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ORIGINAL RESEARCH ARTICLE

Assessing the grey water footprint of pesticide use in the Mendoza wine region (Argentina): implications for sustainable water resources management

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ABSTRACT

This paper assesses the impact of viticulture on water resource quality in the Mendoza wine region using the grey water footprint (GWF) approach to estimate the amount of water required to dilute pesticides commonly used in local vineyards. Our analysis indicates that to progress towards sustainable water management in viticulture, limiting or replacing pesticides with high GWF values is essential. We provide detailed results for 24 fungicides, 7 insecticides, and 7 herbicides, assessed at both microregion and district levels, offering insights into pesticide impacts across both detailed and broader spatial scales. At the microregion level, the herbicide Fluroxypyr-meptyl was found to have the highest GWF (1.10 $m^3\ kg^{-1}$), followed by the fungicide Fosetyl-aluminium (0.59 $m^3\ kg^{-1}$) and the insecticide Imidacloprid (0.41 $m^3\ kg^{-1}$). Our findings also show that pesticide impacts vary at the district level, highlighting the need for localised management strategies. Additionally, the significant variability in GWFs at the local level underscores the necessity for region-specific water quality standards to more accurately assess and manage the environmental impact of pesticide use. This study provides a framework for similar assessments in other viticultural regions, aiding in the development of more informed pesticide management to enhance water resource sustainability.

KEYWORDS: grey water footprint, water resources quality, fungicides, insecticides, herbicides, sustainable water management in viticulture, Mendoza wine region

INTRODUCTION

At the foot of the central Andes, the Mendocinian vineyards cover a total cultivation area of 147,379 hectares, the largest in Argentina (INV, 2022). Known for their cultural and identity values, these green and extensive vineyards are also renowned for the *goût de terroir* or taste of the earth, defining the character of most of their wines and positioning Mendoza as one of the most important wine regions worldwide.

This region, characterised by an arid and semi-arid climate, is experiencing significant variations in temperatures and precipitation because of global warming (IPCC, 2023; Masiokas *et al.*, 2020). Due to the impact on vineyard productivity and wine quality, the increase in average annual temperatures and changes in rainfall patterns raise concerns about the future of viticulture in the region (Castex *et al.*, 2015). The scarcity of irrigation water from climate-related variations is not the only concern, grapevine crops can also be affected by a higher incidence of pests and diseases (Deis *et al.*, 2015).

Numerous studies show that global warming together with CO_2 concentration can cause crop phytosanitary problems and reduce production standards (Hamada & Ghini, 2011; Velásquez *et al.*, 2018; Singh *et al.*, 2023). In Mendoza, this phenomenon can be aggravated due to increased summer rainfall (Boninsegna, 2014; Deis *et al.*, 2015). Various pests and diseases can damage grapevine crops, often requiring chemical management to meet production standards. The use of phytosanitary products (or pesticides; hereinafter, both terms are used interchangeably in the paper) ensures high-quality production with less crop damage and consistent yields. However, often the amount of pesticides reaching target organisms is an extremely small percentage of the applied pesticides, moving the rest throughout the environment (Pimentel, 1995; Pimentel & Burgess, 2012; De Lavôr Paes Barreto *et al.*, 2020). Therefore, pesticides can reach surface or groundwater systems through runoff and leaching from irrigation and rainwater, making them a diffuse pollution source (Sasáková *et al.*, 2018). Faced with the environmental risks posed by these compounds, farmers need tools to assess the efficiency of pesticide management and application to ensure high-quality production while minimising diffuse pollution loads entering water bodies.

Having accurate and reliable information on the impact of pesticides on the quality of water resources may be useful to different stakeholders. For instance, if a wine grower wanted to minimise the risk of diffuse water pollution, what pesticides should receive priority? Or, if a policy maker or land manager were interested in minimising diffuse pollution risk, what critical points should they prioritise in water policy? Moreover, what critical substances should they consider as a priority for efficient phytosanitary regulation in terms of the risks they pose to sustainable water resources management? These are questions that grey water footprint (GWF) can answer.

The GWF has been proposed as a theoretical calculation that indicates the impact of the production system on water resource quality. The GWF refers to the volume of water that is required to assimilate waste, quantified as the volume of water needed to dilute pollutants to such an extent that the quality of the ambient water remains above agreed water quality standards (Hoekstra *et al.*, 2011, p. 31). As an indicator of water resources appropriation through pollution, it provides a tool to help assess the sustainable, efficient and equitable use of water resources (Franke *et al.*, 2013, p. 7). The first GWF assessment was carried out by Chapagain *et al.* (2006) for the worldwide consumption of cotton while a few years later Mekonnen and Hoekstra (2010) reported on the first GWF assessment for grape wines. From this first boost, the GWF of grapes from viticulture to winemaking has been assessed in different wine regions worldwide (Morábito, 2012; Ene *et al.*, 2013; Herath *et al.*, 2013; Lamastra *et al.*, 2014; Novoa *et al.*, 2019; Saraiva *et al.*, 2019). Most of these studies evaluated the GWF associated with fertilisers, particularly nitrogen, ignoring the possible impacts of pesticides on the quality of water resources.

The objective of our study is to assess the impact of viticulture on the quality of water resources. The GWF analysis was used to estimate the amount of water needed to dilute a wide range of pesticides (24 fungicides, 7 insecticides, and 7 herbicides) commonly used in local vineyards. We applied the methodology proposed by Hoekstra *et al.* (2011) to evaluate the GWF of grapevine crops in a viticultural microregion of Mendoza. Our analysis was based on specific information on phytosanitary products marketed from September 2018 to April 2020 provided by the Institute of Agricultural Health and Quality of Mendoza (ISCAMEN, 2021). Our results may be of particular interest to different stakeholders, from wine growers to land managers and policymakers working on the environmental sustainability of viticulture in the field of sustainable water resources management.

MATERIALS AND METHODS

1. Area of study

This research covers a microregion of 2,775 km^2 where grapes are grown for wine production. Located in west-central Argentina, the study area comprises 9 districts: Costa de Araujo, El Carmen, El Central, El Divisadero, El Plumero, Ing. Gustavo André, La Holanda, Nueva California, and Paramillos (Figure 1). Although there is considerable diversity in the crops offered by its agricultural landscapes, only grapevine crops–*Vitis vinifera*–take centre stage: out of the 22,100 cultivated hectares, 13,350 hectares are dedicated to vineyards, which occupy just over 60 % of the cultivated area (INV, 2023).

Following the classification of the Géoviticulture Multicriteria Climatic Classification System, the viticultural microregion under study has an arid and warm climate with cool nights (Tonietto & Carbonneau, 2004), with soils classified as typical torrifluvents with a loamy texture (INTA, 1990).

Both factors, climate and soil types, explain much of the diversity of cultivated grape varieties and the typicity of wines, in terms of their organoleptic characteristics (Tonietto & Carbonneau, 2004; Pose-Juan *et al.*, 2015). Of the 78 grape varieties grown on this soil, 4 are found in 50 % of its vineyards: Bonarda (16.7 %), Cereza (12.8 %), Syrah (10 %), and Pedro Ximénez (9.5 %), with an average annual grape production of 170,633,090 kg between 2018 and 2020. Table 1 shows the annual average of both, grape production and hectares under vines in three consecutive years (2018-2020), distinguishing data at the microregion and district levels (INV, 2023).

Due to the scarce average annual rainfall (220 mm), the agricultural production system was developed using a complex network of irrigation canals that transports water from mountain rivers to vineyards, whose streamflow is the result of the fusion of snow and Andean glaciers, and the groundwater boreholes supporting it (Morábito *et al.*, 2007; Monnet *et al.*, 2022). In 80 % of the farm units with grape cultivation, furrow, flood, or surface irrigation systems are used (INDEC, 2018). These systems are one of the least water-efficient irrigation methods and present a higher risk, especially when compared to other irrigation methods such as drip irrigation, as pesticides that did not reach the target organisms move throughout the environment, contaminating water resources (Franke *et al.*, 2013).

Regarding vineyard training methods, the most traditional and widespread method in grapevine crops in the microregion is the pergola [55 %] (INV, 2022). This technique is associated with higher yield per hectare. In the rest of the vineyards, vertical shoot positioning is used, an increasingly adopted technique, as it allows the incorporation of new technologies such as mechanical harvesting and, in turn, presents a lower probability of the incidence of pests and diseases.

While both irrigation practices and vineyard training methods contribute to diffuse pollution in water bodies, it is crucial to recognise–as demonstrated later in this study–that vineyard training methods directly impact the GWF due to variations in reported yields between methods. However, the influence of irrigation systems on GWF should not be underestimated. Inefficient irrigation practices are widespread in the microregion, with approximately 80 % of farms lacking efficient systems. Improving irrigation efficiency could lead to significant reductions in GWF. Therefore, while vineyard training methods directly affect GWF through productivity differences, the impact of irrigation practices is also critical and warrants attention for reducing GWF.

2. Phytosanitary products

In Argentina, all pesticides are regulated products and must be enrolled in the National Service for Agri-Food Health and Quality (SENASA) before being commercialised. This research focuses on phytosanitary products registered for application in grapevine crops.

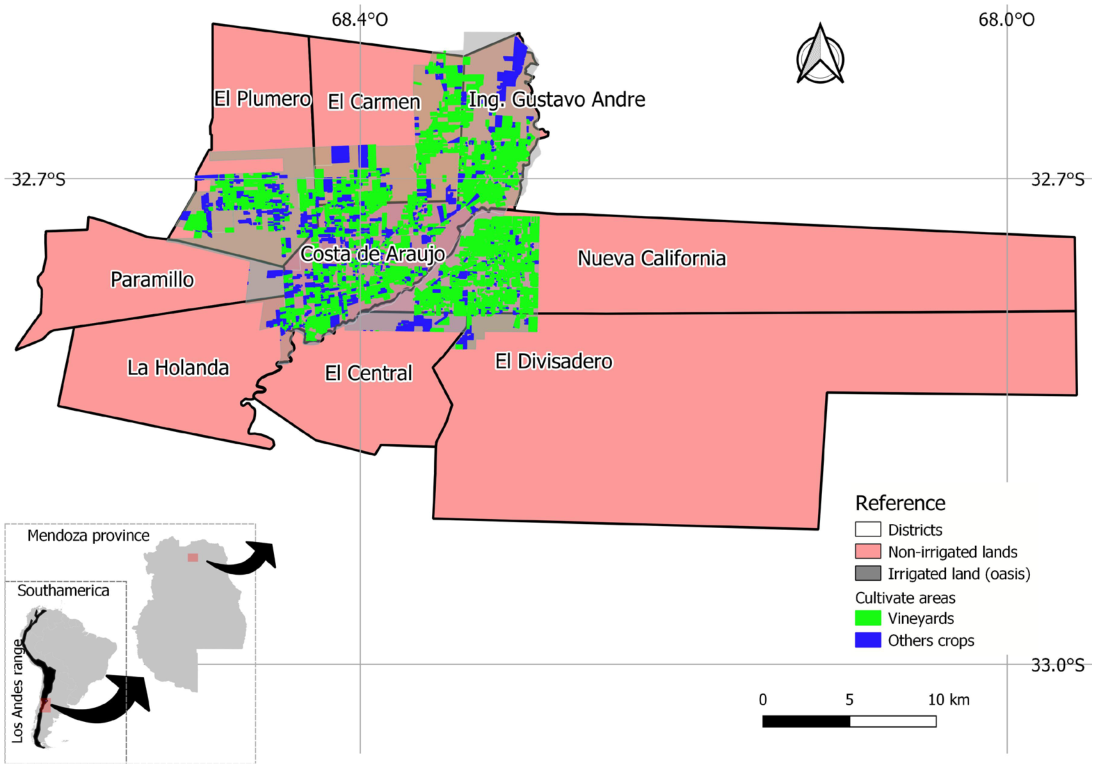

FIGURE 1. Agricultural surface with grapevine crops in the viticultural microregion of the province of Mendoza (Source: Own elaboration based on data obtained from the National Sanitary Registry of Agricultural Producers (RENSPA), the National Institute of Vitiviniculture (INV), and the cartography of the Territorial Environmental Information System (SIAT) and the National Geographic Institute (IGN). The green areas indicate the agricultural surface with grapevine crops).

TABLE 1. Annual average of grape production and hectares under vines in the microregion, grouped by district (2018–2020).

	Hectares under vines (ha)	Production (kg)	Yield per hectare (kg ha^{-1})
	Costa de Araujo		
Annual average	4,137	52,847,234	12,774
	El Carmen		
Annual average	131	2,121,373	16,194
	El Central		
Annual average	1,391	20,617,879	14,822
	El Divisadero		
Annual average	1,402	14,670,995	10,464
	El Plumero		
Annual average	862	7,051,107	8,180
	Ing. Gustavo André		
Annual average	2,523	34,231,330	13,568
	La Holanda		
Annual average	89	1,512,653	16,996
	Nueva California		
Annual average	2,261	33,470,251	14,803
	Paramillos		
Annual average	553	4,110,269	7,433
	Microregion		
Annual average	13,350	170,633,090	12,781

Phytosanitary products are used in grapevine and other crops for the control of pests, diseases, and weeds, and without their application, vineyard productivity could be reduced, compromising the volume and quality of grape production. According to target organisms to control, main phytosanitary products can be classified into herbicides, insecticides, and fungicides. The application rate of pesticides according to target organisms in grapevine crops of the microregion differs from the global trends in agricultural crops. In the microregion, the application rates of herbicides and insecticides are below the global average, at 43.2 % and 17.9 %, respectively, while globally these figures reach 52 % and 23 %, respectively. On the contrary, in the case of fungicides, the situation is reversed, reaching 38.9 % in the area under study compared to the 25 % global average (ISCAMEN, 2021; FAO, 2023).

Phytosanitary products are often a mixture of substances, not all of them critical to the environment. Critical substances are known as active ingredients and their concentrations are reported by the manufacturer on the product label (Franke *et al.*, 2013). Other substances, called inert ingredients, accompany active ingredients, adding qualities that improve the product efficiency, such as increased shelf life, pest attraction, and more uniform dispersion on surfaces, among other things.

This study analyses 38 active ingredients (24 fungicides, 7 insecticides, and 7 herbicides) corresponding to the set of phytosanitary products marketed in the microregion between September 2018 and April 2020. Both the amount of phytosanitary products and the concentration levels of their active ingredients come from sales records of phytosanitary products sold in each district that makes up the microregion. The data are of high quality due to their traceability and their representativeness both temporally and geographically. The recorded compounds correspond to the red, yellow, and blue toxicity classifications (SENASA, 2012).

Table 2 shows the active ingredients marketed in the microregion along with their respective physicochemical properties, that is, the organic carbon adsorption coefficient (*Koc*) and persistence (half-life) in the environment; and maximum allowed concentrations in the receiving freshwater body, grouped by the target organisms to control. The physicochemical properties are useful in predicting the mobility throughout the environment of pesticides that do not reach the target organisms. Thus, the lower the *Koc* value, the lower the adsorption affinity of a critical substance, and then the higher the leaching-runoff potential. Similarly, the longer the half-life of a substance, the more persistent it will be, and therefore, it will have a higher leaching-runoff potential. The maximum allowable concentrations are discussed in the following section.

3. Legislative framework

The GWF indicates the volume of water required to dilute a pollutant load so that the quality of ambient water remains above agreed water quality standards. Therefore, to evaluate the GWF, it is necessary to know the maximum allowable concentrations of the critical substances in the receiving freshwater body. In Argentina, national legislation does not establish maximum allowable concentrations in freshwater bodies. Only the Argentine Food Code sets maximum limits for pesticides: Aldrin, DDT, and Parathion in the water bodies intended for drinking water extraction (CCA, 1969). However, these substances are prohibited for use and commercialisation within the national territory (SENASA, 2019). This underlines the need to modernise

TABLE 2. Physicochemical properties and maximum allowable concentrations in water for active ingredients in the phytosanitary products marketed in the microregion between September 2018 and April 2020.

Pesticides[a]	Physicochemical properties		Maximum allowable concentrations (µg L^{-1})	Referenced guideline
	Environmental persistence (days)	*Koc* (L kg^{-1})		
Fungicides				
Azoxystrobin	78	589	1.8	Rodrigues *et al.* (2017)
Benomyl	67	1,900	90	Australian Government (2011)
Boscalid	484.4	0	0.1[b]	Federal Office of Consumer Protection and Food Safety (2021)
Captan	0.8	200	1.3	Franke *et al.* (2013)
Carbendazim	40	0	100	IPCS (1993)
Chlorothalonil	3.53	2,632	0.18	Franke *et al.* (2013)
Copper (II) hydroxide	0.1	12,000	2,000	PPDB (2006)
Copper oxychloride	0.1	1,000	2,000	PPDB (2006)
Copper sulfate	0.1	9,500	2,000	PPDB (2006)
Difenoconazole	130	0	0.1[b]	PPDB (2006)
Fenhexamid	0.43	475	2,000[b]	EPA (1999)
Folpet	4.7	304	0.1[b]	PPDB (2006)
Fosetyl-aluminium	0.018	0	0.1[b]	PPDB (2006)
Iprodione	36.2	700	100[b]	Australian Government (2011)
Metalaxyl	36	162	100[b]	New Zealand Ministry of Health (2019)
Myclobutanil	560	0	0.1[b]	PPDB (2006)
Penconazole	117	0	0.1[b]	PPDB (2006)
Procymidone	7	378	700[b]	New Zealand Ministry of Health (2019)
Pydiflumetofen	2,416	0	0.1[b]	European Commission (2008)
Pyraclostrobin	41.9	9,304	0.1[b]	Federal Office of Consumer Protection and Food Safety (2021)
Tebuconazole	63	0	0.1[b]	PPDB (2006)
Thiram	4.89	0	7	Australian Government (2011)
Triadimefon	26	300	90	Australian Government (2011)
Zineb	30	1,000	9[b]	Australian Government (2011)
Herbicides				
Fluroxypyr	13.1	0	0.1	Khan *et al.* (2020)
Fluroxypyr-meptyl	1	19,550	0.1	Khan *et al.* (2020)
Glyphosate	15	1,424	800	Franke *et al.* (2013)
Linuron	57.6	842.8	7	Franke *et al.* (2013)
Paraquat	3,000	1,000,000	20	Australian Government (2011)
Paraquat dichloride	365	100,000	10	Franke *et al.* (2013)
Trifluralin	133.7	15,800	0.03	Franke *et al.* (2013)
Insecticides				
Beta-cyfluthrin	28	104,491	50[b]	Australian Government (2011)
Dimethoate	2.5	0	6.2	Franke *et al.* (2013)
Fenamiphos	0.9	446.2	0.5[b]	Australian Government (2011)
Imidacloprid	191	0	0.23	Franke *et al.* (2013)
Pirimiphos-methyl	39	1,100	90[b]	Australian Government (2011)
Propargite	56	0	7[b]	Australian Government (2011)
Spirotetramat	0.19	289	200[b]	Australian Government (2011)

[a] Phytosanitary products enrolled in the SENASA for application in grapevine crops.

[b] Drinking water regulations.

the existing legal framework for establishing water quality standards in state legislation.

Due to the lack of domestic legislation on water quality standards, this study examined the international regulations on the maximum allowable concentrations in freshwater bodies. For some compounds whose maximum limits in natural systems have not been regulated, international drinking water regulations have been used as a reference. Table 2 also shows consulted sources to establish the maximum allowable concentrations for each specific compound in the area under study. By active ingredient, the strictest concentration of the consulted sources was selected.

4. Grey water footprint methodology

The estimation of the overall GWF of viticulture was carried out in accordance with the methodology proposed by Hoekstra *et al.* (2011). The specific GWF for each active ingredient used in local vineyards has been calculated separately. The chronological activities undertaken to evaluate the specific GWF for each active ingredient are described below.

First, the diffuse pollution load entering the surface or groundwater system (L, kg year^{-1}) was calculated. Assuming that a portion of the critical substances reaches the freshwater bodies, the pollutant load for each active ingredient was estimated as a fraction of the amount of the applied critical substance to grapevine crops (Appl, kg year^{-1}).

$L(kg\,\text{year}^{-1}) = \alpha \times Appl$ [1] where, α, a dimensionless factor, represents the fraction of leaching runoff and is defined as the percentage of a particular component lost by leaching in groundwater or by runoff in surface water (Franke *et al.*, 2013). The value of α for each active ingredient of interest was estimated separately following the recommendations of the water footprint network (WFN) expert panel presented by Franke *et al.* (2013).

In this approach, the value of the leaching-runoff fraction is derived from various factors related to the physicochemical properties of active ingredients, the environment, and agricultural practices. Each factor influences individually, to a greater or lesser extent, the value of α. For example, the lower the *Koc* value, the lower the adsorption affinity of an active ingredient, and therefore the higher the leaching-runoff potential. In this study, the determination of the leaching-runoff fraction for each active ingredient was inferred by applying the weights and scores for each influencing factor suggested by Franke *et al.* (2013).

The factors used to calculate the leaching-runoff fraction were selected and grouped in line with the recommendations of the WFN expert panel. These factors are divided into three categories: (1) physicochemical properties of the pesticide, that is, the organic carbon adsorption coefficient (*Koc*) and persistence (half-life) in the environment, (2) environmental factors, such as soil properties (soil texture and organic matter content) and climate (rain intensity and precipitation), and (3) agricultural practices, such as management and application of the compound in the crop, irrigation methods, etc.

In this research, the values of the factors used to calculate the leaching-runoff fractions were derived from local data and global databases. For the physicochemical properties of the active ingredients, PPDB (2006) was chosen (Table 2). For inferring soil texture, rainfall intensity, and precipitation, local data from INTA (1990), Haylock *et al.* (2006), and Morábito *et al.* (2009) were used, respectively. Finally, given the lack of local data on organic matter content and agricultural practices, the supporting information provided by Franke *et al*. (2013) was used. See the Appendix for an example of an α value calculation.

Subsequently, the amount of the applied critical substance (Appl, kg year^{-1}) was derived from Equation [1], which represents the application of the active ingredient of interest to crops of a given area (kg year^{-1}). The variable Appl is calculated by multiplying the application rate (AR, kg ha^{-1} year^{-1}) by the area under analysis (A, ha): $Appl(kg\,\text{year}^{-1}) = AR \times A$ [2].

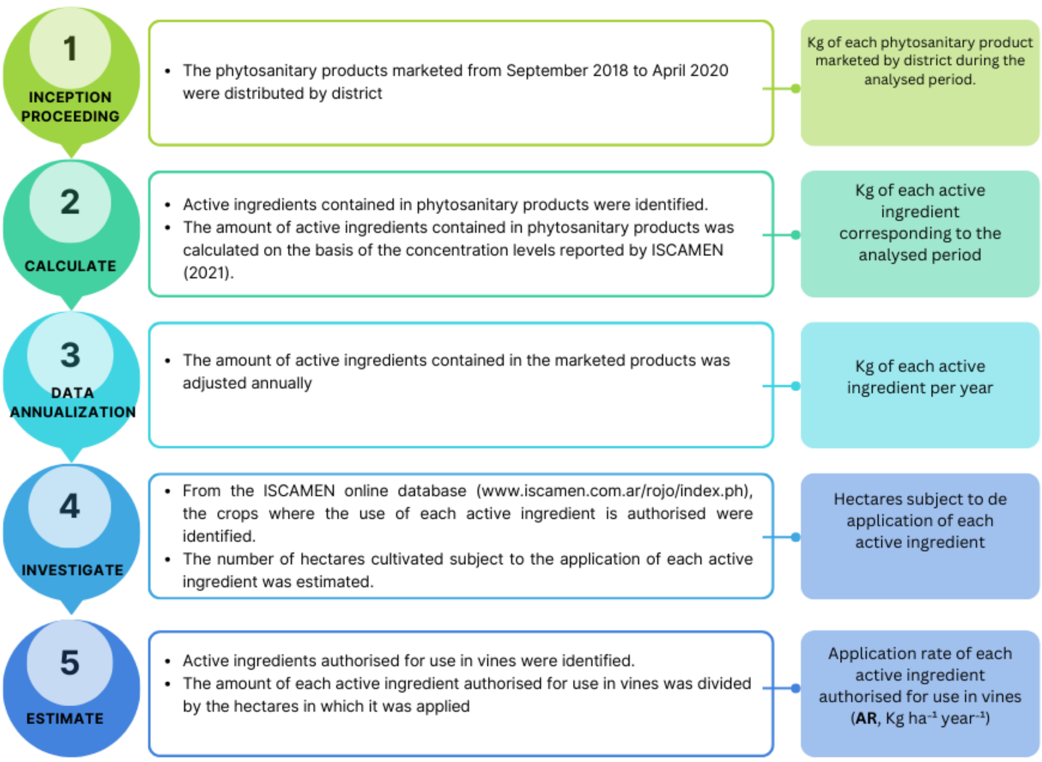

FIGURE 2. Process diagram to calculate the application rate of each active ingredient used in local vineyards (Source: Own elaboration based on data obtained from RENSPA, INV, and ISCAMEN).

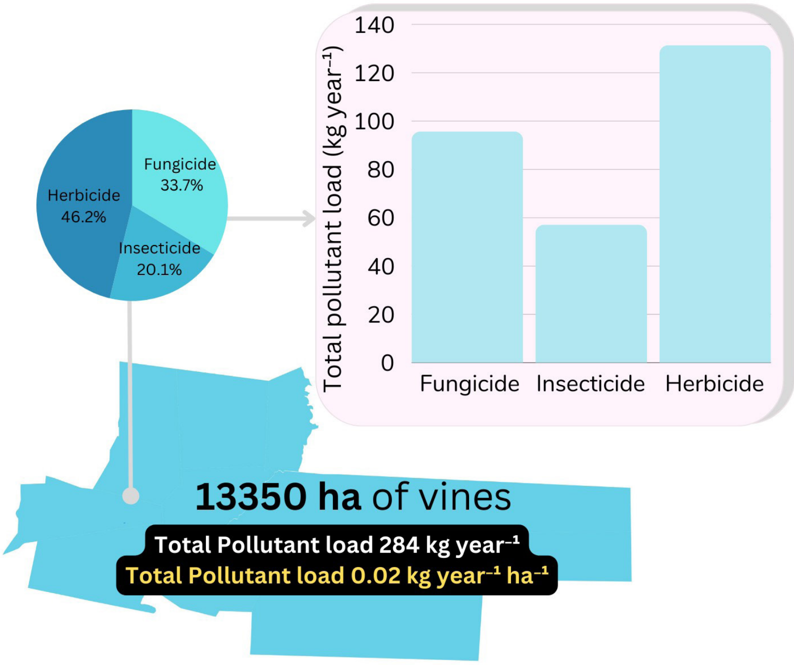

FIGURE 3. Total diffuse pollution load of the microregion (Source: Own elaboration based on data from ISCAMEN, RENSPA, INV, and cartography from SIAT and IGN).

Our analysis is performed at two spatial scales. On the first scale, the study area (A, ha) consists of the entire territory of the viticultural microregion, 13,350 hectares. On the second scale, the analysis area (A, ha) extends separately to each of the 9 districts that make up the microregion.

Figure 2 describes the process for estimating the application rate (AR, kg ha^{-1} $year^{-1}$) of each active ingredient marketed in the microregion between September 2018 and April 2020.

Once the pollutant load (L, kg $year^{-1}$) was estimated using Equation [1], the specific GWF for each active ingredient was calculated. To do this, L was divided by the multiplication of the difference between the maximum allowable concentration (C_{max}, kg m^{-3}) and the natural concentration (C_{nat}, kg m^{-3}) of the active ingredient in the receiving water body by the crop production in the area under study (P, kg $year^{-1}$), formally[1]:

$$GWF(m^3\,\mathrm{kg}^{-1}) = \frac{L}{(C_{max} - C_{nat})P} \quad [3].$$

Natural concentrations (C_{nat}) were zero in the cultivated area because pesticides are not naturally present in the environment. The maximum allowed concentrations (C_{max}) were obtained from the legislative review of the maximum allowable concentrations in different countries (Table 2).

Finally, the overall GWF (m^3 kg^{-1}) of viticulture is equal to the largest GWF found when comparing the specific GWFs of active ingredients commonly used in local vineyards during the analysed period.

RESULTS AND DISCUSSIONS

This section presents the results at two analytical levels. In the first case, the diffuse pollutant load is quantified, while in the second case, the GWF of viticulture is estimated. Both analyses are carried out at two spatial scales: at the microregion level and the district level. The practical implications of the results are discussed in the context of sustainable water resources management.

1. Pollutant load

1.1. Pollutant load at the microregion level

Assuming that the phytosanitary products were fully applied during the analysed period, Table 3 presents the diffuse pollutant load (L, kg $year^{-1}$) of the pesticides listed in Table 2, following Equation [1]. It also shows an approximation of the applied doses (Appl, kg $year^{-1}$; Equation [2]) and the leaching-runoff fractions (α, dimensionless) estimated according to Franke *et al.* (2013).

At the microregion level, the total diffuse pollution load of the 38 active ingredients marketed between September 2018 and April 2020 was estimated at 284 kg $year^{-1}$, or its equivalent of 0.02 kg $year^{-1}$ ha^{-1} (Figure 3). In other words, during the analysed period, it was calculated that approximately 284 kg of applied pesticides to grapevine crops reached surface water by runoff or groundwater by leaching each year.

Figure 3 also shows the contribution of the 38 active ingredients (24 fungicides, 7 insecticides, and 7 herbicides)

1 The GWF of grapevine crops can also be expressed per volume over a period of time (GWF, m^3 $year^{-1}$). To do this, GWF (m^3 kg^{-1}), estimated from Equation [3], is multiplied by the crop production in the area under study (P, kg $year^{-1}$).

TABLE 3. Diffuse pollutant load, applied doses, and leaching-runoff fractions of the active ingredients corresponding to the set of phytosanitary products marketed in the microregion between September 2018 and April 2020.

Pesticides	Application for a given farm unit with grape cultivation (Appl, kg year^{-1})	Leaching–runoff fraction (α)[a]	Pollutant load reaching water bodies (L, kg year^{-1})
Fungicides			
Azoxystrobin	41.69	0.05844	2.44
Benomyl	22.73	0.05185	1.18
Boscalid	22.27	0.07008	1.56
Captan	2.04	0.04171	0.08
Carbendazim	23.55	0.06184	1.46
Chlorothalonil	1.54	0.03511	0.05
Copper (II) hydroxide	410.71	0.03511	14.42
Copper oxychloride	225.37	0.04171	9.40
Copper sulfate	980.00	0.03511	34.41
Difenoconazole	18.02	0.07008	1.26
Fenhexamid	0.36	0.04171	0.01
Folpet	2.63	0.04171	0.11
Fosetyl-aluminium	226.97	0.04510	10.24
Iprodione	1.51	0.05844	0.09
Metalaxyl	13.63	0.06523	0.89
Myclobutanil	9.65	0.07008	0.68
Penconazole	1.77	0.07008	0.12
Procymidone	5.38	0.04171	0.22
Pydiflumetofen	0.39	0.07008	0.03
Pyraclostrobin	49.13	0.05185	2.55
Tebuconazole	80.83	0.06184	5.00
Thiram	0.62	0.04510	0.03
Triadimefon	0.19	0.04995	0.01
Zineb	270.90	0.04995	13.53
Total	2,411.88		95.68
Herbicides			
Fluroxypyr	10.42	0.05335	0.56
Fluroxypyr-meptyl	539.13	0.03511	18.93
Glyphosate	657.10	0.04336	28.49
Linuron	935.98	0.05844	54.70
Paraquat	243.35	0.06525	15.88
Paraquat dichloride	287.17	0.06009	17.26
Trifluralin	2.72	0.06009	0.16
Total	2,675.87		131.4
Insecticides			
Beta-cyfluthrin	6.53	0.04336	0.28
Dimethoate	463.24	0.04510	20.89
Fenamiphos	8.61	0.04171	0.36
Imidacloprid	231.43	0.07008	16.22
Pirimiphos-methyl	1.78	0.05185	0.09
Propargite	229.09	0.06184	14.17
Spirotetramat	167.79	0.04171	7.00
Total	1,108.47		57.13

[a] Since both local data and supplementary information lacked sufficient detail on environmental conditions and agricultural practices at the district level, uniform parameters were applied in calculating the leaching-runoff fraction. Consequently, the value of α reflects only the heterogeneity due to the physicochemical properties of the active ingredients.

to the total pollution load according to the target organisms. In the microregion, 46.2 % of the pollutant load entering the water bodies was estimated to come from herbicides, 33.7 % from fungicides, and 20.1 % from insecticides. In other words, the diffuse load reaching the water bodies from herbicides was higher than the contribution of fungicides and insecticides, at a magnitude of 1.4 and 2.3 times, respectively (Table 3).

Although in the microregion, the distribution of the application rates of herbicides (43.2 %), fungicides (38.9 %), and insecticides (17.9 %) in grapevine crops showed the same behaviour pattern as the contribution to the total pollutant load of the pesticides according to the target organisms (Figure 3), it should be noted that the pollutant load does not depend linearly on the application rate of pesticides. If we consider, for example, two active ingredients with similar application rates, such as the fungicide copper sulfate (0.073 kg ha^{-1} year^{-1}) and the herbicide Linuron (0.070 kg ha^{-1} year^{-1}), it is observed that the pollutant loads of both compounds are different, with the Linuron pollutant load being 1.6 times higher than the copper sulfate pollutant load (Table 3).

Therefore, since the environmental conditions throughout the microregion are the same, the diffuse pollution load entering the surface or groundwater system depends both on the application rate and on the physicochemical properties of the pesticides. This result emphasises that the efficiency of chemical product management should be evaluated not only based on its ability to ensure quality production but also based on its ability to minimise the diffuse load entering water bodies. This may be useful to different stakeholders in this space promoting sustainable water resources management practices while improving viticultural environmental performance.

1.2. Pollutant load at the district level

At the district level, the total pollutant load is observed to be not uniform across the microregion territory (Figure 4). Of the 284 kg year^{-1} of applied pesticides to grapevine crops entering the water bodies of the microregion, 171.6 kg year^{-1} came from the Costa de Araujo vineyards. Although this district indeed has the largest cultivated area with vines–31 % of the vineyards–in the microregion, it should be noted that the pollutant load exceeded by 1–3 orders of magnitude the pollutant load individually contributed by the rest of the districts, accounting for 58.2 % of the total pollutant load reaching the water bodies of the microregion (Figure 4 and Table 3).

Analysing the pollutant load per hectare of vines, it is observed that the individual contribution of most districts was lower than the pollutant load–0.02 kg year^{-1} ha^{-1}–estimated at the microregion level. Of the 9 districts that make up the microregion, only 3–El Divisadero (0.05 kg year^{-1} ha^{-1}), La Holanda (0.05 kg year^{-1} ha^{-1}), and Costa de Araujo (0.04 kg year^{-1} ha^{-1})–had pollutant loads higher than the microregion level (Figure 3 and Figure 4).

With respect to the contribution of pesticides to the pollutant load according to the target organisms, only 4 of the 9 districts of the microregion–Paramillos, El Plumero, Costa de Araujo, and Ing. G. André–showed the same behaviour pattern as that presented at the microregion level (Figure 3 and Figure 4).

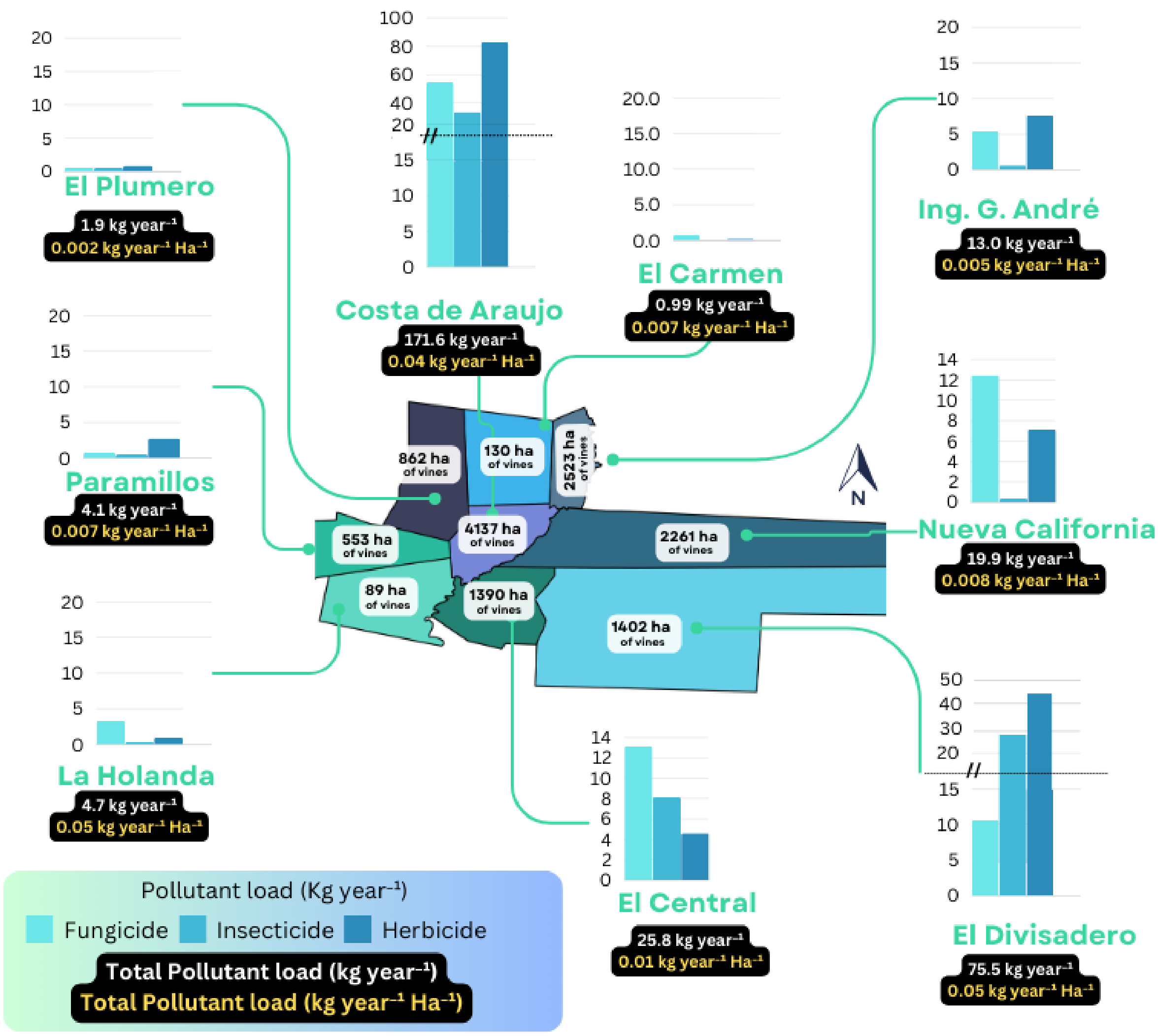

FIGURE 4. Total diffuse pollution load by district (Source: Own elaboration based on data from ISCAMEN, RENSPA, INV, and cartography from SIAT and IGN).

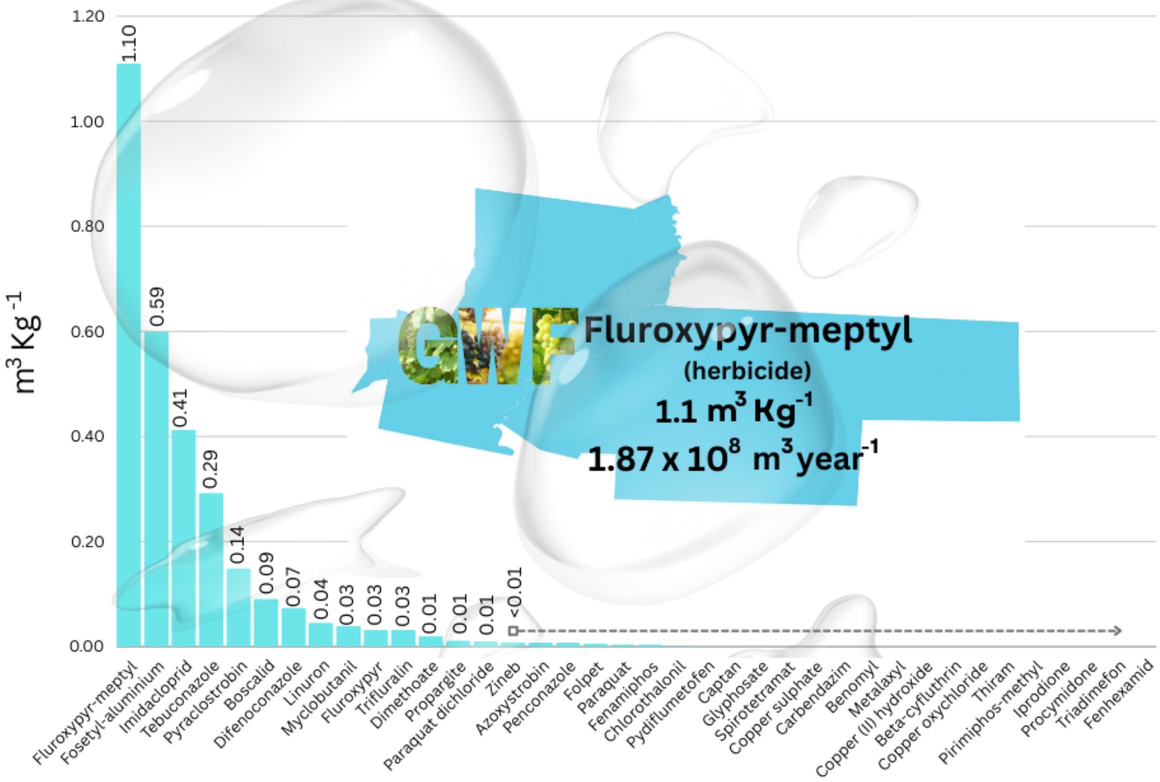

FIGURE 5. Grey water footprint of viticulture in the microregion (Source: Own elaboration based on data from ISCAMEN, RENSPA, INV, and cartography from SIAT and IGN).

Despite being under the same environmental conditions, the different districts that make up the microregion have implemented a variety of chemical management strategies, some with higher diffuse loads than others. Consequently, increased spatial resolution of the analysis provides detailed information that can help identify critical chemical management at the local level in terms of the risks they pose to sustainable water resources management.

2. Grey water footprint

2.1. Grey water footprint at the microregion level

The effect of pesticides on the water resources of the microregion during the analysed period is quantified using Equation [3]. Figure 5 shows the specific GWFs associated with the set of active ingredients that are commonly used in local vineyards (listed in Table 2 and Table 3). The GWF of the herbicide Fluroxypyr-meptyl (1.10 m^3 kg^{-1}) was the highest, followed by the GWF of the fungicide Fosetyl-aluminium (0.59 m^3 kg^{-1}) and the GWF of the insecticide Imidacloprid (0.41 m^3 kg^{-1}). Based on these considerations and in accordance with Hoekstra *et al.* (2011), the GWF of viticulture was estimated at 1.10 m^3 kg^{-1} or 1.87×10^8 m^3 $year^{-1}$. In fact, 1.10 m^3 of water per kg of grapes, or just over 187 million m^3 of water per year, would be required to dilute the herbicide Fluroxypyr-meptyl to a point where ambient water quality remained above established water quality standards.

Despite that the GWF varies depending on the place, applied pesticides, agricultural practices, and analysis scales, among other factors, it is interesting to present some of the findings reported in the literature on the viticultural water footprint. In the same study area, Morábito (2012) estimated the blue, green, and nitrogen-related grey water footprints of two grape varieties at 1.13 m^3 kg^{-1}, 0.11 m^3 kg^{-1}, and 0.1 m^3 kg^{-1}, respectively. Thus, GWF represents 7.2 % of the total water footprint (TWF). Following this line, in the Cachapoal River basin (Chile), Novoa *et al.* (2019) estimated the nitrogen-related GWF of grapevine cultivation at 0.12 m3 kg-1, with a contribution of GWF of approximately 30 %. On a global scale, Mekonnen and Hoekstra (2010) evaluated the nitrogen-related GWF of grapevine crops at 0.09 m^3 kg^{-1}, representing approximately 14.3 % of the TWF. Other studies have estimated the GWF of the wine-making process (Ene *et al.*, 2013; Lamastra *et al.*, 2014; Rinaldi *et al.*, 2016). Most studies on viticultural GWF have estimated the volume of water required to dilute a pollutant load associated with fertilisers, particularly nitrogen, ignoring the possible contamination by pesticides. This could lead to an underestimation of the GWF and therefore increase its contribution to the TWF of viticulture.

Although several studies have evaluated the GWF associated with pesticides for a variety of agricultural products such as sugarcane (Paraiba *et al.*, 2014; De Lavôr Paes Barreto *et al.*, 2020), legumes, cereals, forages (Karandish, 2019), and tea (Ariyani *et al.*, 2022), to the authors knowledge, no GWF involving the wide range of active ingredients examined in this study has been reported. In this regard, Paraiba *et al.* (2014), motivated by the possibility of the contamination of pesticide mixture, proposed an alternative model to Hoekstra *et al.* (2011). The

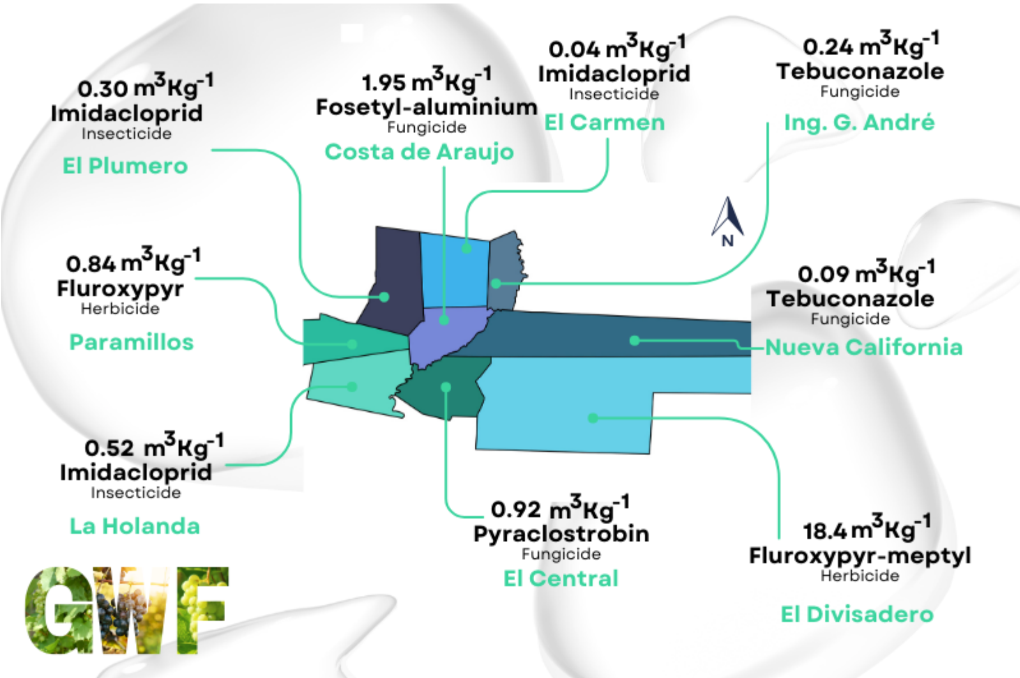

FIGURE 6. Grey water footprint of viticulture by district (Source: Own elaboration based on data from ISCAMEN, RENSPA, INV, and cartography from SIAT and IGN).

alternative model considers in its calculations the volume of water needed to dilute the concentrations of pesticide mixture in freshwater, surface waters, or groundwater, to a level that leads to the protection of aquatic organisms. A few years later, De Lavôr Paes Barreto *et al.* (2020) showed that both models are equally robust in estimating the GWF.

2.2. Grey water footprint at the district level

Finally, the impacts of pesticides on water resources are evaluated in each microregion district during the analysed period. Figure 6 shows viticultural GWF at the district level, indicating the volume of water per kg of grapes required to dilute the compound from which they are derived. When increasing the spatial resolution of the analysis, the variability of the local GWFs was observed not only due to the diversity of the associated active ingredients (Fluroxypyr-meptyl, Fluroxypyr, Fosetyl-aluminium, Pyraclostrobin, Tebuconazole, and Imidacloprid) but also due to the amplitude of the range of estimated values (0.04 to 18.4 $m^3 kg^{-1}$). This local variability can also be higher when considering other factors that influence GWF, such as agricultural practices that can increase production, Equation [3]. For example, districts with a higher proportion of vineyards managed by pergola will have a lower viticultural GWF, further increasing the variability of the local GWFs.

It is important to note that the herbicide Fluroxypyr-meptyl, which was associated with viticultural GWF at the microregion level, was only associated with viticultural GWF in the district of El Divisadero. Furthermore, although the viticultural GWF in El Plumero, El Carmen, and La Holanda districts were associated with the same active ingredient–the insecticide Imidacloprid–differences in the values of their footprints are observed. The GWF associated with Imidacloprid was almost 2 times higher in La Holanda than in El Plumero and just over 10 times higher than in El Carmen. Therefore, since the same environmental factors and agricultural practices have been taken into account for the evaluation of the GWF of viticulture in the microregion, this result indicates that the application rate was not the same, at least in these three units of analysis, indicating different management with respect to the same critical substance. This finding is also evident when looking at the GWF associated with the fungicide Tebuconazole, which was 2.6 times higher in Ing. Gustavo André than in Nueva California.

Consequently, presenting viticultural GWF by district, rather than an aggregated value at the microregion level, may be useful to different stakeholders in the effective development of phytosanitary protocols that prioritise actions aimed at reducing the impact of local production on water quality, improving the competitiveness of local viticulture on the global wine market.

Finally, although pesticides have an impact on water bodies, this impact does not necessarily imply contamination of water resources. According to Heralth *et al.* (2013), this will depend, among other factors, on the dynamics and local hydrological conditions of the receiving water bodies. For instance, in some districts, recharge rates could supply a sufficient volume of water to dilute the pollutant load and prevent contamination of their water resources. However, other districts with the same pollution load may not be able to avoid contamination of water resources because their recharge rates do not provide sufficient dilution of diffuse loads. These considerations highlight the importance of a local design for sustainable water resources management.

CONCLUSIONS

A distinctive feature of our study is that it not only provides results from the GWF analysis of viticulture associated with a wide range of pesticides but also provides results at two spatial scales. The increased spatial resolution of analysis provides detailed information that can help identify critical chemical management at the local level in terms of the risks they pose to sustainable water resources management. This may be particularly useful to different stakeholders. For example, if faced with a higher incidence of pests and diseases in different areas, land managers may want to design specific chemical management strategies that ensure local quality production while minimising the diffuse load entering the water bodies. Likewise, policymakers may be interested in evaluating the efficiency of a phytosanitary protocol considering the different local hydrological dynamics and conditions to reduce environmental risks.

Our study found that at the microregion level, during the analysed period, 284 kg year^{-1} of applied pesticides to grapevine crops (24 fungicides, 7 insecticides, and 7 herbicides) reached surface or groundwater systems, according to theoretical calculations following Equation [1]. It was estimated that 46.2 % of the pollutant load that entered the water bodies came from herbicides, 33.7 % from fungicides, and 20.1 % from insecticides. At the district level, it was observed that the total pollutant load was not uniform throughout the territory of the microregion. For example, when analysing the pollutant load per hectare of vines, it was observed that the individual contribution of most districts was below the pollutant load per hectare of vines–0.02 kg year^{-1} ha^{-1}–estimated at the microregion level.

On the other hand, when comparing the specific GWFs of these compounds at the microregion level, the GWF of the herbicide Fluroxypyr-meptyl (1.10 m³ kg^{-1}) was the highest, followed by the GWF of the fungicide Fosetyl-aluminium (0.59 m³ kg^{-1}) and the GWF of the insecticide Imidacloprid (0.41 m³ kg^{-1}). Based on these considerations and in accordance with Hoekstra *et al.* (2011), the GWF of viticulture was estimated at 1.10 m³ kg^{-1} or 1.87×10^8 m³ year^{-1}. In fact, 1.10 m³ of water per kg of grapes or just over 187 million m³ of water per year would be needed to dilute the herbicide Fluroxypyr-meptyl to such an extent that the quality of the ambient water remains above agreed water quality standards. However, when increasing the spatial resolution of the analysis, the variability of the local GWFs was observed not only due to the diversity of the active ingredients (Fluroxypyr-meptyl, Fluroxypyr, Fosetyl-aluminium, Pyraclostrobin, Tebuconazole, and Imidacloprid) from which they are derived but also due to the amplitude of the range of estimated values (0.04 to 18.4 m³ kg^{-1}). These findings emphasise the importance of considering the appropriation of water resources through pesticide pollution on a local scale.

Our GWF evaluations are contingent on the standards used with respect to the maximum allowable concentrations. Due to the absence of local standards, international regulations were used in line with the recommendations of Franke *et al.* (2013). However, the application of standards established by other countries can underestimate or overestimate GWF value by not considering dynamics and local hydrological conditions. Consequently, the inclusion of local water quality standards can strengthen the contribution of the GWF to empirical applications aimed at reducing the impact of local production on water resource quality, and improving environmental sustainability.

Following the recommendations of Hoekstra *et al.* (2011) and other experts (Franke *et al.*, 2013; Paraiba *et al.*, 2014; De Lavôr Paes Barreto *et al.*, 2020), the GWF analysis has been carefully applied to ensure a state-of-the-art application. For example, in estimating the assimilation capacity of a receiving water body, natural concentrations were used as reference values rather than actual concentrations of a critical substance. Therefore, the appropriate assimilation capacity was evaluated against the remaining assimilation capacity. Furthermore, the leaching-runoff fractions were estimated from available local information on agricultural practices and data on soil and climate characteristics. This allowed for more specific estimates of the leaching-runoff fractions from the study site. However, our estimates were based on aggregated statistical data. This forced the use of some restrictive assumptions, for example, that the phytosanitary products marketed and authorised for use in grapevine crops were fully applied during the analysed period. Therefore, our results should be considered as approximations to the orders of magnitude of the GWFs in the context of the assumptions adopted.

In summary, our results highlight the importance of conducting GWF analyses in the context of a wide range of pesticides at multiple spatial scales. Limiting the analysis to a few pesticides and a single spatial scale produces limited knowledge that can affect the efficiency of sustainable water resources management. Analyses such as those carried out in this study can improve the GWF as a tool for managing sustainable water resources by providing more global information on the appropriation of water resources through pollution. For example, our results show that if we want to move towards a sustainable use of water in viticulture, we need to limit or replace the use of higher-GWF pesticides such as Fluroxypyr-meptyl, Fosetyl-aluminium, and Imidacloprid. In response to predictions of an increased incidence of pests and diseases due to global warming, it is essential to develop chemical management strategies that are more respectful of the environment and its natural resources. Otherwise, the GWFs of pesticides will probably increase, which will affect the availability and future quality of water resources, ultimately affecting human well-being.

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APPENDIX

Example of how to calculate the leaching-runoff fraction

In this example, the leaching-runoff fraction (α) of the herbicide Fluroxypyr-meptyl is calculated following the guidelines of

Franke *et al.* (2013). They suggest that if local data on the factors influencing the leaching-runoff fraction are available, the value of α can be inferred using the following equation (Franke *et al.*, 2013, p. 17): $\alpha = \alpha_{min} + \left(\frac{\sum_i s_i \times w_i}{\sum_i w_i}\right) \times (\alpha_{max} - \alpha_{min})$.

The value of α, in the case of pesticides, will be somewhere between the minimum leaching-runoff fraction (α_{min} = 0.0001) and the maximum leaching-runoff fraction (α_{max} = 0.1). The minimum and maximum leaching-runoff fractions are inferred by the WFN expert panel. For factor i, the score of the leaching-runoff potential (s) is multiplied by the weight of factor (w).

Table 4 shows the score and weight of each influencing factor. A weight w for factor i denotes the importance of the factor. The status of factor i determines the leaching-runoff potential, expressed as a score (s) between 0 and 1. A score of 0 means very low leaching-runoff potential, a score of 0.33 means low, a score of 0.67 means high, and a score of 1 means very high leaching-runoff potential.

Based on Table 4, the following scores were found for the leaching-runoff potential per factor:

- The average *Koc* value of Fluroxypyr-meptyl is 19,550 L kg^{-1} (Table 2). Therefore, the score for the leaching-runoff potential is 0.
- The persistence is 1 day (Table 2), which implies a score for the leaching-runoff potential of 0.
- The soil type in the area under study is classified as typical torrifluvents with a loamy texture (INTA, 1990). Therefore, the score for leaching-runoff potential is 1 for leaching and 0.33 for runoff. The probability therefore that Fluroxypyr-meptyl can reach groundwater is higher than that in surface water.
- The organic matter content is between 21 and 40 tonnes ha^{-1} (Franke *et al.*, 2013, map 8); therefore, the score for the leaching-runoff potential is 0.67.
- For the rainfall intensity is strong, resulting in a score for the leaching-runoff potential of 0.67 (Haylock *et al.*, 2006; Morábito *et al.*, 2009).
- Net-precipitation is equal to 220 mm per year (Haylock *et al.*, 2006; Morábito *et al.*, 2009), equivalent to a score for the leaching-runoff potential of 0.
- For agricultural management practice, there is no information available. Franke *et al.* (2013) suggest classifying according to the development stage of the region. In our case, Argentina is a developing country, so we assume that wine growers in the area under study have average training in management practices. Therefore, the score for the leaching-runoff potential is 0.67.

To obtain the value of α, the scores and weights for all influencing factors can be inserted into the previous equation as follows:

$$\alpha = 0.0001 + \left[\frac{(0\times 20)+(0\times 15)+(0\times 10)+(1\times 15)+(0.33\times 10)+(0.67\times 10)+(0.67\times 5)+(0\times 5)+(0.67\times 10)}{20+15+10+15+10+10+5+5+10}\right] \times (0.1 - 0.0001)$$

$$\alpha = 0.0001 + \left[\frac{35.05}{100}\right] \times (0.0999)$$

$$\alpha = 0.03511$$

TABLE 4. Factors influencing the leaching-runoff potential of pesticides.

Category		Factor	Pesticides				
			Leaching-runoff potential	Very low	Low	High	Very high
			Score (*s*)	0	0.33	0.67	1
			Weight (*w*)				
Chemical properties		*Koc* (L kg^{-1})	20	> 1000	1000-200	200-50	< 50
		Environmental persistence (days) (relevant for leaching)	15	< 10	10-30	30-100	> 100
		Environmental persistence (days) (relevant for runoff)	10	< 10	10-30	30-100	> 100
Environmental factors	Soil	Texture (relevant to leaching)	15	Clay	Silt	Loam	Sand
		Texture (relevant to runoff)	10	Sand	Loam	Silt	Clay
		Organic matter content (kg m^{-2})	10	> 80	41-80	21-40	< 20
	Climate	Rain intensity (relevant for runoff)	5	Light	Moderate	Strong	Heavy
		Precipitation (mm) (relevant for leaching)	5	0-600	600-1200	1200-1800	> 1800
Agricultural practice		Management practice (relevant for runoff)	10	Best	Good	Average	Worst

Source: Franke *et al.* (2013).

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