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# Evaluating point source pesticide contamination via sprayer washing water dispersal: A northern Italian vineyard area case study

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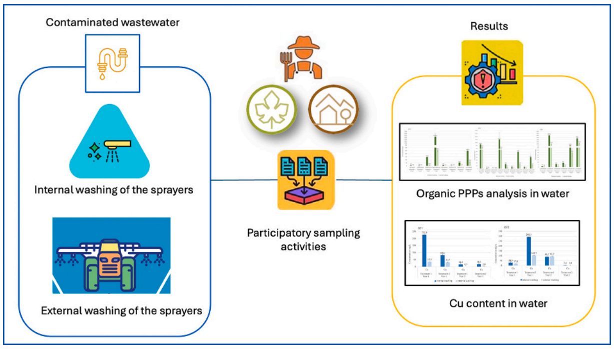
## HIGHLIGHTS

- Internal washing water had PPPs concentrations up to 38 times higher than external
- Sprayers features and poor BMP adoption by farmers influenced the results.
- Estimated PPPs concentrations in FOCUS "stream" surface water were above $EQS_{SW}$
- The toxicological endpoints for a single PPP were never exceeded.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Wastewater contaminated by plant protection products (PPP) from sprayer cleaning operations must be properly managed and disposed of, as it could represent a point source of environmental PPP pollution and pose risks to non-target organisms. Three conventionally and two organically managed farms in hilly vineyards of North-West Italy engaged in a participatory activity for sampling sprayer washing and resultant water. In total 52 samples of wash water (internal and external) were collected during two agricultural seasons and analyzed for six organic pesticides and metallic Cu. PPP concentrations in water collected after internal washing were up to 37.9 times higher than in water collected after external washing. Concentrations in water after external washing were surprisingly high. This may be explained by the characteristics of the sprayers, but also by farmers failing to

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*Abbreviations:* BMPs, best management practices; PPPs, Plant Protection Products; MMs, mitigation measures; RDP, Rural Development Program; LOD, limit of detection; LOQ, limit of quantification; CF, Conventional Farm; OF, Organic Farm; FOCUS, Forum for the Coordination of pesticide fate models and their Use; EQS, environmental quality standard; NOEC, no observed effect concentration.

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comply with good practices during PPP use. To evaluate the possible impact on the aquatic environment of dispersal of wash water into a water body, the FOCUS "Stream" approach was followed. The concentrations thus estimated were almost always higher than the environmental quality standard for surface waters but below the toxicological endpoints for fish and *Daphnia magna*. With reference to the Italian guidelines for waste classification, only one sample would be classified as ecotoxicological hazardous waste and need to be properly managed. In conclusion, due to the nature of contamination, which is point source but diffuse in the territory, analytical data confirms the need for additional joint efforts to improve awareness in managing wastewater containing PPP and to decrease the impact of the agricultural sector.

## 1. Introduction

Point source pesticide contamination can result from spillages, leakages, and pesticide-contaminated water discharge from in-farm and post-farm activities (Mosthaf et al., 2024; Beltran-Flores et al., 2023; Bagheri et al., 2023; Suciu et al., 2020). Such contamination may cause adverse effects on non-target soil organisms and natural water resources (Smalling et al., 2021; Wang et al., 2024; Pamanji et al., 2024).

Pesticide contamination is difficult to manage due to the environment and socio-economic context and its influence on farmer behavior and compliance to best management practices (BMPs) (De Wilde et al., 2007; Liu et al., 2018; Suciu et al., 2020).

Directive 2009/128/CE on sustainable use of pesticides provides specific measures to be implemented by the Member States addressing activities like handling, storage, diluting and mixing of pesticides, cleaning of application equipment after use, recovery and disposal of tank mixtures, empty packaging, and remnants. External washing focuses on the outside of the sprayer while internal washing cleans internal components. Both external and internal cleaning are important to minimize pesticide residues, prevent cross-contamination, and maintain the efficiency of the sprayer (Balsari and Marucco, 2017). Post-treatment internal washing must be conducted when changing crops and/or if the plant protection products (PPP) used for the previous crop are not registered for the next crop to be treated. Internal washing is also advised when PPP may be phytotoxic or if the residual mixture in the sprayer poses a risk of clogging filters and nozzles or of other mechanical malfunctions. Mixture residues can accumulate on the external surfaces of the sprayer and tractors due to splash and drip deposits during treatment. Periodic washing the external surfaces of equipment used for PPP treatment helps prevent residue built up. Cleaning operations generate PPP contaminated water that must be managed and disposed of following appropriate good practices and mitigation measures (MM) (EC, 2009). Even so, just a few studies reported data about PPPs' presence in washing water of equipment. De Wilde et al. (2007) reported PPP concentrations in the washing water of equipment ranging from 0.2 to 61 mg $L^{-1}$ for four herbicides. No specific information about the type of washing (external vs internal) was provided. Balsari and Marucco, 2017) by applying a test solution of water and yellow dye E102 Tartrazine showed that up to 0.94 % of applied PPPs deposits on the machine. Very recently, Beltran -Flores et al. Bagheri et al. (2023) reported values between 4.5 and 19.2 mg $L^{-1}$ for four PPPs, with the highest value for thiacloprid, a neonicotinoid insecticide. These cleaning activities contribute to the contamination of surface and ground water (Bagheri et al., Bagheri et al., 2023 and E. Nilsson 2021). European projects WATERPROTECT and INNOSETA were funded to improve pesticide management at the farm level and reduce human and environmental risks. Policy measures (as those included in the Directive 128/2009 CE on sustainable use of pesticides) to support Integrated Pest Management (IPM) include training professional users and advisors and providing incentives for the transition to organic farming and precision farming. Nevertheless, the Report of European Commission on CAP Strategic Plan Bagheri et al., 2023–2027, published in November 2023, still highlights the need of additional joint efforts to improve the water quality and decrease the impact of the agricultural sector (EC, 2023). Indeed, pesticides are still present in ground and surface waters (Zambito Marsala et al., 2020; Herrero-Hernández et al., 2020; Suciu et al., 2023; Bagheri et al., 2023). The European Environment Agency (EEA) detected one or more pesticides above their EU environmental quality standards as set by The Water Framework Directive (WFD) in 10 % to 25 % of surface water monitoring sites between 2013 and 2021 (EEA, 2024).

Tackling farming wastewater-related problems requires a coordinated cooperative effort among farmers and other stakeholders, such as policy makers and researchers, to preserve and improve local natural water resources (Chen et al., 2022; Calliera et al., 2021). Indeed, experience and local farmers' awareness of the environmental risk associated with pesticide use play a significant role in successful and effective implementation of measures. In this framework several experiences at European levels show that participatory monitoring through the collection and sharing of data is an established and accepted way to make informed and trustful decisions that can led to behaviors change and to the adoption of BMPs (Belmans et al., 2021; Campling et al., 2021; Calliera et al., 2023; Bagheri et al., 2023).

Participatory monitoring and evaluation involve self-evaluation, collective knowledge generation and cooperative actions by stakeholders in a program or an intervention. Stakeholders collect and analyze data and act based on what they learn through this process (Onyango, 2018). In Italy, local environmental agencies monitor PPP in water to help assess the chemical status of water bodies with respect to the Water Framework Directive (EC, 2000) and the Italian legislation (D. lgs. 172/2015) (DL, 2015). D.lgs. 172/2015 sets the limit of 0.1 μg/L for all the pesticides (including metabolites) for EQS in surface water and, for the sum of pesticides, the limit of 1 μg/L, if not explicitly regulated by Directive 2008/105/EC (EC, 2008). The monitoring program does not assess the effectiveness of any measures introduced to prevent or limit the input of pollutants. Involving farmers in the design and set up of water monitoring is crucial to increased credibility of monitoring data and helps reduce the information gap between farmers and monitoring agencies (Belmans et al., 2018). In addition to a qualitative-quantitative environmental survey method, participatory monitoring represents an important method of communication and an essential tool to generate trust and increase the awareness among operators (Calliera et al., 2021; Campling et al., 2021).

In this context, the main objective of the present study is to improve the understanding of the impact of *point sources* on PPPs environmental occurrences and to increase local farmers' awareness for a better adoption of behavioral and technical preventive solutions. In particular, the study aims (i) developing a participatory monitoring campaign of the wastewater resulting from PPPs application equipment cleaning operations in hilly vineyards of Piedmont Region, (ii) investigating the farmers behavior during cleaning operations and their awareness regarding the environmental impact of *in farm point source contamination*, and (iii) using the analytical data to evaluate the exposure of aquatic organisms to PPPs in case of improper disposal of the wastewater resulted from the washing operations. The present study is part of a Rural Development Program (RDP) project of Piedmont Region, northern Italy, called VITA - Viticoltura Armoniosa and developed in an area characterized by intensive viticulture production.

## 2. Materials and methods

### 2.1. Study area description

The study area is Colli Tortonesi, located in north-west of Italy, in Piemonte Region in the province of Alessandria (Fig. 1 A) a hilly area with an elevation level between 120 and 450 m above sea level, characterized by deeply rooted tradition and vocation viticulture, where vines production seems to date back to over 2000 years ago. It includes seven valleys and 46 municipalities. The grapes grown are Cortese and Barbera, some Dolcetto and the recently reintroduced Timorasso. Vineyards cover around 1200 ha of the area. Production is mainly for the local and national Italian market with 30–35 % destined for export.

Soils are predominantly calcareous and clayey. From a hydrographic point of view, the project study area is in the sub-basin of the Po - Scrivia - Curone. The main tributary of the Scrivia stream is the Borbera stream. Other tributaries are the Ossona and the Grue. Important although not a tributary of the Scrivia, the Curone which crosses and delimits the eastern borders of the study area (Fig. 1 B). The chemical status of the water over 2014–2019 was good for most streams in the study area. The VITA project partner involved in this study is Consortium "Tutela Vini Colli Tortonesi", currently represented by sixty-five members. One of the members is Cantina Sociale di Tortona which in turn associates >250 producers. Therefore, The Consortium "Tutela Vini Colli Tortonesi" today represents 98 % of the total grape production of the area.

### 2.2. Participatory monitoring: farmer involvement and wastewater samples collection

In the present study, five farms (3 conventionally and two organically managed) engaged in participatory sampling activities aimed at measuring the content of PPPs in the wastewater resulted from the internal and external washing of the sprayers. The involvement of organic farms allowed Cu in washing wastewater, an inorganic chemical classified as a candidate for substitution due to intrinsic characteristics of danger, including persistence (EU, 2018) to be studied.

Twenty-six internal and twenty-six external washings of two types of sprayers were conducted: low-volume sprayer and fan sprayer. To ensure safe washing and facilitate the collection of both internal and external washing water, an impermeable pad with lateral barriers was used (Suciu et al., 2020). A volume of 20 to 40 L and 30 to 50 L of tap water was used for internal and external washing, respectively. After internal washing, the washing water was collected in containers of 50 L. The collected washing water was manually homogenized and three samples of 1 L each were collected. Later, the external washing was made, and the washing water was collected in the impermeable pad. As for internal washing, washing water was manually homogenized and three samples of 1 L each were collected. Right after sampling, the washing water samples were kept at 4 °C before reaching the laboratory facilities. The container and the impermeable pad were suitable cleaned after and before each washing. A total of twenty-six controlled washings were conducted throughout the spraying seasons of 2022 and Bagheri et al., 2023.

The PPPs investigated in the study were selected based on their real use in the field. Metallic Cu was reported by local farmers as the most used active ingredient to combat *Plasmopara viticola* in organic viticulture, whereas the use of other products is limited.

For each PPP application reported in the study, an information form was produced providing information about the treated surface with PPPs, sprayer type, spraying speed, air flow rate, volume of distribution, commercial formulates used for the treatment and quantity of water used for internal and external washing. Furthermore, for a proper identification of the contamination drivers an additional survey with the following questions was conducted:

1. How often do you wash the sprayer externally?
2. How often do you wash the sprayer internally?
3. Where is the sprayer washed?
4. Where is the washing water disposed/dispersed?
5. Are there any sensitive areas nearby?
6. Are there wells in the surrounding areas?

### 2.3. Reagents and standards

Methanol and acetonitrile HPLC grade were purchased from Carlo Erba reagents S.R.L (Milan, Italy). Formic acid was purchased from Sigma-Aldrich S.R.L. (Milan, Italy). SPE Bond Elut PPL cartridges were purchased from Agilent Technology (Milan, Italy). Plant protection products (PPPs) standards were supplied by VWR International S.R.L. (Milan, Italy). Individual stock solutions (100 mg $L^{-1}$) of each analyte were prepared in methanol and then mixed standard solutions (0.01–10 mg $L^{-1}$) of all analytes were prepared in methanol.

### 2.4. Plant Protection Product analysis

12 and 14 controlled washings were conducted following phytosanitary treatments in the period May–August 2022 and May–August Bagheri et al., 2023, respectively. Thirty-six washing water samples were collected in three conventional farms and analyzed for the content of six organic PPPs, whereas sixteen samples were collected in two organic farms and analyzed for metallic Cu content.

#### 2.4.1. Cu content in water

For Cu analysis, within 12 h after sampling, the washing water was centrifuged for 1 h at 21 °C and 4500 rotations, filtered through a 0.45-μm glass membrane and acidified by adding 1 % of nitric acid. Until analysis, within 72 h, the samples were stored at 4 °C. Cu analyses were conducted by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, 7800 Agilent).

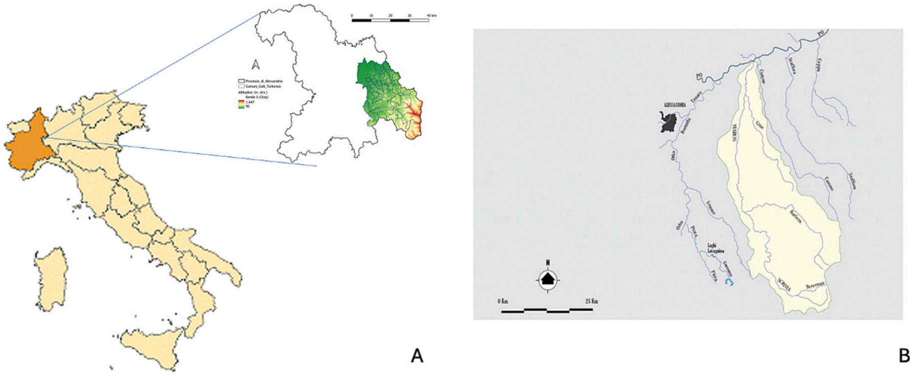

**Fig. 1.** Study area (A) and Sub-basin of the Po - Scrivia – Curone (B).

### 2.4.2. *Organic PPPs analysis in water*

The washing water samples collected at the farms, within 4 h after sampling, were frozen at −18 °C and thawed at ambient temperature only before the extraction process. Firstly, the samples were filtered with glass fiber filters (Pore dimensions 1,6 μm) three times. The six PPPs were extracted using the SPE (solid phase extraction) method, transferred into *vials* and analyzed by liquid chromatography coupled with triple quadrupole tandem mass spectrometry (LC-MS/MS).

*2.4.2.1. SPE – Solid phase extraction.* The protocol developed by Zambito Marsala et al. (2020) and slightly modified was used for SPE activities. First, Bond Elut PPL (styrene-divinylbenzene) cartridges were conditioned with 2.5 mL of methanol and 2.5 mL of ultrapure Milli-Q water at a flow rate of 2.5 mL/min, without allowing the cartridges to dry out. Subsequently, 10 mL of previously filtered sample was transferred to the conditioned cartridges and percolated under vacuum through the solid phase at a flow of about 8 mL/min. The cartridges were then washed with 1.5 mL of ultrapure water and dried for 1 h under vacuum. Finally, the active ingredients were eluted from the solid phase with 10 mL of methanol. 1 mL of methanol containing the active substances was transferred into amber glass vials and used for LC-MS/MS analysis.

*2.4.2.2. LC-MS/MS analysis.* The system consisted of a Vanquish pump and autosampler, and a TSQ Fortis triple-quadrupole mass spectrometer (Thermo-Fisher Scientific, San Jose, CA, USA). The separation was performed with an EC-C18 column (2.1 × 50 mm, 5 μm, Agilent technologies, Milan, Italy). Injection volume was 10 μL, run time was 20 min and the flow rate was 0.2 mL/min. The mobile phases were ultra-pure water with 0.2 % formic acid (phase A) and 0.2 % formic acid in Acetonitrile (phase B). The gradient of solvent B was set up as follows: 0–9 min from 30 to 70 %, 9–13 min from 70 to 90 % and finally 13–20 min at 45 %. The precursor and product ions used for the identification and the quantification of each compound, were taken from literature (Zambito Marsala et al., 2020; Lazic et al., 2018; Fang et al., 2020). The collision energy was below 35 V, and the retention times were within 15 min (Table SM1).

*2.4.2.3. Quality control.* For organic PPPs extraction and quantifications, the proposed method was validated by evaluating linearity, matrix effect, limit of detection (LOD), limit of quantification (LOQ), accuracy (in terms of recovery) and precision (in terms of repeatability). The linearity was evaluated through the coefficient of determination ($R^2$) of the analytical curves at concentration levels between 0.01 and 10 mg $L^{-1}$ (Table SM2). Matrix effect (ME) was calculated comparing the slope of curves prepared in solvent and in the blank extracts (tap water was used as blank). <2 % of ME was observed for all analytes. Precision was evaluated in terms of repeatability and intermediate precision, by estimating the relative standard deviation (RSD) of the recovery percentage. For the recovery tests, two standard solutions containing the six active ingredients in tap water were prepared at concentrations of 0.5 and 1 mg $L^{-1}$. Subsequently, 10 mL of solution was used for extraction following the method indicated above. Results showed a recovery percentage varying from 50 to 108 %, with a standard deviation $\leq$21 % (Table SM2). The LOD and LOQ were calculated using the method of signal-to-noise ratio, and the LOD was defined as the lowest concentration at which the analytical signal could be reliably differentiated with a signal-to-noise ratio of 3:1. The LOQ was established as the lowest spiked level concentration, which produced a signal-to-noise ratio of 10:1. The LOD and LOQ of the method was determined for all target active ingredients (Table SM2). Factors of 1:10, 1:100 and 1:1000 dilution/concentration were applied to samples found out of the range of quantification.

## 3. Results and discussion

### 3.1. *Organic PPPs concentration in washing water*

The content of the six active substances acetamiprid, cyflufenamid, cyprodinil, flupirodifurone, penconazole and metalaxyl-M in thirty-six washing water samples collected in 2022 and Bagheri et al., 2023 in the three conventional farms are presented in the figure SM1 in the supplementary material. In general, the analytical results showed up to 37.9 times higher PPPs concentrations in internal washing water than those found in the external washing water. At conventional farm 1 (CF1), the highest concentration in both internal and external washing waters was observed for flupyradifurone, with values equal to 4799.6 mg $L^{-1}$ and 259.1 mg $L^{-1}$, respectively. At conventional farm 2 (CF2), the insecticide acetamiprid showed the highest concentration in both internal and external washing waters, with values equal to 1611.1 mg $L^{-1}$ and 368.9 mg $L^{-1}$, respectively. Similar results were observed at conventional farm 3 (CF3), with the insecticide acetamiprid showing the highest concentration, 1073.2 mg $L^{-1}$ in internal washing water and 337.2 mg $L^{-1}$ in external washing water. However, the washing waters collected at CF3 showed the lowest difference between the concentrations found in the internal and external washing waters (3.7 times higher values in internal washing water). If the concentrations resulting from internal washing were not surprising, considering the concentrations of the active ingredients in the application solutions, the concentrations resulting from external washing were surprisingly high. Such results may be, partially, explained by the characteristics of the sprayers. Indeed, all four types of sprayers used, due to their shape and the distribution of the nozzles and fan, are particularly exposed to external contamination during the distribution of the PPPs solution. This aspect was underlined by the farmers involved in participatory monitoring, who also highlighted the significant exposure of the front part of the tractor during the application.

When examining the PPPs content in the external washing water, together with the declared PPPs used, the presence of residues of other PPPs was also observed (Fig. 2–4). For samples collected at CF1, the active ingredients detected were penconazole (0.01 mg $L^{-1}$), acetamiprid (4.4 mg $L^{-1}$) and flupirodifurone (30.4 mg $L^{-1}$) (Fig. 2). In the external washing water collected at CF2 the active ingredients detected were metalaxyl-M (0.01 mg $L^{-1}$), acetamiprid (5.6 mg $L^{-1}$) and cyflufenamid (0.02 mg $L^{-1}$) (Fig. 3). At CF3, acetamiprid (year 1) and flupyradifurone (year 2) were detected, with concentrations up to 3.3 mg $L^{-1}$and 4.9 mg $L^{-1}$, respectively (Fig. 4). To understand the reason for these occurrences, the farmers were asked to provide the field management book with all the PPPs applications made during the growing season. In most of the cases, the information provided highlighted the use of the active ingredients found in the external washing water during the applications made before the date of sampling. Therefore, the results might give ground to the hypothesis that different active compounds have different adherence to the sprayers surface, and therefore giving differences in their removal efficiency when washing. However, for CF1 and CF3 four active ingredients found in the external washing water, acetamiprid (CF1), penconazole (CFs 1 and 3), cyprodinil (CFs 1 and 3) and flupirodifurone (CF3) were not reported in the field management book during the season of sampling. When looking at the list of the active ingredients used in the previous seasons, all four compounds were present. These observations underline the long-term persistence of certain active ingredients on the surface of spraying equipment even after external cleaning post-application.

Trying to compare our results with data previously reported in literature, very little information was available. De Wilde et al. (2007) reported PPP concentrations in the washing water of equipment ranging from 0.2 to 61 mg $L^{-1}$ for four herbicides. No specific information about the type of washing (external vs internal) was provided. Very recently, Beltran -Flores et al. Bagheri et al. (2023) reported values between 4.5 and 19.2 mg $L^{-1}$ for four PPPs, with the highest value for thiacloprid, a

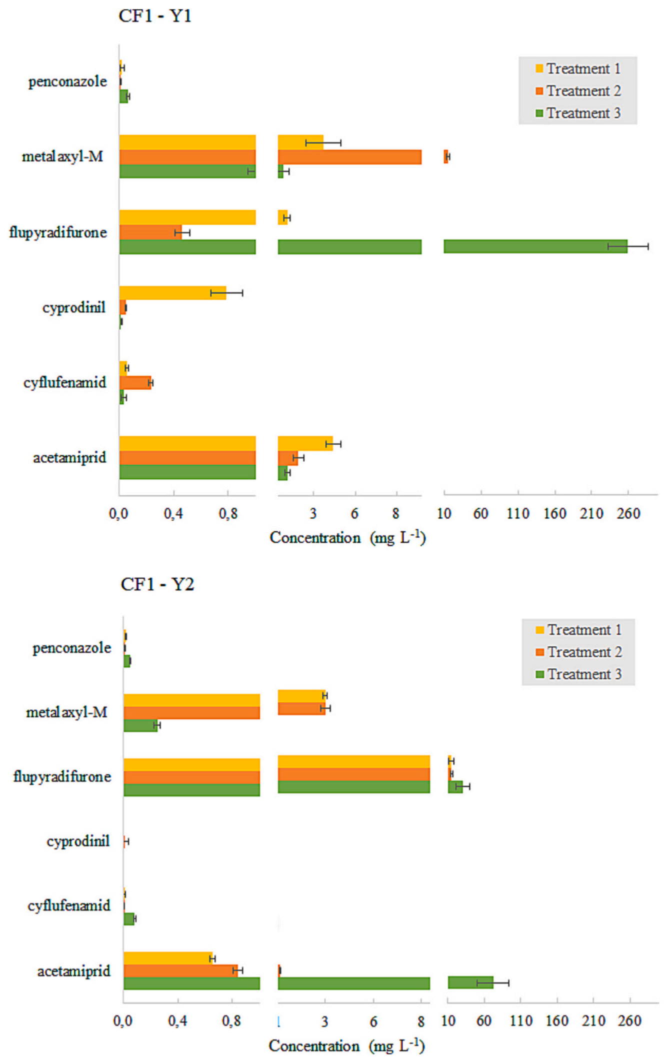

**Fig. 2.** Organic PPPs concentrations in external washing water samples collected at CF1 during the year 2022 (Y1) and year Bagheri et al., 2023(Y2).

neonicotinoid insecticide. These are much lower than the concentrations of six organic PPP monitored in the external and internal washing water in the present study. However, they were similar to the residues found for the other PPPs.

### 3.2. Cu concentration in washing water

The content of Cu in sixteen washing water samples collected in 2022 and 2023 in the two organic farms (OF1 and OF2) are presented in figure SM2. In general, the analytical results showed up to 10.3 times higher Cu concentration in internal washing water than those found in the external washing water. For OF1 the concentration of Cu in internal washing water was up to 227.3 mg $L^{-1}$ whereas in external washing water was up to 35.9 mg $L^{-1}$. The concentrations found in washing water collected at OF2 were up to 292.3 mg $L^{-1}$ in internal washing water and up to 102 mg $L^{-1}$ in external washing water. Also, Cu concentrations in external washing water were surprisingly high. The sprayers used for the applications have similar characteristics to those used for the application of organic PPPs in conventional farms; therefore, the characteristics of the sprayers could have determined the contamination of the external parts of the sprayers in this case too.

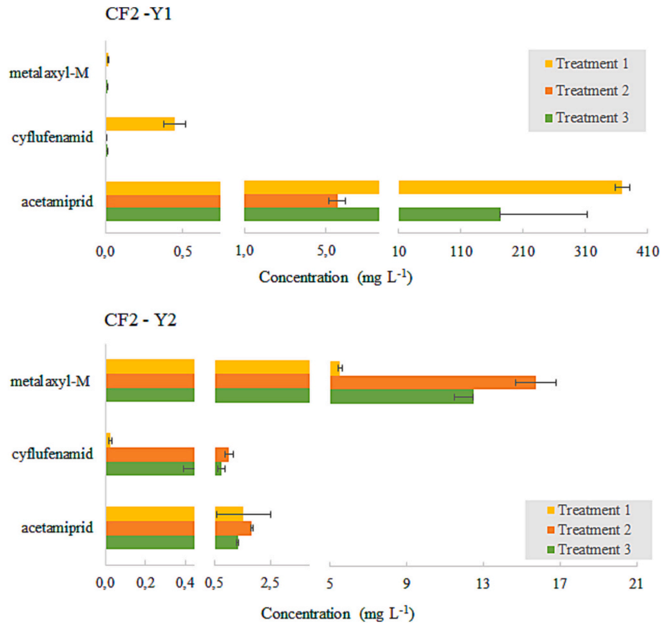

**Fig. 3.** Organic PPPs concentrations in external washing water samples collected at CF2 during the year 2022 (Y1) and year 2023 (Y2).

### 3.3. Mass balance analysis

Considering the volumes of water used for sprayers washing (Tables SM3 and SM4), the concentrations found in the washing water, the quantity of the active ingredient used for each treatment, and the vineyard area treated, it was possible to quantify the percentage of the active ingredient remaining in the sprayer and possibly dispersed in the environment by washing. For CF1, the PPPs dispersion percentage ranged between 0.02 % (for cyflufenamid, year 1) and 53.9 % (for flupyradifurone, year 1) whereas for CF2 was lower, ranging from 0.001 % (for cyflufenamid, year 1) to 2.9 % (for acetamiprid, year 1). For CF3, the PPPs dispersion percentage was higher than the losses observed in farm 2 but still lower than those observed in farm 1, and ranged between 0.03 % (for cyflufenamid, year 1) and 5 % (for acetamiprid, year 1).

For OF1 Cu dispersion percentage ranged between 0.02 % and 0.14 % whereas for OF2 Cu losses were higher, ranging from 0.01 % and 0.3 %.

### 3.4. Assessment of the impact on the aquatic environment

To evaluate the impact on the aquatic environment of a possible dispersion of the washing water into a water body, a standard-sized water body was considered, which is generally used by Forum for the Co-ordination of pesticides fate models and their Use (FOCUS) models for the assessment of the environmental fate of PPPs. The FOCUS "Stream" water body is characterized by a length of 100 m, a width of 1 m, and a water depth of 0.5 m (FOCUS, 2015). The "Stream" water body was selected as considered the most representative for the area under study. Under these conditions, the volume of the water column of the water body is 50 $m^3$. If we assume a point discharge of the washing water with the highest concentrations found for each active ingredient and a homogeneous distribution over the entire water column, it is possible to estimate the maximum concentrations of the active ingredients in water. Table 1 shows the quantities of PPPs present in the washing water, both total (internal + external) and external, that have been considered for the estimates. The concentrations thus estimated ranged from 0.06 μg/L to 2112 μg/L, generally higher than the environmental quality standard for surface water (EQS) of 0.1 μg/L. The lowest value (the only one lower than the EQS) was estimated for

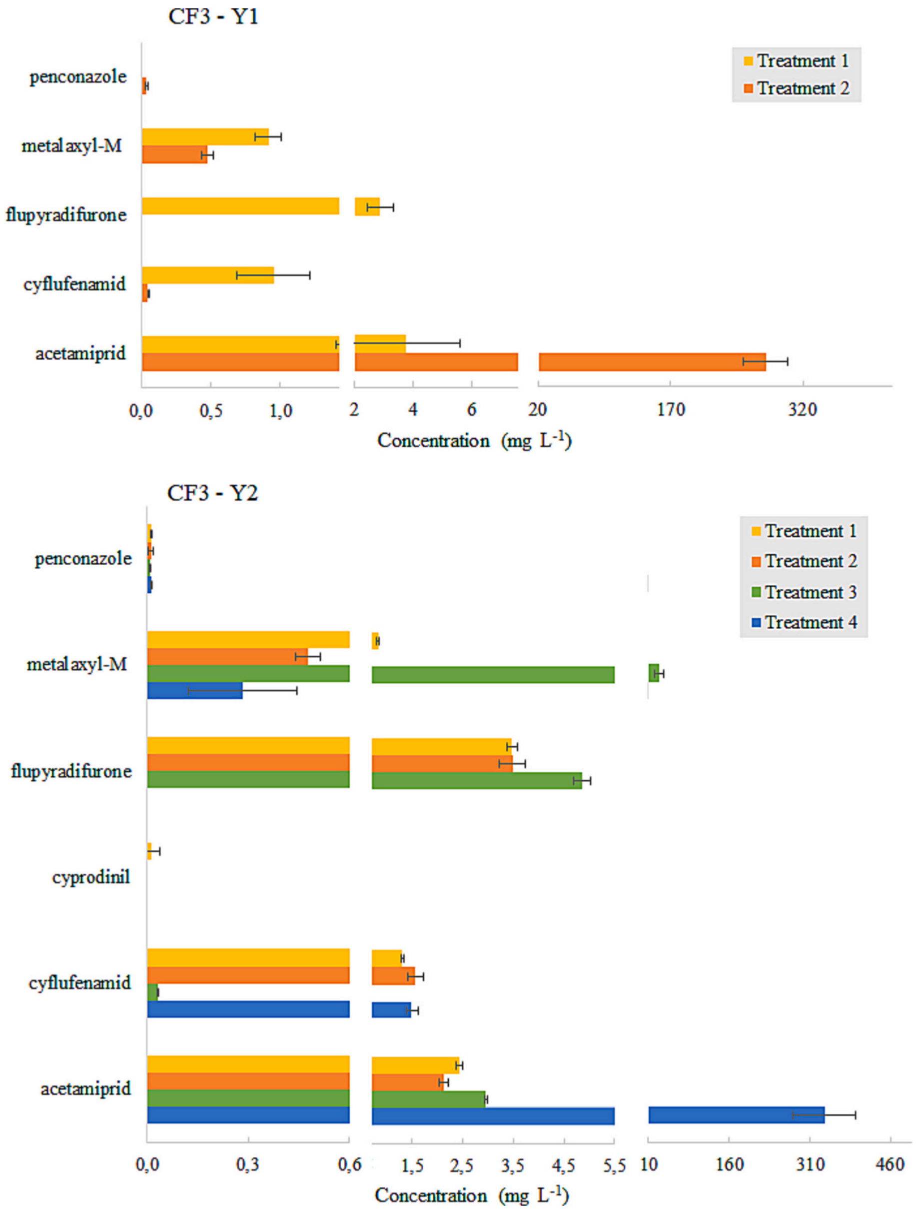

**Fig. 4.** Organic PPPs concentrations in external washing water samples collected at CF3 during the year 2022 (Y1) and year 2023 (Y2).

penconazole when considering the quantity present in the external washing water. The highest value was estimated for flupirodifurone, 2112 μg/L, when considering the total amount present in both internal and external washing water. However, when evaluating the impact on aquatic organisms, the estimated concentrations were always below the toxicological endpoints (NOEC – no observed effect concentration) for both fish (*Pimephales promelas*) and *Daphnia magna* (Table 3). Nevertheless, flupirodifurone exhibits toxicological endpoints values in the same order of magnitude as the estimated concentrations. Moreover, considering that during the agronomic year several treatments with flupyradifurone can be conducted and that its degradation time in water is >200 days (table 3), an exceedance of the toxicological endpoints may be expected.

For the definition of ecotoxicological hazards of PPP-contaminated water the Italian indications of Decree n. 47 del 9 of 9th of August 2021 and guidelines SNPA 24/2020 were followed. These legislative papers identify methodological criteria and indicate the threshold values to consider when evaluating the hazard characteristics and consequent classification of the waste.

The PPP analyzed in the washing water are classified as substances with aquatic chronic toxicity (H411 for penconazole and H410 the others). The threshold value (cut-off) for these substances is 0.1 % but the waste should be classified as hazardous (HP14) only if is satisfied the formula:

$100 \times \_\Sigma c(H410) + 10\times \_\Sigma c(H411) + \Sigma c(H412) \geq 25\ \%$.

In the present study only three samples, all deriving from internal washing, have had PPPs content greater than the cut off value, but just one, (flupyradifurone, treatment 3 Year 1) satisfied the aforementioned formula and therefore must be considered as ecotoxicological hazardous waste and be properly managed.

## 4. Conclusion

During two agricultural seasons 52 samples of washing water were collected in five farms involved in the participatory monitoring program. Three samples, out of the 52 analyzed, deriving from internal washing showed concentrations of the active ingredients >0.1 %. This value represents the cut-off for substances with the H410 hazard

**Table 1**
Estimated concentrations of the organic PPPs in a standard water body and ecotoxicological thresholds.

| Active ingredient | Water Body Volume (L) | Total amount of active ingredient in wash water (g) | Conc. in the water body after internal and external wash water dispersal (μg/L) | Total amount of active ingredient in external wash water (g) | Conc. in the water body after external wash water dispersal (μg/L) | Toxicity for fish: *Pimephales promelas* (μg/L) | Toxicity for Invertebrates: *Daphnia magna* (μg/L) | DT50 in water (days) |
|---|---|---|---|---|---|---|---|---|
| Cyprodinil | 50,000 | 0.2 | 4.4 | 0.02 | 0.4 | 231 NOEC (EFSA.2005) | 8.2 NOEC (EFSA. 2005) | 16.3 (EFSA. 2005) |
| Cyflufenamid | | 0.3 | 6 | 0.06 | 1.2 | 24 Growth NOEC (EFSA. 2009) | 246 Reproduction NOEC (EFSA. 2009) | 4.95 (EFSA. 2009) |
| Flupirodifurone | | 105.6 | 2112 | 10.4 | 208 | 4410 Survival NOEC (EFSA (European Food Safety Authority), 2015a, b) | 3200 Reproduction NOEC (EFSA (European Food Safety Authority), 2015a, b) | 228 (EFSA (European Food Safety Authority), 2015a, b) |
| Penconazole | | 0.3 | 6 | 0.003 | 0.06 | 320,000 NOEC (EFSA. 2008) | 60,000 Reproduction NOEC (EFSA. 2008) | 706 (EFSA. 2008) |
| Acetamiprid | | 39.2 | 784 | 14.8 | 296 | 9400 Hatchability NOEC (EFSA. 2016) | 5000 Reproduction or development NOEC (EFSA. 2016) | 27 (EFSA. 2016) |
| Metalaxyl-M | | 4.5 | 89.8 | 1.2 | 24 | 9100 Growth NOEC (EFSA (European Food Safety Authority), 2015a, b) | 1000 Reproduction NOEC (EFSA (European Food Safety Authority), 2015a, b) | 47.1 (EFSA (European Food Safety Authority), 2015a, b) |

statement, as six of the seven PPPs considered in the present study and must be taken into consideration for the classification of the waste as hazardous. In general, PPP concentrations in the internal washing water were up to 37.9 times higher than the concentration in the external washing water. However, the latter concentrations were surprisingly high and unexpected, in some cases even just under two times lower. This may be, partially, explained by the characteristics of the sprayers, particularly exposed to external contamination during the distribution of the PPPs but, also, to failure to comply with the BMPs. Indeed, as confirmed by farmers in the additional survey conducted for a proper identification of the contamination drivers, the external washing of the sprayer is commonly conducted only once a year.

Regarding the impact on the aquatic environment of a possible dispersal of the washing water into a water body, the estimated concentrations, calculated using the FOCUS “Stream” water body, are almost always higher than the environmental quality standard (EQS) of 0.1 μg/L, but below the toxicological endpoints (NOEC – no observed effect concentration) for both fish (*Pimephales promelas*) and *Daphnia magna*. Nevertheless, for some active ingredients used several times during the agricultural season and characterized by high degradation time in water, such as flupyradifurone, it can be supposed that the toxicological endpoints could be exceeded. Flupirodifurone exhibits toxicological endpoint values in the same order of magnitude as the estimated concentration in the water body and has a degradation time in water >200 days.

Although a two-year monitoring period may not be enough to fully assess the effectiveness of reducing environmental contamination of PPPs, involving farmers in participatory monitoring, along with consultants and managers is an effective method of gaining valuable insights, building trust, and fostering positive relationships.

The data collected through the surveys confirmed that local farmers' awareness of the environmental risk associated with PPP use plays an important role in successful compliance with BMPs and the difficulty of managing PPP point source contamination due to its specific context nature and its strong link with environmental and socio-economic factors. Having spraying equipment that complies with the minimum legal and technical requirements may not be sufficient to mitigate the risk of point source pollution by PPPs resulting from the internal and external washing of the sprayers. Behavioral deviations from good practices are difficult to control and, therefore, achieving changes requires efforts, not only in informing about BMPs, which could lead to the reduction of contamination, but also in disseminating a culture of pollution anticipation and prevention. Furthermore, from a long-term perspective, it is crucial to understand the factors that influence farmers' decisions and behavior in a specific context (Calliera and L'Astorina, 2018). For instance, to effectively prevent “in-farm” PPP pollution from point sources, the implementation of “bio-purification systems” could be a technically feasible and controllable solution. However, these systems must be authorized at the national level, be economical and reliable, easy to use with low labor and time inputs, have low waste disposal costs, and, when technologically possible, should allow for the reuse of treated water. This is especially important in recent years, as water scarcity has become a more acute problem.

The viticulture territory considered in the present study is quite common nationwide. It is characterized by a high variability of farm structures, risk attitude, and economic availability. Due to the nature of contamination by PPPs, which is point source but diffuse in the territory, analytical data confirms the need for additional joint efforts to improve awareness in managing washing water containing PPPs and to decrease the impact of the agricultural sector.

## CRediT authorship contribution statement

**Maura Calliera:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Ettore Capri:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Anastasia Lomadze:** Writing – review & editing, Writing –

original draft, Formal analysis, Data curation. **Terenzio Bertuzzi:** Writing – review & editing, Formal analysis. **Gian Maria Beone:** Writing – review & editing, Formal analysis. **Emanuela Delpero:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Alessandro Varotto:** Writing – review & editing, Methodology, Investigation, Data curation, Conceptualization. **Stefano Bergaglio:** Writing – review & editing, Project administration, Funding acquisition. **Elena Anselmetti:** Writing – review & editing, Validation, Conceptualization. **Nicoleta Alina Suciu:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

## Declaration of competing interest

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

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2025.178551.

## Data availability

Data will be made available on request.

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