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Assessing the Gray Water Footprint Impact of Pesticide Use in Tommy Atkins Mango Cultivation: A case study in the Semi-Arid Region of São Francisco Valley, Brazil

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ABSTRACT

Mango production, particularly of the Tommy Atkins variety, is prominent in the São Francisco Valley region of Northeast Brazil due to favorable conditions and year-round cultivation facilitated by irrigation and growth regulators. However, concerns arise over its significant water footprint and heavy pesticide usage, prompting a study on the gray water footprint of pesticides applied to Tommy Atkins mangoes in Sub-middle São Francisco Valley-Pernambuco, Brazil. Utilizing models by Hoekstra et al. (2011) and Paraíba et al. (2014), the study estimated the Gray Water Volume (GWV) and assessed potential water contamination using the GUS Index and GOSS method. Results suggest minimal groundwater pollution risk but moderate surface water contamination risk. The GWV ranged from 10^6 to 10^7 m³ ha⁻¹, with the model of Paraíba et al. (2014) showing higher environmental sustainability due to considering toxicity to aquatic non-target organisms. Despite this, both models indicate a high gray water footprint. The pesticide ranking derived from these findings can aid in selecting environmentally safer pesticide mixtures for mango cultivation, aiming to balance water protection and agricultural productivity.

Keywords: Gray Water Footprint, Pesticides, Tommy Atkins Mango, Water contamination.

Avaliando o Impacto da Pegada Hídrica Cinza do Uso de Pesticidas no Cultivo de Manga Tommy Atkins: Um Estudo de Caso na Região Semiárida do Vale do São Francisco, Brasil

RESUMO

A produção de manga, principalmente da variedade Tommy Atkins, é proeminente na região do Vale do São Francisco, no Nordeste do Brasil, devido às condições favoráveis e ao cultivo durante todo o ano, facilitado pela irrigação e reguladores de crescimento. No entanto, surgem preocupações sobre sua significativa pegada hídrica e uso intensivo de pesticidas, o que levou a um estudo sobre a pegada hídrica cinza de pesticidas aplicados à manga Tommy Atkins no Submédio Vale do São Francisco-Pernambuco, Brasil. Utilizando os modelos de Hoekstra et al. (2011) e Paraíba et al. (2014), o estudo estimou o Volume de Água Cinza (VAC) e avaliou a potencial contaminação da água utilizando o Índice GUS e o método de GOSS. Os resultados sugerem um risco mínimo de poluição das águas subterrâneas, mas um risco moderado de contaminação das águas superficiais. O VAC variou de 10^6 a 10^7 m³ ha⁻¹, tendo o modelo de Paraíba et al. (2014) mostrado maior sustentabilidade ambiental por considerar a toxicidade para organismos aquáticos não-alvo. Apesar disso, ambos os modelos indicam uma elevada pegada hídrica cinza. A classificação de pesticidas derivada destas descobertas pode ajudar na seleção de misturas de pesticidas ambientalmente mais seguras para o cultivo da manga, com o objetivo de equilibrar a proteção da água e a produtividade agrícola.

Palavras-chave: Pegada Hídrica Cinza, Agrotóxicos, Manga Tommy Atkins, Contaminação da água.

Abbreviation:

A_C , cultivated area; A_D , pesticide dose; A_F , attenuation factor; A_{SF} , assessment factor; CA , concentration addition; C_{max} , maximum allowable concentrations; C_{nat} , natural concentrations; D , deep irrigation; $EC50$, median effective concentration; ET_0 , reference evapotranspiration; ET_r , actual evapotranspiration; f_{oc} , soil organic carbon content; GWF , gray water footprint; GWF^{ha}_i , gray water footprint of the pesticide per hectare; GWF_{PM} , gray water footprint of the pesticide mixture; $GOSS$, Potential risk of contamination of surface waters; GUS , Groundwater Ubiquity Score; I , daily irrigation J_w , water daily net recharge of the soil area; k , pesticide degradation rate; K_C , crop coefficients; K_d , partition distribution coefficient; K_{OC} , organic-water carbon partition coefficient; L , pollutant load; M , pesticide mass; P , daily precipitation; PEC , Predicted Environmental Concentration; $PNEC$, Predicted No Effect Concentration; $PT50$, inflection point of the curve; r , pesticide rank; R_F , retardation factor; R_O , surface runoff; $T_{1/2}$, half-life of the pesticide; z , depth of the soil; α_H , leaching-runoff coefficients of the pesticides; α_P , fraction of the pesticide that undergoes runoff; ρ_s , soil dry bulk density; θ_{cc} , soil–water content at field capacity.

Introduction

The Brazilian Northeast is a major producer of mangoes (*Mangifera indica* L.), especially the Sub-middle São Francisco Valley region. This region stands out for producing mangoes all year round due to the irrigation system and the artificial management of mango flowering, which is achieved through applying growth regulators. The need for high irrigation in the region and the use of pesticides for mango production results in a high water footprint (Araújo et al., 2018; Dias et al., 2018; Oliveira et al., 2010; Pereira et al., 2006). Moreover, the climatic and soil conditions prevalent in the region are conducive to the emergence of pests and weeds, which possess the potential to inflict harm upon agricultural produce. Therefore, the use of pesticides is a determining factor in ensuring agricultural productivity (Ferracini et al., 2001; B. L. F. da Silva, 2022).

According to Ferreira (2022), the Tommy Atkins mango is one of the main cultivars serving domestic and export markets. The Tommy Atkins variety is adapted to the hot climate of the Sub-middle São Francisco Valley, presenting elevated resistance to pests and diseases, greater post-harvest durability; regularity in production and resistance to mechanical impacts, which is a fundamental characteristic for exportation, as it becomes less perishable (Mouco et al., 2011; Oliveira et al., 2010; Pereira et al., 2006).

The extensive use of pesticides in food production has sparked apprehension within the environmental and public health sphere. One of the primary consequences stemming from the application of pesticides is the pollution of the atmosphere, soil, and water, which not only proves detrimental to non-target organisms but also exerts adverse effects on human well-being (Barreto et al., 2020; Lopes & Albuquerque, 2018; Vale et al., 2019).

Furthermore, when combating diseases and pests in crops, it is common for farmers to use a mixture of different pesticides, thus obtaining a more efficient result in controlling pests and reducing the final cost of production. However, this mixture can be more toxic due to the interaction between the different substances and active components (Barreto et al., 2020; Hernández et al., 2017; Paraiba et al., 2014; Vale et al., 2019).

Pesticides can reach water bodies through surface runoff and leaching. As such, it is imperative to evaluate the probable contamination of water bodies by pesticides. This assessment is necessary to comprehend the hazards associated with their usage, as suggested by the GUS index (Gustafson, 1989), which gauges the likelihood of groundwater contamination by pesticides, and the Goss method, which assesses the potential for surface water contamination by pesticides (Goss, 1992).

The water footprint is an indicator of water use that considers its multiple uses and is classified into three types: blue water, which refers to water taken from rivers and lakes (surface and groundwater); green water, which is rainwater stored in the ground; and gray water, which is the volume of contaminated water resulting from a particular process. In this context, an alternative to estimate the volume of water contaminated by the mixture of pesticides is the Gray Water Footprint, which was introduced to express water pollution in terms of polluted volume (Barreto et al., 2020; Hoekstra et al., 2011; Paraiba et al., 2014).

The calculation of the Gray Water Footprint can be used as an indicator of agricultural sustainability and as an index of water pollution, seeking to encourage a better choice of pesticide mixture used in crops and protect water resources.

Numerous studies conducted in Brazil and various countries worldwide have examined the topic of the Gray Water Footprint in agriculture, recognizing it as a significant management tool.

Various crops have been evaluated, including rice, mango, sugarcane, and peanuts. Furthermore, some studies have comprehensively calculated the gray water footprint for all crops within a specific study region. The majority of these studies have focused on assessing the Gray Water Footprint with fertilizer usage, as demonstrated by the works of (Arunrat et al., 2022; Herath et al., 2013; Karandish, 2019; Meng et al., 2022; Ribeiro, 2014; Shi et al., 2020).

Recently, assessments have been conducted on the Gray Water Footprint of various pollutants, including pesticides and fertilizers. This has been demonstrated in studies such as those undertaken by Ariyani et al. (2022), Deepa et al. (2022), Roudbari et al. (2023), and Scarpore et al. (2023). Additionally, certain studies have solely focused on calculating the Gray Water Footprint resulting from pesticide application, as exemplified by Vale et al. (2019) and Barreto et al. (2020). Thus, the primary aim of the current study was to assess the Gray Water Footprint of the pesticide mixture applied in the cultivation of Tommy Atkins mango (*Mangifera Indica* L.), situated in the Sub-middle São Francisco Valley region, using the models of Hoekstra et al. (2011) and Paraiba et al. (2014) in a comparative way.

Material and methods

Characterization of the study area

The study area is located at coordinates 9°23'28.43"S and 40°44'57.22"W, has approximately 4 hectares, and was reserved on a

farm where Tommy Atkins Mango (*Mangifera Indica* L.) is grown for exportation, located in the city of Casa Nova, Bahia, belonging to the Sub-middle São Francisco Valley region. The Casa Nova – BA municipality has an area of approximately 9,647 km² and a population of 64,940 inhabitants (IBGE, 2023). The city is part of the caatinga biome and follows the climatic characteristics of the semi-arid region: high temperatures, low precipitation, critical periods of prolonged drought, a high rate of evapotranspiration and low water retention capacity. The agricultural sector holds significant importance for the local economy of the municipality. The sustenance of this activity is contingent upon the irrigation system sourced from the São Francisco River, given the semi-arid climatic conditions. Additionally, the application of pesticides is necessary to manage pests and diseases effectively (Ferracini et al., 2001; Ferreira, 2022; IBGE, 2023; Queiroz, 2013).

The municipality of Casa Nova is part of the Integrated Administrative Development Region (RIDE) of the Petrolina and Juazeiro Hub (Figure 1), which is a hub for the technological development of irrigated fruit growing in Brazil, standing out for the cultivation of vegetable crops, mainly onions, watermelon and melon and fruits such as mango and grapes. The Petrolina and Juazeiro Hub RIDE also includes the cities of Sobradinho, Juazeiro, and Curaça in Bahia and the cities of Petrolina, Lagoa Grande, Santa Maria da Boa Vista, and Orocó belonging to the territory of Pernambuco (R. J. De Lima & De Sousa, 2017; Queiroz, 2013; B. L. F. da Silva, 2022).

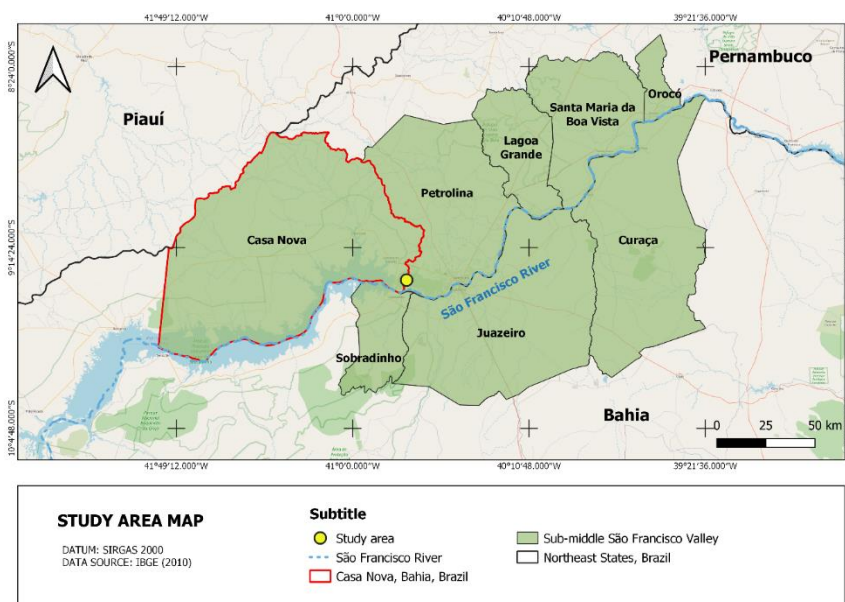


Figure 1. Study Area Map.

In the reserved area, both disturbed and undisturbed soil samples were gathered from a plot that encompasses an area of approximately four hectares. A total of 15 disturbed samples were randomly collected from the soil layers of 0 to 20 cm and 20 to 40 cm, to form a composite sample per layer, as recommended by Figueiredo et al. (2013). Additionally, 5 undisturbed samples were collected from the same layers using 50 cm³ volumetric rings for further physical analysis (Figueiredo et al., 2013).

The samples were appropriately stored and sent to the Physics and Soil Chemistry laboratories of the Federal Rural University of Pernambuco. Subsequently, physicochemical analyses of the soil were performed, leading to a thorough characterization of the soil within the designated study area. This characterization is necessary to apply the model by Paraiba et al. (2014) to estimate the gray water footprint.

The physical characteristics were determined following the Embrapa methodology (P. C. Teixeira et al., 2017), namely: soil particle and dry bulk densities, total porosity, volumetric soil water content, and particle size, as well as the standardization of methods for particle size analysis in Brazil (Almeida et al., 2012). The water content at field capacity was determined by subjecting the samples to a tension of 100 centimeters of water column, employing the Haines funnel method (Cássaro et al., 2009; Haines, 1930).

The chemical analyses consisted of determining pH in water and KCl, exchangeable Ca²⁺, Mg²⁺, K⁺, Na⁺, and Al³⁺, available P, and potential acidity (H+Al), which resulted in calculations of effective and potential cation

exchange capacities, base saturation, aluminum and sodium saturations and soil organic carbon and organic matter contents (Teixeira et al., 2017).

Assessment of the potential for contamination of water bodies by pesticides applied to crops

The product application data was acquired from a comprehensive report on the application of pesticide mixtures in mango cultivation provided by the individual accountable for the designated research area. This report encompasses all applications conducted within 2021-2022, detailing the specific pesticides employed in the mixtures, the respective application dates, the dosage administered for each constituent pesticide, and the corresponding growth stage of cultivation during which they were applied. Additional data required for the investigation were sourced from various literature, notably the International Union of Pure and Applied Chemistry (IUPAC, 2023) database, AGROFIT, which is the phytosanitary pesticide system of the Ministry of Agriculture, Livestock and Supply of Brazil (MAPA, 2023), and the outcomes of physical-chemical assessments of the soil.

It was possible to assess the potential for contamination of water bodies (groundwater and surface water) using the GUS index (Groundwater Ubiquity Score) (Gustafson, 1989) and the Goss Method (Goss, 1992), for each pesticide used in the period.

The GUS Index classifies them according to the leaching tendency and expresses the vulnerability of groundwater to contaminants present in the locations. This index is applied according to Table 1 (Gustafson, 1989).

Table 1. Groundwater Ubiquity Score (GUS) index.

Equation	Classification		
	NL	I	L
$GUS = \log(T_{1/2})(4 - \log K_{OC})$	< 1.8	$1.8 < GUS < 2.8$	> 2.8

$T_{1/2}$: Pesticide half-life; K_{OC} : Organic-water carbon partition coefficient (L kg⁻¹); NL: Non-leachable; I: Intermediate; L: Leachable.

The Goss method (1992) expresses the potential risk of contamination of surface waters, classifying each pesticide as large, medium, or small risk of contamination associated with sediment and dissolved in water. Table 2 presents the criteria used to classify pesticides by this

method. According to (Souza e Silva et al., 2017), this method is essential for defining which environmental monitoring programs should be prioritized in the Sub-middle São Francisco Valley region.

Table 2. Potential risk of contamination of surface waters (Goss method).

Flow form	Pesticide runoff potential		
	Large	Small	Medium
Sediment transport	$Se\ T_{1/2} \geq 40$ and $K_{oc} \geq 1000$ or $Se\ T_{1/2} \geq 40$ and $K_{oc} \geq 500$ and $S \leq 0,5$	$Se\ T_{1/2} \leq 1$ or $Se\ T_{1/2} \leq 2$ and $K_{oc} \leq 500$ or $Se\ T_{1/2} \leq 4$ and $K_{oc} \leq 900$ and $S \geq 0,5$ or $Se\ T_{1/2} \leq 40$ and $K_{oc} \leq 500$ and $S \geq 0,5$ or $Se\ T_{1/2} \leq 40$ and $K_{oc} \leq 900$ and $S \geq 2$	Everything else
		$Se\ K_{oc} \geq 100000$	
		or	
		$Se\ K_{oc} \geq 1000$ and $T_{1/2} \leq 1$	
		or	
Solution-phase transport	$Se\ S \geq 1$ and $T_{1/2} > 35$ and $K_{oc} < 100000$ or $Se\ S \geq 10$ and $S < 100$ and $K_{oc} \leq 700$	$Se\ S < 0,5$ and $T_{1/2} < 35$	Everything else

$T_{1/2}$: Pesticide half-life; K_{oc} : Organic-water carbon partition coefficient; S: Solubility. (Goss, 1992).

Gray Water Footprint assessment models

The models employed for assessing the gray water footprint of the pesticide mixture were those proposed by Hoekstra et al. (2011) and Paraiba et al. (2014), as elucidated in Figure 2. Henceforth, the model developed by Hoekstra et al. (2011) shall be referred to as the H-model, while the one formulated by Paraiba et al. (2014) shall be denoted as the P-model. The procedure for implementing both models is delineated in Figure 2.

The maximum concentrations of pesticides allowed in drinking water, used in the application of the model by Hoekstra et al. (2011), were obtained through consultations with Brazilian legislation: Resolution No. 357 of the National Environmental Council (Resolução CONAMA N° 357, de 17 de Março de 2005, 2005), with updates

by Resolutions No. 410/2009 and 430/2011; Attachment XX of Consolidation Ordinance No. 5/MS/GM of 09/28/2017 (former Ordinance No. 2,914, of 12/2011, by the Ministry of Health) and CONAMA Resolution No. 396 of 04/03/2008 (Resolução CONAMA No 396, de 3 de Abril de 2008, 2008). European legislation for the maximum concentration of copper in water for human consumption was also considered (IUPAC, 2023). Upon discovering that none of the above regulations contained the maximum concentration of the pesticide, the standard implemented by the European Union was consulted. This standard stipulates that the concentration of any pesticide in water must not exceed $0.1\ \mu\text{g L}^{-1}$ (Presença de Agrotóxicos Em Água Potável No Brasil: Parecer Técnico Do GT de Agrotóxicos Da Fiocruz Para a Revisão Do Anexo XX Da Portaria de Consolidação N° 05, 2017).



where ET_O is the reference evapotranspiration of the crop in mm day^{-1} , K_c is the crop coefficient, T_i is the irrigation shift in day and E_f is the efficiency of the irrigation system, considered as 0.9 for micro sprinkler (L. O. Lima et al., 2012).

$$GIB = \frac{ET_0 K_C T_i}{Ef} \quad \text{Eq. 2}$$

The reference Evapotranspiration was obtained by the Embrapa Semiárido agrometeorological data platform (*Dados agrometeorológicos do Vale do São Francisco*, 2023). Potential Evapotranspiration (ET_0) data for the years 2021 and 2022 were obtained from the Salitre Station, located in Juazeiro, Bahia, at coordinates 9°30'0.00"S and 40°37'60.00"W, as it is the closest to the plot. The crop coefficients (K_C) adopted were those defined by Teixeira et al. (2008) in a study on the cultivation of Tommy Atkins mango in the Petrolina region – PE (Table 3).

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Table 3. Crop coefficients (K_c) adopted for Tommy Atkins mango.

Stage of cultivation	K_c
Rest	0.7
Vegetative Growth	0.8
Branch maturation	1
Floral Induction	1
Pre-flowering	1
Full flowering	1
End of flowering	0.9
Fruit development	0.9
Fruit maturation	0.8

Source: Adapted from Teixeira et al. (2008).

Furthermore, ET_r , which is the actual evapotranspiration of the crop, was calculated by the product between the reference evapotranspiration (ET_0) and the crop coefficient (K_c), as presented in Equation 3.

$$ET_r = ET_0 K_c \quad \text{Eq. 3}$$

As depicted in Figure 2, after acquiring the gray water volumes derived from the pesticide mixture (GWV_{PM}) from the H-model and P-model, the relative positioning of each pesticide within the mixtures was determined utilizing the pesticide ranking. The primary objective of this ranking is to present the pesticides with the highest impact within the mixtures that are employed for crop application. For each method, the GWV_i (m³) for each pesticide will be divided by the pesticide application area A_c (ha) to calculate the gray water footprint of each pesticide per hectare (GWV_i^{ha}), as determined by Equation 4:

$$r_i = \log(GWV_i^{ha}) \quad \text{Eq. 4}$$

Results and discussion

Table 4 illustrates the outcomes of the soil characterization analysis conducted on the crop plot under investigation. The findings indicate that the predominant particle size composition in the 0-20 cm and 20-40 cm layers is sand, leading to the classification of the soil as loamy sand. The ratio of silt to clay was found to be less than 0.7, thereby indicating a significant level of soil weathering (H. G. dos Santos et al., 2018). The soil dry bulk density (ρ_s) measured 1.26 g cm⁻³ in the 0-20 cm layer and 2.00 g cm⁻³ in the 20-40 cm layer. It is noteworthy that sandy soils or layers exhibit higher soil dry bulk density values. The significant increase in soil dry bulk density observed in the 20-40 cm layer indicates a susceptibility to

compaction (Queiroz et al., 2013; N. G. N. dos Santos, 2015).

The particle density (D_p) measures at 0-20 and 20-40 cm layers were 2.49 and 2.60 g cm⁻³, respectively. These findings align with the results obtained by Queiroz et al. (2013) during their investigation and classification of the five predominant soil classes in Casa Nova - BA, which ranged from 2.48 to 2.66 g cm⁻³. Total Porosity (P_t) is based on soil dry bulk density and particle density and was 49.58% in the 0-20 cm layer and 22.90% in the 20-40 cm layer.

Soil volumetric water at field capacity (θ_{cc}) measures the maximum amount of water retained by the soil and is an essential parameter for applying the P-model. It was determined to be 24.55% for the 0-20 cm layer and 21.40% for the 20-40 cm layer. Furthermore, the determination of the Volumetric Water Content (VWC), which is the relationship between the volume of water in a sample and the total volume of the sample, was 14.34 m³ mg⁻³ and 19.78 m³ mg⁻³ for the 0-20 and 20-40 cm layers, respectively.

The pH values obtained from measurements conducted on both water and KCl solutions for both layers exhibited a range of 6.85 to 7.70. It is a common characteristic of soils in semi-arid regions to possess an alkaline pH, which can be attributed to the presence of bicarbonate released into the soil and the water utilized in the irrigation system (Maia, 2013). However, this is not a problem for the mango tree, as it produces relatively well in soils with a wide pH range (D. J. Silva et al., 2004). Furthermore, the ΔpH was negative in both layers, indicating the predominance of negative charges capable of adsorbing ions with positive charges (Ca²⁺, Mg²⁺, K⁺, among others). Regarding electrical conductivity, the two layers studied presented low values (Table 4), which is a relevant parameter since high electrical conductivity can indicate saline soils (Queiroz, 2013).

The exchangeable Ca^{2+} was $0.86 \text{ cmol}_c \text{ kg}^{-1}$ in the most superficial layer and $0.82 \text{ cmol}_c \text{ kg}^{-1}$ in the deepest layer. Calcium is an essential nutrient of significant importance in the cultivation of mangoes, as it plays a crucial role in both the growth and development of the plant and the fruits it produces. The values obtained for Mg^{2+} were 0.12 and $0.10 \text{ cmol}_c \text{ kg}^{-1}$ for layers 0-20 and 20-40 cm, respectively. In the semi-arid region, the levels of calcium and magnesium in the soil are inherently low. Therefore, liming is employed to fulfill the requirements of mango production by enhancing the accessibility of these essential nutrients (Silva et al., 2004).

K^+ and Na^+ presented low values in both layers, requiring corrective fertilization attention. The presence of Al^{+3} was not detected in the soil samples, which is detrimental to the growth and development of the crop. The neutralization of exchangeable aluminum is also a key objective of the liming process (Silva et al., 2004). The potential acidity measured $1.98 \text{ cmol}_c \text{ kg}^{-1}$ in the uppermost layer and $2.48 \text{ cmol}_c \text{ kg}^{-1}$ in the deepest layer, signifying its significance as a crucial parameter in estimating the soil's Cation Exchange Capacity (CEC). The sum of exchangeable bases (S) and the effective CEC had the same value, given the absence of exchangeable aluminum concentration within the soil.

The total soil CEC (T) was $2.98 \text{ cmol}_c \text{ kg}^{-1}$ in the 0-20 cm layer and $3.41 \text{ cmol}_c \text{ kg}^{-1}$ in the 20-40 cm layer. According to Silva et al. (2004), soil CEC in regions with a semi-arid climate are usually low, while base saturation (V) is generally high, with values close to 100%. However, this fact was not identified in soil samples from the region, so the V values were 33.46% and 27.45% for the 0-20 and 20-40 cm layers, respectively. Liming can also be used to increase V values.

The available phosphorus was 89.68 mg kg^{-1} in the 0-20 cm layer and 55.05 mg kg^{-1} in the 20-40 cm layer. The most superficial layer tends to have higher phosphorus values, and this variation is due to the supply of this nutrient by external sources in areas under different agricultural uses, as observed by Queiroz (2013). According to Silva et al. (2004), mango has a low demand for phosphorus, especially in sandy soils.

The organic carbon values were 14.97 g kg^{-1} in the 0-20 cm layer and 8.95 g kg^{-1} in the 20-40 cm layer. Based on the premise that organic matter has 58% organic carbon, the transformed values were 25.81 and 15.43 g kg^{-1} in the 0-20 and 20-40 cm layers, respectively. According to Queiroz (2013), soils in the semi-arid region have low levels of organic matter due to the physical and climatic conditions of the study region.

Table 3. Physicochemical characterization of the soil in the study area.

Soil Layer	Granulometric composition (%)			Classe Textural	S/A	ρ_s	Dp	Pt	θ_{cc}	CVA	pH			EC
(cm)	Sand	Silt	Clay			g cm^{-3}		%		$\text{m}^3 \text{ mg}^{-3}$	H_2O	KCl	ΔpH	$\mu\text{s cm}^{-1}$
0-20	85.27	4.71	10.02	Loamy Sand	0.47	1.26	2.49	49.58	24.55	14.34	7.70	7.05	-0.65	746.70
20-40	81.31	3.91	14.78		0.26	2.00	2.60	22.90	21.40	19.78	7.76	6.85	-0.91	604.90

Soil Layer	Ca^{2+}	Mg^{2+}	K^+	Na^+	Al^{+3}	H+Al	SB	t	T	V	P	OC	MO
(cm)	$\text{cmol}_c \text{ kg}^{-1}$									%	mg kg^{-1}	g kg^{-1}	
0-20	0.86	0.12	0.0054	0.0068	0	1.98	1.00	1.00	2.98	33.46	89.68	14.97	25.81
20-40	0.82	0.10	0.0056	0.008	0	2.48	0.94	0.94	3.41	27.45	55.05	8.95	15.43

According to ABRASCO (2012), the soil characteristics in the São Francisco Valley region facilitate the process of pesticide leaching, thereby potentially promoting groundwater contamination.

During the period under study, 67 product applications were carried out on the crop, 60 of which involved the presence of pesticides in the form of a mixture with other pesticides or with other components, such as fertilizers. Among the applications with pesticides, 29 of them were carried out in 2021 and 31 in 2022. In each year, 13

products were applied, totaling 16 different active ingredients in the period: Abamectin; Acetamiprid; Azoxystrobin; Chlorpyrifos; Deltamethrin; Difenconazole; Spinosad; Ethephon; Fenpyroximate; Glyphosate; Glufosinate; Copper hydroxide; Lambda-Cyhalothrin; Copper oxychloride; Paclobutrazol and Tebuconazole. The active ingredients Acetamiprid, Copper Hydroxide and Paclobutrazol were only applied in 2021, while Chlorpyrifos, Deltamethrin and Fenpyroximate only in 2022.

The chemical properties of the pesticides studied, the maximum concentration (C_{max}) permitted by legislation for these pesticides in water bodies, and the class, environmental, and toxicological classification are presented in Chart 1. Among the pesticides applied in the area, 38%

were insecticides, 31% fungicides, 13% were acaricides, 13% growth regulators, 13% herbicides, and 6% bactericides, it is worth noting that some pesticides are classified into two classes, as can also be seen in Chart 1.

Chart 1. Pesticide properties.

Pesticide	$T_{1/2}$ (days) ²	K_{oc} (mL g ⁻¹) ²	Solubility (mg L ⁻¹) ²	Class ³	C_{max} (mg L ⁻¹) 1,2,4	Environmental classification ³	Toxicological classification ³ (Category)
Abamectin	14.00	5	0.01	Insecticide and Acaricide	0.0001	III	4
Acetamiprid	3.00	200	2950.00	Insecticide	0.0001	I	
Azoxystrobin	180.70	589	6.70	Fungicide	0.0001	III	
Chlorpyrifos	27.60	5509	1.05	Insecticide	0.03	II	
Deltamethrin	21.00	10240000	0.0002	Insecticide	0.0001	I	
Difenoconazole	91.80	7734	15.00	Fungicide	0.0001	II	
Spinosad	0.99	2000	235.00	Insecticide	0.0001	III	
Ethephon	13.50	2540	1000000.00	Growth regulator	0.0001	III	
Fenpyroximate	6.80	12000	0.02	Insecticide	0.0001	II	
Glyphosate	6.45	1424	100000.00	Herbicide	0.065	III	
Glufosinate	7.00	600	500000.00	Herbicide	0.0001	III	
Copper (II) hydroxide	0.10	12000	0.50	Fungicide e Bactericides	2	II	
Lambda- Cyhalothrin	26.90	283707	0.01	Insecticide	0.0001	I	3
Copper oxychloride	0.10	1000	1.19	Fungicide	2	III	5
Paclobutrazol	140.00	400	22.90	Growth regulator	0.0001	III	4
Tebuconazole	47.10	6000	36.00	Fungicide	0,18	II	5

$T_{1/2}$: Pesticide half-life; K_{oc} : Organic-water carbon partition coefficient; S: Solubility; C_{max} : maximum concentration limit in water.

(CONAMA, 2005¹; IUPAC, 2023²; MAPA, 2023³; MINISTÉRIO DA SAÚDE, 2011⁴).

Regarding environmental classification, three pesticides are considered hazardous products for the environment: Acetamiprid, Deltamethrin, and Lambda-Cyhalothrin. Regarding the toxicological classification, Chlorpyrifos and Lambda-Cyhalothrin are classified as moderately toxic products, and the others are in categories 4 and 5, low toxic products and unlikely to cause acute harm, respectively.

The active ingredient with the most extended half-life was Azoxystrobin, with 180.7 days for degradation in the soil, which, according to field tests, can be considered persistent (IUPAC, 2023). Regarding the Organic Carbon Partition Coefficient (K_{oc}), a high value indicates that the compound is firmly fixed to the organic matter in the soil and has less chance of contaminating water bodies (surface and groundwater), so a lower K_{oc} value suggests a greater possibility of contamination (Ferracini et al., 2001). The lowest

K_{oc} value was that of the active ingredient Abamectin (5 mL kg⁻¹).

Regarding solubility, it is noteworthy to emphasize that the higher the solubility of the active ingredient, the increased likelihood of its dissolution in adjacent water bodies and subsequent contamination (Mendes et al., 2020). Consequently, it is pertinent to highlight that Ethephon, Glyphosate, and Glufosinate are the most soluble compounds in pure water.

The assessment of the risks associated with the contamination of groundwater resources due to product leaching, utilizing the GUS index (Gustafson, 1989), has revealed that the pesticides employed in the examined cultivation area possess a minimal likelihood of groundwater contamination. This conclusion is drawn from the fact that 81.25% of the compounds investigated exhibit no potential for leaching (NL) (Table 2). Out of the pesticides examined, only Abamectin and Paclobutrazol exhibit the characteristic of

Probable Leaching (PL), while Azoxystrobin falls within the Transition Range (FT). The categorization of Abamectin and Azoxystrobin supports the findings presented by Souza e Silva et al. (2017) in their investigation on the potential pollution of water reservoirs due to pesticide usage in grape farming, specifically within the São Francisco Valley region.

Concerning the assessment of the potential contamination risks of surface water resources using the Goss method (Goss, 1992) (Chart 2), it has been determined that out of the 16 pesticides examined within the study area, 25% exhibit a significant likelihood of contaminating the dissolved surface water, while 31.25% pose a moderate risk, and 43.75% present a low risk. Additionally, 12.5% of the pesticides demonstrate a high risk of adsorption to sediments, 50% indicate a medium risk, and 37.5% display a low

risk. Consequently, it can be concluded that most of the pesticides investigated in this study pose a relatively low to moderate risk of contaminating surface water bodies.

According to the Goss method, Difenconazole and Tebuconazole pose the greatest risk of contaminating surface water bodies. This risk is significant independent of whether these compounds are dissolved in water or adsorbed to sediments. On the other hand, the compounds Azoxystrobin and Paclobutrazol, besides posing a risk to groundwater, are also classified as high risk for contaminating surface waters in their dissolved form. This information can serve as a foundation for selecting pesticides for monitoring purposes, mainly when there is a requirement to establish a program for analyzing the water quality of water bodies in the region.

Chart 2. Results of GUS index and Goss method.

Pesticide	GUS		GOSS	
	Result	Classification	Solution-phase transport	Sediment transport
Abamectin	3.78	PL	Small	Medium
Acetamiprid	0.81	NL	Medium	Small
Azoxystrobin	2.78	I	Large	Medium
Chlorpyrifos	0.37	NL	Medium	Medium
Deltamethrin	-3.98	NL	Small	Medium
Difenconazole	0.22	NL	Large	Large
Spinosad	0.00	NL	Small	Small
Ethephon	0.67	NL	Medium	Medium
Fenpyroximate	-0.07	NL	Small	Medium
Glyphosate	0.69	NL	Medium	Medium
Glufosinate	1.03	NL	Medium	Small
Copper (II) hydroxide	0.08	NL	Small	Small
Lambda-Cyhalothrin	-2.08	NL	Small	Medium
Copper oxychloride	-1.00	NL	Small	Small
Paclobutrazol	3.00	PL	Large	Small
Tebuconazole	0.37	NL	Large	Large

GUS classification: NL - non-leachable; I - intermediate; PL – potentially leachable.

Numerous studies have already provided evidence of the existence of pesticide residues in aquatic environments, including those designated for human consumption (Mateo-Sagasta et al., 2017; Medkova et al., 2023; Pathak et al., 2022; Rajmohan et al., 2020; Tudi et al., 2021). Due to this environmental and public health predicament, the São Paulo Environmental Agency (CETESB) undertakes comprehensive water surveillance in São Paulo, Brazil, to detect the occurrence of

pesticides in surface and groundwater reservoirs and sedimentary deposits. Values above national and international criteria were identified for the insecticide Chlorpyrifos (CETESB, 2021)

A study on the risk of contamination of surface and groundwater by pesticides in Onion cultivation in the municipalities of Casa Nova and Sento Sé in Bahia (Souza e Silva et al., 2019), concluded that, among the pesticides applied to the crop, Chlorpyrifos, Difenconazole and Lambda-

Cyhalothrin pose a significant risk of contamination through adsorption to sediments. Additionally, Azoxystrobin, Chlorpyrifos, and Tebuconazole have been identified as having a high risk of contamination when dissolved in water.

The study conducted by Pinheiro et al. (2010) investigated the occurrence of pesticides in both surface and groundwater within the Itajaí basin, Santa Catarina, Brazil. Samples were collected from various locations along the river as well as from wells. These study findings revealed that herbicides were detected at a relatively low frequency in both surface and groundwater. On the other hand, fungicides such as Metconazole and Tebuconazole, as well as the insecticide Lambda-Cyhalothrin, exhibited a high detection frequency. Furthermore, concentrations were high, exceeding the maximum limits established by the European Union. The authors also pointed out that, regarding the majority of active ingredients that have been authorized in the country, Brazilian legislation had not established any maximum limits.

In their study, Britto et al. (2015) assessed the potential risk of water contamination by pesticides in the Bitume irrigated perimeter, a tributary of the São Francisco River. The study revealed the presence of Chlorpyrifos, Tebuconazole, and Tetraconazole in the water. The authors emphasized that the issue of contamination becomes increasingly severe when the contaminated water is utilized for human consumption, thereby exposing the population to potential risks. Consequently, it is imperative to make informed decisions to ensure the preservation of water quality.

Chart 3 presents the non-target organism most affected by each active ingredient, based on the premise that the sensitivity of the ecosystem depends on the most sensitive species. The EC_{50} and LC_{50} values were obtained from the IUPAC database (2023) and, when absent in this database, from the Chemical Product Safety Information Sheet of the pesticides made available on the internet by the product manufacturers. For fish, the values obtained were LC_{50} , which represents the mean lethal dose of the substances, specifically the concentration that induces mortality in 50% of the organisms exposed. As for daphnia and algae, the values obtained were EC_{50} , which is the concentration that produces an adverse effect on 50% of exposed organisms. Utilizing this data, it became feasible to compute the Unpredicted Effect

Concentration ($PNEC$) for each active component, as outlined in the methodology.

According to $PNEC$ values, Chlorpyrifos, Deltamethrin, and Lambda-Cyhalothrin are the most toxic to non-target organisms. It is worth noting that all of these are part of the insecticide class. The active ingredients Acetamiprid, Glufosinate, and Glyphosate exhibit lower toxicity due to their elevated $PNEC$ values.

Chart 3 also presents the values of the Retardation Factor (R_F), the values of daily water recharge (J_w) for the two years under study, and the calculation of the Attenuation Factor (A_F) of the pesticide from the soil to the groundwater. The R_F is directly linked to the K_{oc} value of the active ingredient. The highest R_F value was that of the pesticide Deltamethrin, which also has the highest K_{oc} value.

R_F is a relevant parameter for calculating the attenuation factor so that high R_F values reflect lower A_F values. The A_F values were significantly low, confirming the outcome obtained through the GUS method. This method has demonstrated that the pesticides employed in the examined cultivation plot possess a minimal capacity for groundwater contamination through leaching. The pesticides Abamectin and Paclobutrazol, which were classified as likely to be leached, and Azoxystrobin, which was in the transition zone, presented the highest A_F values, although still low.

Table 5 shows the number of times each pesticide was applied and how much this represents in terms of pollutant load. Furthermore, it presents the leaching-runoff coefficients used in the H-model and the pesticide runoff coefficient used in the P-model, calculated as described in the methodology.

In the study area during the year 2021, the most commonly utilized pesticide on the crop plot was Lambda-Cyhalothrin, an insecticide with 13 applications. Conversely, Glyphosate, Glufosinate, and Paclobutrazol were the least utilized, with only one application each during the mentioned period. It is noteworthy, however, that despite its singular application, Paclobutrazol exhibited the highest pollutant load applied (Apl) at 34.88 kg, followed by Glyphosate with an Apl of 22.71 kg. In 2022, Spinosad was the most widely applied pesticide, which falls under insecticides. Notably, Paclobutrazol was not employed during this period. However, it is worth mentioning that Glyphosate, accounted for the highest pollutant load, measuring an Apl of 45.42 kg, despite being applied twice a year.

Chart 3. Toxicity, retardation factor, daily water recharge and attenuation factor.

Pesticide	Non-target organism	¹ EC50/CL50 (mg L ⁻¹)	PNEC (kg m ⁻³)	RF	J _w (m d ⁻¹)		A _F	
					2021	2022	2021	2022
Abamectin	Daphnia Similis	5.60E-03	5.60E-09	1.38	1.30E-03	3.49E-04	5.57E-12	1.28E-42
Acetamiprid	Daphnia magna	4.98E+01	4.98E-05	16.40	3.21E-03	*	1.52E-252	*
Azoxystrobin	Daphnia magna	2.30E-01	2.30E-07	46.34	1.15E-03	4.35E-04	8.80E-34	5.93E-88
Chlorpyrifos	Daphnia magna	1.00E-04	1.00E-10	425.11	*	4.93E-03	*	0.00E+00
Deltamethrin	Oncorhynchus mykiss (Fish)	1.50E-04	1.50E-10	788335.01	*	2.73E-03	*	0.00E+00
Difenoconazole	Scenedemus subspicatus (Algae)	3.20E-02	3.20E-08	596.41	7.28E-04	4.91E-04	0.00E+00	0.00E+00
Spinosad	Navicula sp. (Algae)	1.70E-01	1.70E-07	154.97	8.48E-04	6.85E-04	0.00E+00	0.00E+00
Ethephon	Navicula pelliculosa (Algae)	2.86E+00	2.86E-06	196.54	1.94E-03	1.89E-03	0.00E+00	0.00E+00
Fenpyroximate	Oncorhynchus mykiss (Fish)	1.05E-03	1.05E-09	924.83	*	7.64E-04	*	0.00E+00
Glyphosate	Pseudokirchneriella subcapitata (Algae)	1.90E+01	1.90E-05	110.63	4.23E-04	2.22E-03	0.00E+00	0.00E+00
Glufosinate	Pseudokirchneriella subcapitata	3.07E+01	3.07E-05	47.19	4.23E-04	2.22E-03	0.00E+00	0.00E+00
Copper (II) hydroxide	Pseudokirchneriella subcapitata	9.00E-03	9.00E-09	924.83	9.76E-04	*	0.00E+00	*
Lambda-Cyhalothrin	Lepomis macrochirus (Fish)	2.10E-04	2.10E-10	21842.39	9.17E-04	8.88E-04	0.00E+00	0.00E+00
Copper oxychloride	Daphnia magna	2.90E-01	2.90E-07	77.99	9.76E-04	3.43E-03	0.00E+00	0.00E+00
Paclobutrazol	Pseudokirchneriella subcapitata (Algae)	7.20E+00	7.20E-06	31.79	1.01E-02	*	4.77E-04	*
Tebuconazole	Scenedemus subspicatus (Algae)	1.96E+00	1.96E-06	462.91	7.78E-04	4.32E-04	0,00E+00	0.00E+00

* Period without applications.
(IUPAC, 2023¹)

Table 4. Number of pesticide applications; *Apl* (kg); leaching-runoff coefficient a_H (H-model) and runoff coefficient a (P-model).

Pesticide	Number of applications		<i>Apl</i> (kg)		a_H	a
	2021	2022	2021	2022		
Abamectin	7	7	8.85	8.85	6.00E-02	9.89E-02
Acetamiprid	5	*	5.05	*	4.52E-02	1.56E-02
Azoxystrobin	5	6	1.80	2.16	6.33E-02	5.87E-03
Chlorpyrifos	*	2	*	7.97	4.00E-02	7.40E-04
Deltamethrin	*	4	*	4.36	4.00E-02	9.36E-05
Difenoconazole	6	5	10.85	9.04	4.85E-02	5.55E-04
Spinosad	3	10	2.93	9.17	3.18E-02	1.86E-03
Ethephon	3	5	2.51	4.62	4.00E-02	1.49E-03
Fenpyroximate	*	1	*	3.30	3.18E-02	3.91E-04
Glyphosate	1	2	22.71	45.42	3.18E-02	2.42E-04
Glufosinate	1	2	14.61	29.22	3.18E-02	5.77E-03
Copper (II) hydroxide	1	*	3.32	*	3.18E-02	3.91E-04
Lambda-Cyhalothrin	13	7	2.07	1.12	4.00E-02	1.06E-04
Copper oxychloride	2	3	13.28	19.92	3.84E-02	3.57E-03
Paclobutrazol	1	*	34.88	*	6.33E-02	8.40E-03
Tebuconazole	6	6	19.80	19.80	4.85E-02	6.87E-04

* Period without applications.

The Gray Water Volume (GWV) was calculated for the H-model and the P-model for the years 2021 (Table 6) and 2022 (Table 7). For the pollutant load applied in 2021, the H-model indicated Paclobutrazol as the one with the highest GWV, followed by the pesticides Abamectin, Difenoconazole, and Glufosinate, all with the same order of magnitude of GWV (10^6 m^3). It is worth mentioning that Paclobutrazol was applied once and obtained the highest *Apl*. Furthermore, its susceptibility to leaching and surface runoff justifies its placement in the pesticide ranking.

According to the pesticide ranking produced by the P-model, the pesticide with the highest pollution level was Abamectin (7.59), which, as indicated by the GUS index, is likely to have leaching effects. Following closely behind are the pesticides Lambda-Cyhalothrin (5.42) and Difenoconazole (4.67). A study conducted by Novelli (2010) has already indicated that Abamectin exhibits significant toxicity even at minimal concentrations. This finding suggests implementing measures that limit its usage and further validate its placement within the pesticide ranking. One of the reasons why Paclobutrazol does not occupy a prominent

position in the pesticide ranking from the P-model is because the model considers toxicity as a determining factor for calculating the GWV, and Paclobutrazol is not one of the most toxic pesticides among those used in the area. Moreover, Lambda-Cyhalothrin exhibited greater prominence within the GWV according to the P-model, owing to its status as one of the active constituents possessing the lowest Predicted No-Effect Concentration (*PNEC*) value. Additionally, it is classified as highly hazardous to the environment and moderately toxic.

Still, for the pesticide load applied to the cultivation plot in 2021 (Table 6), the H-model demonstrated that the lowest GWV values were for the pesticides Glyphosate, Tebuconazole, Copper Oxychloride, and Copper Hydroxide. The ranking of pesticides that they hold exerts a significant influence on the C_{max} values attributed to them. These values are notably higher than those assigned to most active ingredients currently under investigation. This is because the European Union's standard, as outlined in Directive 2015/1787 of 10/06/2015, has been adopted for pesticides lacking a standardized C_{max} value in Brazilian

legislation. This directive mandates a uniform C_{max} value of 0.0001 mg L^{-1} for all active ingredients, which is a more stringent standard. The C_{max} of Tebuconazole was adopted as 0.18 mg L^{-1} (Presença de Agrotóxicos Em Água Potável No Brasil: Parecer Técnico Do GT de Agrotóxicos Da Fiocruz Para a Revisão Do Anexo XX Da Portaria de Consolidação No 05, 2017) that of Copper Oxychloride and Copper Hydroxide as 2 mg L^{-1} , following the European standard for copper in water for human

consumption (IUPAC, 2023), and that of Glyphosate as 0.065 mg L^{-1} (Resolução CONAMA N° 357, de 17 de Março de 2005, 2005).

The P-model does not consider the C_{max} permitted by legislation. Thus, the lowest GWV was for the active ingredients Glyphosate, Ethephon, and Acetamiprid, which are products with higher $PNEC$ values. That is, they are less toxic to non-target organisms.

Table 5. Gray Water Volume of pesticides applied in 2021.

Pesticides applied in 2021	Gray Water Volume (GWV) H-model		Gray Water Volume (GWV) P-model	
	$GWV i^{ha}$ ($\text{m}^3 \text{ ha}^{-1}$)	r_i	$GWV i^{ha}$ ($\text{m}^3 \text{ ha}^{-1}$)	r_i
Abamectin	1.33E+06	6.12	3.91E+07	7.59
Acetamiprid	5.71E+05	5.76	3.95E+02	2.60
Azoxystrobin	2.85E+05	5.45	1.15E+04	4.06
Difenoconazole	1.32E+06	6.12	4.70E+04	4.67
Spinosad	2.33E+05	5.37	8.01E+03	3.90
Ethephon	2.51E+05	5.40	3.26E+02	2.51
Glyphosate	2.77E+03	3.44	7.24E+01	1.86
Glufosinate	1.16E+06	6.06	6.86E+02	2.84
Copper (II) hydroxide	1.32E+01	1.12	3.61E+04	4.56
Lambda-Cyhalothrin	2.08E+05	5.32	2.62E+05	5.42
Copper oxychloride	6.37E+01	1.80	4.08E+04	4.61
Paclobutrazol	5.52E+06	6.74	1.07E+04	4.03
Tebuconazole	1.33E+03	3.13	1.74E+03	3.24

In the assessment of pesticide ranking using the two models employed to estimate the GWV for the year 2021, as previously discussed, significant disparities were also evident for Glufosinate, Acetamiprid, Ethephon, Copper Oxychloride, and Copper Hydroxide (Figure 3). In the H-model, Glufosinate exhibits the most value of the pesticide ranking, whereas in the P-model, it exhibits the lowest value. This disparity may be attributed to Glufosinate's high application rate and solubility despite

possessing a high $PNEC$ value, indicating low toxicity. Acetamiprid and Ethephon are also low-toxic products and, therefore, had lower GWV values in the P-model. Copper Oxychloride and Copper Hydroxide have a high C_{max} value, which caused them to have a low GWV value by the H-model, but they are toxic products with low $PNEC$ values for the most sensitive non-target organism, which increased their position in the pesticide ranking.

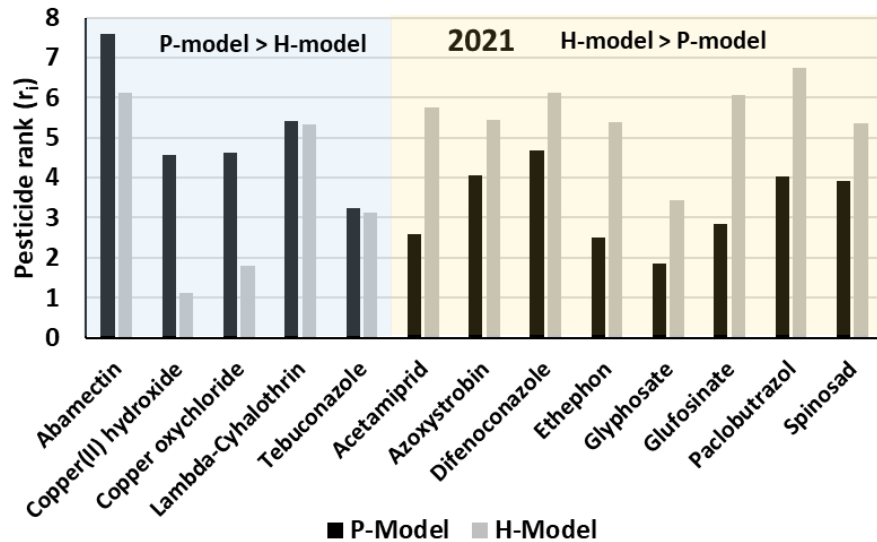


Figure 3. Comparison between the pesticide rankings obtained by the P-model and H-model - 2021.

In 2022, the H-model calculation of pesticide rankings revealed Glufosinate to have the highest GWV, followed by Abamectin and Difenoconazole, all with a magnitude of 10^6 m^3 . It is important to note that Paclobutrazol, which had the highest GWV in 2021, was not utilized during this period. On the other hand, the P-model generated pesticide rankings highlighted Abamectin as having the highest GWV, followed by the active ingredients Chlorpyrifos and Deltamethrin, all exhibiting very low $PNEC$ values.

According to the H-model, the applications with the lowest GWV values for the year 2022 were Chlorpyrifos, Copper Oxychloride, Tebuconazole, and Glyphosate. Similarly, to the explanation provided for the year 2021, this ranking is closely linked to the C_{max} values adopted. In terms of the P-model ranking, the pesticides Glufosinate, Ethephon, and Glyphosate exhibit the lowest GWV values, all of which are associated with low toxicity towards non-target organisms.

Table 6. Gray Water Volume of pesticides applied in 2022.

Pesticides applied in 2022	Gray Water Volume (GWV) H-model		Gray Water Volume (GWV) P-model	
	$VACI^{ha}$ ($\text{m}^3 \text{ ha}^{-1}$)	r_i	$VACI^{ha}$ ($\text{m}^3 \text{ ha}^{-1}$)	r_i
Abamectin	1.33E+06	6.12	3.91E+07	7.59
Azoxystrobin	3.42E+05	5.53	1.38E+04	4.14
Chlorpyrifos	2.66E+03	3.42	1.47E+07	7.17
Deltamethrin	4.36E+05	5.64	6.80E+05	5.83
Difenoconazole	1.10E+06	6.04	3.92E+04	4.59
Spinosad	7.29E+05	5.86	2.51E+04	4.40
Ethephon	4.62E+05	5.66	6.00E+02	2.78
Fenpyroximate	2.62E+05	5.42	3.07E+05	5.49
Glyphosate	5.55E+03	3.74	1.45E+02	2.16
Glufosinate	2.32E+06	6.37	1.37E+03	3.14
Lambda-Cyhalothrin	1.12E+05	5.05	1.41E+05	5.15
Copper oxychloride	9.55E+01	1.98	6.13E+04	4.79
Tebuconazole	1.33E+03	3.13	1.74E+03	3.24

The pesticide rankings of both models in 2021 exhibited similar differences to those observed in 2022 for Glufosinate, Ethephon, Lambda-Cyhalothrin, and Copper Oxychloride. Furthermore, notable variations in the outcomes for Chlorpyrifos, Deltamethrin, and Fenpyroximate were also evident despite their non-application in the preceding year (Figure 4).

Based on the H-model, Chlorpyrifos occupies the 11th position, Deltamethrin occupies the 6th and Fenpyroximate the 8th. Conversely, in the P-model Chlorpyrifos is ranked 2nd, Deltamethrin in the 3rd, and Fenpyroximate in the 4th in the pesticide ranking. Chlorpyrifos was not applied during 2021, and in the subsequent 2022, it was employed merely on two occasions within the cultivation area. This insecticide is categorized as moderately toxic and poses a significant environmental threat. On the other hand, Deltamethrin is classified as highly hazardous to the environment. Furthermore, the three active ingredients are toxic to non-target organisms, as they have low *PNEC* values.

Among the pesticides in the insecticide and acaricide class, those with the highest GWV were Abamectin and Chlorpyrifos. The active ingredient Abamectin is categorized as having a high likelihood of leaching, as per the GUS index. It possesses a low Predicted No-Effect Concentration (*PNEC*) value, indicating its toxicity, and exhibits a low retardation factor due to its low K_{oc} value. Consequently, Abamectin reached the highest positions in the pesticide ranking for both the H-model and the P-model during the two years of examination. Chlorpyrifos is the most toxic, with the lowest *PNEC* value among the pesticides applied to the cultivation area.

Among the fungicides, it is worth highlighting Azoxystrobin, as it has been found to exhibit leaching tendencies according to the GUS method. Moreover, when dissolved in water, there is a significant risk of contaminating surface water bodies. Due to its

relatively low application load, Azoxystrobin was not highlighted as the highest GWV in any of the models.

To herbicides, it has been observed that Glufosinate exhibits a greater volume of GWV in comparison to Glyphosate across all models. This phenomenon can be attributed to its lower K_{oc} value, resulting in a lower retardation factor and higher solubility in water. Nevertheless, despite Glyphosate's ability to generate a reduced gray water footprint and exhibit lower toxicity toward aquatic organisms, numerous studies have already shed light on its potential carcinogenic properties, particularly when it comes to the occupational exposure of individuals working in rural areas (Siqueira & Bressiani, 2023).

The success of mango floral induction in the semi-arid region depends on growth regulators such as Paclobutrazol and Ethephon. The main growth regulator used is Paclobutrazol (Oliveira, 2020). Nevertheless, it is worth mentioning that despite its limited application, the substance above achieved the highest GWV in the year 2021. This can be attributed to its propensity to leach and disperse when diluted in water. Ethephon, on the other hand, has a lower GWV value in both the H-model and P-model but is inefficient when applied alone. There are already several studies that demonstrate the efficiency of combining Paclobutrazol with Ethephon, as well as other products such as potassium nitrate and potassium sulfate, including in the Tommy Atkins mango crop (Mendonça et al., 2001, 2003; J. A. L. da Silva & Neves, 2011). Furthermore, Ethephon also has good efficiency when combined with water stress (Mouco et al., 2021). Thus, reducing the applied dose of Paclobutrazol, when it does not compromise agricultural production or replacing it with Ethephon combined with water stress, will reduce the gray water footprint of the crop.

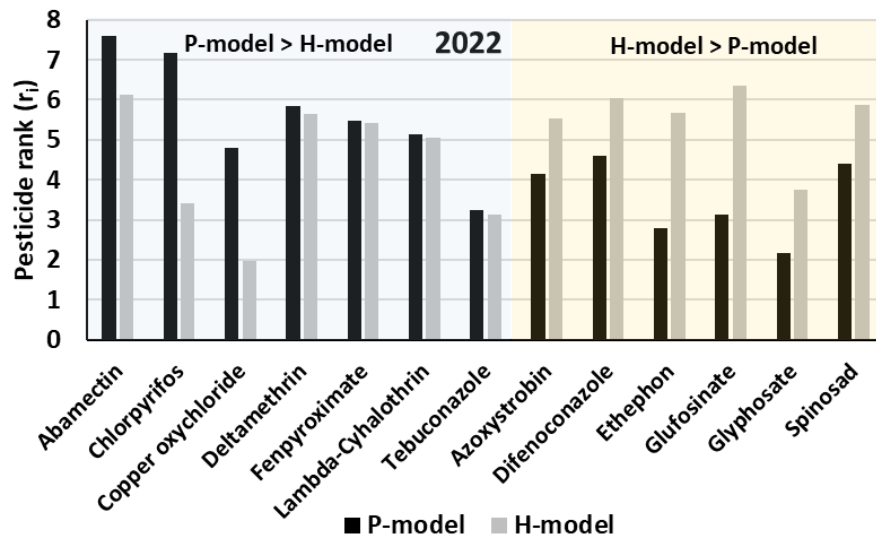


Figure 4. Comparison between the rankings obtained by the P-model and H-model - 2022.

In the case of the H-model, which considers that the volume of gray water in the mixture will be the highest volume of gray water per hectare among the volumes calculated for each pesticide used in the mixture, the generated GWV_{ha} was $5.52 \times 10^6 \text{ m}^3 \text{ ha}^{-1}$. This value pertains explicitly to the GWV_{ha} resulting from the application of Paclobutrazol in December 2021. In 2022, the volume of Glyphosate and Glufosinate mixture applied resulted in a GWV_{ha} of $1.16 \times 10^6 \text{ m}^3 \text{ ha}^{-1}$. For the P-model, which uses the concentration addition principle, the GWV_{ha} was $3.95 \times 10^7 \text{ m}^3 \text{ ha}^{-1}$ in 2021 and $5.51 \times 10^7 \text{ m}^3 \text{ ha}^{-1}$ in 2022.

The Volume of Gray Water found by the P-model was greater than that calculated by the H-model. This observation may be attributed to the environmental sustainability of the P-model, which considers the toxicity of active ingredients in indicator aquatic organisms, as previously expounded by Barreto et al. (2019). Paraíba et al. (2014) also pointed out in their study that the potency of the mixture calculated using the concentration addition model is greater than when using the independent action model.

For both models, the GWV of the pesticide mixtures applied to the four hectares in the Tommy Atkins mango crop is generally considerably high. To make a comparison, it is worth noting that the GWV of the P-model in 2022 amounts to $2.20 \times 10^8 \text{ m}^3$. Thus, this volume is equivalent to the capacity of approximately 11 million water tankers, each capable of holding 20 m^3 of water.

There is a lack of regional studies estimating the Gray Water Footprint of pesticides used on Tommy Atkins mango crops and other mango cultivars for comparison. Therefore, the findings of this study hold significant value as they can serve as a crucial resource for selecting less environmentally harmful pesticides to be employed in conjunction with other sustainable techniques in mango cultivation. An exemplary instance is the implementation of biological control in the region, exemplified by the Moscamed project. This initiative employs the release of sterile male fruit fly insects in infested areas to outcompete their wild counterparts, thereby diminishing the pest population. Consequently, this method can potentially supplant the reliance on insecticides like Deltamethrin for combating fruit flies, mitigating the crop's gray water footprint. It is still possible to think about combining different pesticides to reduce the dose of the most polluting pesticides, as is the case of combining Paclobutrazol and Ethephon or Ethephon with water stress for the floral induction of mango, as already discussed.

In modern agriculture, the use of pesticides plays a vital role in safeguarding and enhancing food production. Nevertheless, due to their harmful properties, it is imperative for farmers to comprehend the ecological repercussions of pesticide usage and investigate sustainable approaches to avert contamination of surface and groundwater.

Excessive use of fertilizers and pesticides contributes significantly to the gray

water footprint. Consequently, by minimizing this footprint, enables farmers to make well-informed choices and adopt practices that promote environmental well-being and their agricultural operations, ensuring long-term sustainability.

Policymakers can utilize the findings of this study to improve pesticide regulations. However, economic constraints often compel farmers to prioritize productivity rather than ecological concerns. To address this, governments should offer incentives to promote sustainable practices, such as agroecology and biopesticides. Additionally, implementing stringent monitoring mechanisms is crucial to ensure compliance with these practices.

The evaluation conducted in this research on the gray water footprint of pesticides used in cultivating Tommy Atkins mangoes in the Sub-middle São Francisco Valley region highlights the importance of this indicator. It provides technical guidance to promote the responsible application of pesticides, emphasizing the need for environmentally conscious agricultural practices.

Conclusions

The soil in the study region is sandy, which makes it more vulnerable to leaching. However, according to the assessment of the potential contamination of water bodies by pesticides applied to the crop carried out using the GUS Index and the GOSS method, the pesticides that were applied to the Tommy Atkins mango crop have a low potential for underground water contamination by leaching and present a low to medium risk of contaminating surface water bodies.

The pesticides Difenoconazole and Tebuconazole have the highest risk of contaminating surface water bodies among the 16 pesticides applied in the area over a period of 2 (two) years. The pesticide Abamectin was classified as likely to be leached. The pesticides Azoxystrobin and Paclobutrazol, in addition to presenting a risk of contaminating groundwater through leaching, are also classified as having a high risk of contaminating surface waters when dissolved in water. Although they were not classified as likely to leach and pose a risk to surface waters in this study, Chlorpyrifos and

Lambda-Cyhalothrin require attention due to their low *PNEC* values and because they are cited in the literature as active principles found when water from water bodies nearby cultivation areas is analyzed, including the São Francisco River.

In 2021, according to the H-model, Paclobutrazol was responsible for the highest GWV. For the P-model it was Abamectin. In 2022, the highest GWV value for the H-model was Glufosinate; according to the P-model, it was, again, Abamectin. The disparity between the models primarily stems from the fact that the model developed by Hoekstra et al. (2011) considers the maximum concentration allowed by pesticide regulations in water bodies. Conversely, the model developed by Paraíba et al. (2014) focuses on the toxic impact on indicator organisms.

The GWV_{ha} of the pesticide mixtures applied to the Tommy Atkins mango crop was about $10^6 \text{ m}^3 \text{ ha}^{-1}$ for the H-model and $10^7 \text{ m}^3 \text{ ha}^{-1}$ for the P-model. In general, considering the two models applied, it can be observed that the GWV_{ha} of the pesticide mixtures applied to the Tommy Atkins mango crop was high. It is also possible to conclude that the P-model is more environmentally conservative, as it considers the toxicity of pesticides to aquatic organisms.

Therefore, the pesticide ranking derived from the computation of the gray water footprint, in conjunction with the potential evaluation of water body contamination caused by pesticides, can serve as a valuable instrument for facilitating decisions regarding the selection of pesticide combinations for mango cultivation. This approach aims to safeguard water bodies while simultaneously ensuring agricultural productivity.

Author contributions

Flávia Fernanda Santos Gomes: Methodology, Formal Analysis, Investigation, Writing – Original Draft. André Maciel Netto: Conceptualization, Methodology, Formal Analysis, Investigation, Resources, Writing – Review & Editing, Supervision, Project Administration. Ademir Amaral: Writing – Review & Editing. Lourival Costa Paraíba: Methodology, Formal Analysis, Writing – Review & Editing.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethics approval and consent to participate

The authors declare that this manuscript is in accordance with the ethical responsibilities of the journal and the Committee on Publication Ethics (COPE).

Data availability

Data will be made available on request.

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