorrentía previa o por infiltración, y que pueden ser medidas en el cauce final del río Pisque antes de su desembocadura. Para conocer los pesticidas utilizados se han realizado encuestas a los productores florícolas. Las mediciones se realizaron en los ríos Granobles y Guachalá, afluentes del río Pisque, y en dos puntos separados en el mismo río Pisque, uno inmediatamente después de la conjunción entre los dos afluentes y un punto antes de su desembocadura al siguiente río. Los aforos de caudal fueron mensuales desde junio 2018 hasta mayo 2019; cómo método de muestreo se usaron dispositivos pasivos *SPMD* y *POCIS* durante los tres meses secos, de junio a agosto de 2018. Para obtener las tasas de retención de los dispositivos pasivos se realizó una calibración con los plaguicidas en laboratorio mediante un canal hidrodinámico. De las encuestas se identificaron 24 ingredientes activos principales, en su mayoría compuestos con toxicidades Tipo III y Tipo IV. Según los resultados del modelo, la carga fluvial de pesticidas en aguas superficiales fue de 2982,24 *Kg* entre los meses de junio de 2018 a mayo de 2019, existiendo degradación ambiental de varios compuestos a lo largo del tramo del río.

Palabras clave: Floricultura, muestreadores pasivos SPMD y POCIS, degradación ambiental de pesticidas.

Suggested citation:	Sánchez Proaño, R., Cerón Pánchig, C. and Landeta Jibaja, K. (2023). Fluvial loads of pesticides in the Pisque River (Ecuador) between June 2018 and May 2019. La Granja: Revista de Ciencias de la Vida. Vol. 38(2):94-103. http://doi.org/10.17163/lgr.n38.2023.07.

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1 Introduction

Pesticides are almost universally applied on agricultural crop lands, plots and in the floriculture industry, focusing this research on this economic activity, since it is one of the main economic activities within the Pisque river basin.

The Pisque river basin is a valley in which two main cities are located, Cayambe and Tabacundo, with a population of 152,153 inhabitants for the year 2018 (GAD Municipal de Pedro Moncayo, 2018; GADIP Cayambe, 2020), in addition to having 3,201.73 hectares of flowers grown in greenhouses in 2017 (Cachipuendo, 2018). It is located in the province of Pichincha and its waters flow into the Guayllabamba River, which subsequently flows into the Esmeraldas River and the Pacific Ocean. The greenhouses dedicated to flower production are more common in Cayambe and Tabacundo, as seen in the orthophoto in Figure 1.

In the basin, floricultural crops by the 1980s occupied 25 hectares (Bravo and Flores, 2006), and increased in the mid-1990s due to economic factors such as the elimination of exporting tariffs to the United States (Corrales, 2016) and environmental factors, such as the great sun exposure that occurs at 2800 and 2900 m.a.s.l, stable temperatures throughout the year (Bravo and Flores, 2006), and proximity to air ports; this increase in flower production led to an increase in the use of pesticides.

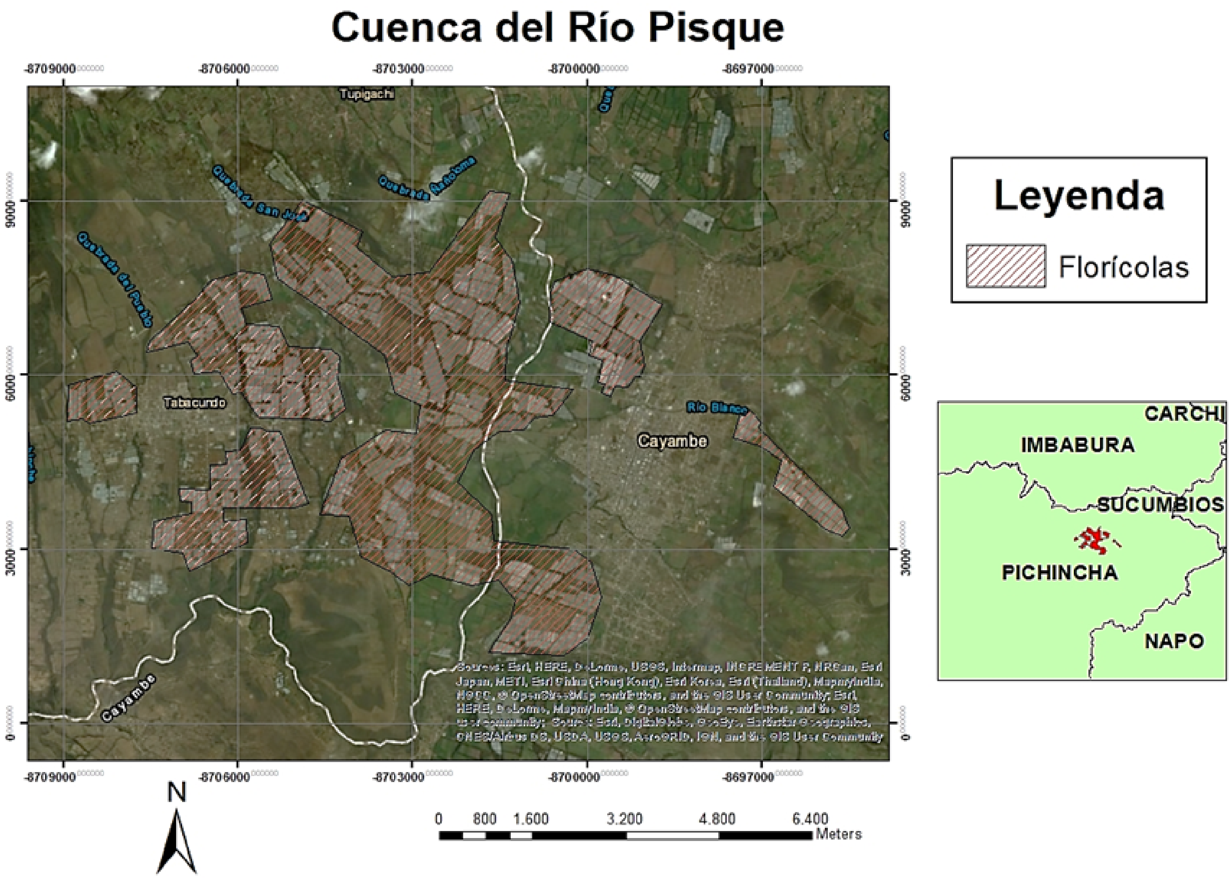

Figure 1. Area occupied by flower growers in the cities of Cayambe and Tabacundo in 2018.

It is estimated that less than 0.1% of the pesticides applied to crops reach their target, while the rest end up contaminating the air, soil and water (Arias et al., 2008). Much of this pesticide release is transported to water, affecting its quality and human health. Among the effects on water is the increase in toxicity, non-biodegradable organic carbon, electrical conductivity and solid matter (Calamari and Barg, 1993); while the main effects on human health are damage to the nervous system, hormonal alterations, cancer, damage to the immune system, reproductive damage, among others (Badr, 2020). It is therefore necessary to monitor pesticides, which is generally done through active sampling and only Persistent Organic Compounds (POPs) (Alvarez et al., 2014; Miège et al., 2012). Therefore, the aim is to sample the most commonly used chemicals in the flower industry to evaluate their permanence, and using passive sampling techniques to record continuous discharges, avoiding point discharges (Alvarez et al., 2007).

A useful technique for evaluating organic compounds in natural water bodies was used for sampling pesticides, such as passive sampling methods (Narváez et al., 2013). These can remain in the water for extended periods of time, passively adsorbing contaminants by diffusion and partitioning processes (Vrana et al., 2005). The use of a passive sampler to monitor contaminants in the aquatic environment is simpler and more practical than the measurement of bioaccumulated pesticides in living organisms (Alvarez et al., 2004; Vrana et al., 2005; Fedorova et al., 2014; Kot et al., 2000). However, its use in the environment requires a previous laboratory calibration to determine the value of the sampling rate of the specific compound (Morin et al., 2012), obtaining the entrainment or fluvial load that each chemical has in a surface water flow.

2 Materials and Methods

This section explains the protocols used for flow measurement, passive water sampling, laboratory analysis and calibration of sampling devices. First, the pesticides to be evaluated were defined through a survey of 20 floricultural producers.

For the gauging, a small section was sought in each river where the water flows continuously and unidirectionally, without interruption by rocks or obstacles; the cross-sectional area of the water body was measured by bathymetry (Swanson et al., 2009), and a Simtech micromoline, model FP111, was used to measure the velocity. This procedure was performed once a month for one year, starting in June 2018. There were three gauging points, one in the Granobles river, another in the Pisque river (point 1) after the junction with the Guachalá river and a last one in the Pisque river (point 2) before contributing its flow to the Guayllabamba river. To calculate the flow of the Guachalá river, the flow of the Granobles river was subtracted from the flow of the Pisque river (point 1), since there are no significant contributions within the section studied, as shown in Figure 2.

To measure the polar pesticides, SPMD (Semipermeable Membrane Devices) and for non-polar POCIS (Polar Organic Chemical Integrative Sampler) devices were used. The difference of chemical potentials of the analyte between the liquid and solid media of the samplers makes that these balance in the time in which the analysis is performed, obtaining in the passive sampler the average concentration of analyte that was in the water body (Górecki and Namieśnik, 2002). To calculate the mass of the accumulated analyte with respect to the concentration in the water the Equation 1 proposed by Vrana et al. (2005) was used.

$$M_s(t) = C_w R_s t \tag{1}$$

Where $M_s(t)$ is the mass of analyte accumulated in the sampler after the exposure time. R_s is the proportionality constant, C_w is the concentration of analyte in the aqueous environment and t is the exposure time. The devices used are those distributed by the company "EST-Lab" located in St. Joseph, Missouri, USA. The POCIS devices are the "Oasis HLB rectangular" model and the SPMD devices are the "99% purity 15cm with loops" model; both membranes were held by a metal structure and placed inside a plastic casing made of PVC pipe (Figure 3).

Figure 2. Sampling area and gauging points at the junction of the Granobles and Guachalá rivers to form the Pisque.

There were four passive sampling points, three located at the sites where the flow gauges were obtained, and a fourth in the Guachalá river. Two sampling points were carried out in the Pisque river in order to know which chemicals remain in the water and which chemicals are degraded. An SPMD sampler and a POCIS were placed in each of the four sampling points with a 28-day permanence in the water in each month during the three dry months, i.e., June to August. The objective of sampling during the dry months is to detect lower concentrations of pesticides, which is difficult if there are concentration dilutions due to precipitation.

As for the analysis of pesticides, an extraction procedure known as dialysis was performed, in which analytes are separated from membranes with different methods for SPMD and POCIS, according to the procedure proposed by Narváez et al. (2013). The sample preparation technique for measurement used was the one recommended by Aguilar (1998); López-Roldán et al. (2004) and Rodrigues et al. (2007), among others. The measurement was performed by the High Performance Liquid Chromatography (HPLC) method. For this, pesticide techniques developed by Kiso et al. (1996); Hernández et al. (2001) and Ferrer and Thurman (2007), among others, were considered. These techniques were applied both in the normal phase of polar compounds, for which a polar stationary phase and a non-polar mobile phase are used, and for non-polar compounds in which the stationary phase is non-polar and the mobile phase is polar.

A Waters HPLC equipment was used for the measurement, the models of its components are 1525 of the binary pump, 2998 of the photodiode array detector and the Empower 3 software developed by the same brand. A Restek brand C18 with code 9534565 was used as the column.

Figure 3. Passive samplers placed in water bodies.

According to Huckins et al. (1999); Luellen and Shea (2002) and Murdock et al. (2001), the calibration of exchange kinetics in passive sampling can be performed in the laboratory. Hence, the experimental method is the best to know the transfer coefficients, since the transfer rate depends on several hydrodynamic factors such as turbulence, environmental properties, shape and permeability of the casing, among others, which are simplified into a single factor (Yabuki et al., 2016). Experimentally, the obtaining of this single factor in the laboratory was performed in an Armfield model S16-11-b hydrodynamic channel. The degradation values of each analyte were obtained with the degradation of pesticides in the same channel. The ingredients to be analyzed were placed in the hydrodynamic channel at a concentration of 1 ppm using commercial products; the initial concentration was verified and three SPMD devices and three POCIS devices were placed, and a pair was removed and analyzed every three days. Finally, quantifying the pesticides in the water bodies, the laboratory proportionality constants corrected by the data obtained from the SPMD devices and the field POCIS will be used, obtaining an average pesticide concentration in the water for each month, which when multiplied by the flow rate of the same month gives the value of the pesticide load in the moving water body in magnitudes of mass over time.

3 Results

The results in flow measurements in cubic meters per second (m^3/s) of the gauging for each month are shown in Table 1, with one measurement made in the Granobles river and two in the Pisque river, at two different points; in the case of the Guachará river, the flow value corresponds to the mathematical calculation explained above.

The surveys conducted with flower growers revealed the use of 24 pesticides in greater quantities, which are presented in Table 2. None of these ingredients were found to have Type I toxicity or compounds classified as POPs; out of those three had Type II toxicity, 13 Type III and 9 Type IV. However, it was decided to increase the measurement of DDT 4,4' in order to check the permanence of this chemical in the soil that presents contact with water and that was possibly used in previous decades.

The SPMD and POCIS passive samplers were calibrated with these pesticides. Table 2 shows the type of sampling device used for their analysis according to the polarity of the ingredient, the temporary concentrations measured directly in the water after mixing the chemical, and the measurements obtained from the passive devices at 3, 6 and 9 days.

The proportionality constants were obtained from the above values, and with these rates and the monthly flow rates, the river loads of pesticides transported per year at the four measurement points were obtained, which are presented in Table 3.

Table 1. Results of river gauging in m^3/s.

No.	Source	2019					2018						
		Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1	Granobles river	1.2	3.4	2.8	3.6	5.4	2.1	1.6	1.4	0.8	2.1	2.4	3.6
2	Guachalá river	3.1	5.9	21.9	24.4	13.5	0.2	4.7	0.4	2	5.6	7.5	7.1
3	Pisque river (point 1)	4.3	9.3	24.7	28	18.9	2.3	6.3	1.8	2.8	7.7	9.9	10.7
4	Pisque river (point 2)	9.6	15.4	20.9	25.8	35.5	6.3	11.2	5.2	6.5	12.9	13.4	15

4 Conclusions and Discussion

Out of the 25 pesticides measured, all were detected by SPMD and POCIS devices excepting Cyproconazole, of these Thiabendazole was previously detected in the watershed by direct composite sampling in the Granobles River in the study conducted by Breilh et al. (2009); thus, 24 chemicals have not been characterized before in the watershed due to their commercial production of less than ten years (Securities and Exchange Commission, 2017).

The chemical with the highest concentration in the Granobles River was the acaricide Hexythiazox with a discharged amount of 1.2 T/year, also acaricide Clofentezine and the fungicide-bactericide Kasugamicin with concentrations higher than half a ton per year. The chemical with the highest con-

Table 2. Pesticides measured, devices used for this measurement and concentrations obtained at 0, 3, 6 and 9 days.

Ingredient	Tool used to measure	Water sample			
		From 0 days (μg/L)	At 3 days (μg/L)	At 6 days (μg/L)	At 9 days (μg/L)
Abamectina	SPMD	0.646695501	0.53849858	0.54167056	0.47745176
Bifenazato	SPMD	0.518783287	0.340566	0.273792	0.150416
Captan	SPMD	0.560243903	0.46804891	0.46794318	0.41566033
Carboxina	SPMD	0.693843997	0.68067431	0.49621795	0.42715263
Clofentezine	SPMD	0.563645605	0.47704974	0.45991542	0.38852853
Clorotalonil	POCIS	0.619721452	0.55072321	0.56884298	0.53318026
Clorfenapir	SPMD	0.562550269	0.51234852	0.43466815	0.40084613
Ciproconazol	SPMD	0.96418066	0.84196316	0.86543625	0.68150459
Dazomet	SPMD	0.712663906	0.57978667	0.59948895	0.59945474
DDT 4,4’	POCIS	0.80498488	0.7250131	0.7246846	0.7596978
Diafentiuron	SPMD	0.917674635	0.5788426	0.46744052	0.39246549
Difenoconazol	SPMD	0.760377939	0.6463111	0.62050694	0.53513305
Furalaxyl	SPMD	0.615093338	0.55017808	0.47513903	0.41824266
Hexythiazox	POCIS	0.886933592	0.60465611	0.46895995	0.38146892
Imidacloprid	POCIS	0.56145588	0.51898931	0.50362015	0.52374401
Isopyrazam	SPMD	1.079953092	0.96459406	0.96196111	0.97657145
Kasugamicina	SPMD	0.961088186	0.82968248	0.84669486	0.89287705
Mancozeb	SPMD	0.999337494	0.8777455	0.83864724	0.72522865
Mandipropamida	SPMD	0.727720428	0.68136426	0.64661057	0.64078673
Metalaxil-M	SPMD	0.70121361	0.55710826	0.51705397	0.52321987
Oxicarboxina	SPMD	0.6815315	0.56779358	0.51636684	0.54778815
Tiabendazol	SPMD	0.814691604	0.49154876	0.42893184	0.33380668
Tiametoxam	SPMD	0.536073681	0.35322476	0.29355718	0.23723684
Thiocyclam	SPMD	1.067956414	0.87624062	0.90435532	0.78547042
Thiram	SPMD	0.505084445	0.41808088	0.37347192	0.34748851

centration in the Guachalá river was the acaricide Hexythiazox with a measured discharge of 5.5 tons/year, while the insecticide-acaricide Abamectin has a discharge of half a ton per year. The chemical with the highest concentration at the mouth of the Pisque River was the acaricide Clofentezine with a permanence in the river of 0.605 T/year, while the fungicide Diafeconazole and the fungicide-bactericide Kasugamicin exceeded the permeance of entrainment in the river by more than 0.4 T/year. The results confirm that insecticides and fungicides in Ecuador are the most widely used pesticides (Valarezo and Muñoz, 2011).

The highest DDT carryover in surface water was in the Granobles River with 0.194 T/year, because this sub-basin is home to the floriculture industry. However, this carryover value is low compared to the rest of the agrotoxins, because since 2008 in Ecuador this persistent pesticide has not been imported; therefore, the contamination of soils and water with persistent chemicals and residues is the result of many years of its unrestricted application, finding metabolites such as DDT 4,4’ still in water bodies (Cairns and Sherma, 1992; Kouzayha et al., 2013).

There is a decrease in pesticide concentrations downstream comparing points 1 and 2 of the Pisque River, maybe related with the decreases in concentrations found in laboratory (Table 2). In field analysis this may be due to environmental factors in addition to variable climatic conditions including drought, desertification and other factors present in the study area (Aisha et al., 2017). The acaricide Clofentezine has a longer permanence in water bodies despite having Type IV toxicity, with a decrease of only 37% between points 1 and 2 of the Pisque River. It is not possible to compare the presence and degradation of these chemicals with other basins or micro-basins in the country, since there are no similar studies.

Table 3. Riverine pesticide loads from June 2018 to May 2019 at the Granobles, Guachalá, Pisque (point 1) and Pisque (point 2) sampling points.

Agrotoxic	Mass transported to the river every year (Kg/year)			
	Granobles river	**Guachalá river**	**Pisque river (Point 1)**	**Pisque river (Point 2)**
Abamectin	6.653528	505.477019	629.176347	122.808668
Bifenazate	6.620319	160.148325	77.819682	64.863366
Captan	144.33157	0.360573	160.588781	28.004311
Carboxine	39.944796	18.24502	96.992282	370.995619
Clofentezine	852.05047	1.020008	953.89041	605.280247
Chlorothalonil	29.324674	117.808407	103.970527	0.051113
Chlorfenapyr	16.68012	0.833866	10.451968	12.665925
Ciproconazol	0	0	0	0
Dazomet	12.829044	10.348819	30.244102	14.955096
DDT 4,4’	194.122733	0	15.599694	0.533583
Diafenthiuron	17.144261	354.515585	264.258417	235.911596
Difeconazol	121.341225	0.244132	322.424488	430.743341
Furalaxyl	347.413055	4.556359	491.844465	253.193159
Hexythiazox	1207.15446	555.134675	935.364327	1.356934
Imidacloprid	467.290891	68.016049	965.451402	35.350273
Isopyrazam	68.172396	21.459916	129.310744	131.940685
Kasugamicin	644.610004	84.379842	956.951816	441.095821
Mancozeb	205.192694	0	78.173762	29.875791
Mandipropamid	2.579379	0	4.215016	2.875818
Metalaxyl-M	6.479502	0.240234	7.657236	1.748932
Oxycarboxine	463.488287	0.879675	178.184092	82.686197
Thiabendazole	7.520012	3.113556	10.797758	6.585262
Tiametoxam	21.313513	14.81764	49.24951	11.928538
Thiocyclan	11.820493	2.312543	37.89562	20.001449
Thiran	84.577268	6.421586	144.596888	76.786843

The chemical profile of the Pisque River is relatively similar to those observed in Lake Ziway in Ethiopia, which also has the presence of the flower industry in its watershed parenciteLamessa2021. Knowing the type and quantity of pesticides present in the basin allows evaluating their effect on human health and ecosystems by analyzing the complete life cycle of pesticides in the basin, analyzing their final destinations and the exposure of humans and other species through different media and pathways, such as food, evaporation into the air, transfer to soil or groundwater (Margni et al., 2002).

Acknowledgments

This project was financed by Universidad Politécnica Salesiana in Quito, Ecuador.

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