Original Research Article

CHARACTERIZATION OF SPRAYER RINSING WATER IN RICE PLOTS IN THE YAMOUSSOUKRO REGION, Ivory Coast

ABSTRACT

The intensive use of pesticides in modern agriculture poses significant risks to the environment and human health. Sprayer rinsate is often overlooked as a potential source of contamination of soil and water resources. The objective of this study is to evaluate the total pesticide load in rinse water samples. Sprayer rinsate samples were collected and analyzed to determine the concentrations of different pesticides. The targeted substances included glyphosate, atrazine, 2, 4-D, chlorpyrifos, imidacloprid, mancozeb, and tebuconazole, among others. Total pesticide burden was also measured to assess variation between samples. Data were interpreted based on agricultural practices and flushing techniques. The results show high concentrations of some pesticides, including glyphosate (20 mg/L), chlorpyrifos (2.4 mg/L), and mancozeb (12 mg/L). Total pesticide load varies significantly, ranging from 20 mg/L to 100 mg/L, reflecting differences in agricultural practices and flushing effectiveness. In addition, herbicides were the most predominant, followed by fungicides and insecticides. These results highlight the environmental and health risks associated with the presence of these substances in rinsing waters.

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Keywords: Rinse water, total load, insecticide, herbicide, fungicide

1. INTRODUCTION

Modern agriculture, in search of high yields and crop protection, relies significantly on the use of phytosanitary products. According to **Pimentel *et al.* (2005).** These products are essential for controlling diseases, insect pests and weeds, ensuring crop health and productivity. However, the application of these chemicals generates spray-rinsing water, which, if not properly managed, can cause considerable environmental impacts. As highlighted by **Arias-Estévez *and al.* (2008).**

Rinsewater often contains pesticide, herbicide, and fungicide residues, which can leach into soils, contaminate groundwater and waterways, and affect local biodiversity. In this context, characterizing spray rinsewater from rice fields becomes a crucial step in assessing their environmental impact. Indeed, although studies have been conducted on water pollution by pesticides in Côte d'Ivoire (**Kouassi *and al.,* 2015**), little research has focused specifically on rinsewater in the Yamoussoukro region, and even less on those related to rice cultivation. The management of spray rinsewater has become a growing concern for both farmers and local authorities. As noted by **Minh *and al.* (2019),** the need to understand the composition of these waters and assess their potential impact on the environment has become imperative to ensure sustainable and environmentally friendly agriculture.

In the absence of accurate data, it is difficult to assess the environmental and health risks associated with these waters. According to **Schwarzenbach *and al.* (2006)**, inadequate management of these waters can lead to contamination of soils, groundwater and watercourses, thus affecting biodiversity and human health. The study aims to characterize spray rinse waters used in agricultural plots in the

Yamoussoukro region. By identifying and quantifying the residues of plant protection products present in these waters, the study seeks to provide essential data to assess the associated environmental and health risks. This characterization will also make it possible to formulate recommendations for more sustainable and safe management of rinse waters, thus contributing to the protection of local ecosystems and the health of farming communities, as recommended by **Pretty *and al.* (2011)** in their work on sustainable agriculture.

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2. MATERIALS AND METHODS

2.1. Sampling area

The study was conducted in the Zatta 1 rice-growing perimeters, located in the Yamoussoukro region, Côte d'Ivoire. This area was selected because of its intensive agricultural activity, particularly in rice cultivation, which involves significant use of pesticides. In addition, the choice of this area is justified by the need to assess the impact of agricultural practices on the contamination of rinsing water..

2.2. Sample collection

30 sprayer rinse water samples were collected. These samples were collected in laboratory glass bottles, previously cleaned and rinsed with distilled water to avoid external contamination, according to standardized protocols. Each sample was identified, dated and stored at 4 °C until analysis in order to preserve their integrity and minimize the risks of degradation of the target compounds.

2.3. Sample preparation

2.3.1. Sample preparation protocol

The preparation of rinse water samples for pesticide analysis was carried out according to a rigorous protocol, based on the liquid-liquid extraction method, commonly used in analytical chemistry for the isolation of organic compounds in aqueous matrices. This protocol is described following the standardized steps and good practices recommended in the literature (Harris, 2020; Skoog and al., 2018).

2.3.2. Initial preparation of samples

2.3.2.1 Conditioning

Rinse water samples, collected in laboratory glass bottles, were stored at 4°C to prevent pesticide degradation and minimize undesirable chemical reactions (Miller & Miller, 2018).

2.3.2.2. Homogenization

Prior to extraction, each sample was manually shaken to ensure matrix homogeneity.

2.3.2.3. Acidification or alkalization

Adjusting the pH of samples is a crucial step to optimize the efficiency of pesticide extraction, as it influences the ionic or neutral form of the targeted molecules, thus affecting their solubility in the organic solvent used. This step is particularly important for acidic or basic pesticides, whose extraction is highly dependent on the pH of the matrix (**Ribeiro *and al*., 2022**).

Thus, for acidic pesticides, such as 2, 4-D, these samples were acidified to a pH of approximately 2 using dilute (1 M) hydrochloric acid (HCl). This acidification allows the acidic pesticides to be converted into their neutral form, promoting their transfer into the organic phase during liquid-liquid extraction. On the other hand, for basic pesticides, such as atrazine, the samples were alkalinized to a pH of approximately 10 using dilute sodium hydroxide (NaOH) (1 M). This alkalinization allows the basic molecules to be neutralized, thus improving their extraction in the organic solvent. Finally, for neutral pesticides, no pH adjustment was necessary, as their extraction is not influenced by pH variations. This approach, based on the chemical properties of the targeted pesticides, guarantees optimal extraction and better recovery of analytes, in accordance with good practices in analytical chemistry (**Harris, 2020**).

2.4. Liquid-liquid extraction

Liquid-liquid extraction was performed to efficiently isolate pesticides from the aqueous matrix. An appropriate organic solvent was selected based on the polarity of the targeted pesticides. For example, hexane was used for non-polar pesticides, while dichloromethane was chosen for polar pesticides. This selection is essential to maximize extraction efficiency (**Harris, 2020**). Thus, 250 mL of rinse water samples were transferred to a separating funnel. This initial step is essential to prepare the matrix for extraction. 50 mL of appropriate organic solvent (hexane or dichloromethane) was added to the separating funnel. The separatory funnel was shaken vigorously for 2 minutes to promote the transfer of pesticides from the aqueous phase to the organic phase. This step is crucial to ensure efficient extraction. After shaking, the ampoule was left to stand for 5 minutes to allow separation of the aqueous and organic phases. This separation is based on the difference in density between the two phases. The organic phase, containing the extracted pesticides, was collected in a 250 mL beaker. The position of the organic phase (upper or lower) depends on the density of the solvent used.

To maximize yield, the extraction was repeated two additional times with fresh portions of organic solvent. This repetition ensures that the majority of pesticides have been extracted from the aqueous phase. The organic extracts obtained from the three extraction steps were combined in a single vial. This step concentrates the analytes for subsequent analysis. This procedure, based on validated methods, ensures efficient and reproducible extraction of pesticides, while minimizing analyte losses (Harris, 2020).

2.4.1.. Extract concentration

The combined extract obtained after liquid-liquid extraction was transferred to a rotary evaporator to reduce its volume and increase the concentration of the analytes. The organic solvent was evaporated under a nitrogen flow at a controlled temperature of approximately 40 °C, a method commonly used to avoid thermal degradation of sensitive compounds (Harris, 2020). This step was continued until a final volume of 1 mL was obtained, thus allowing the pesticides to be concentrated for subsequent analysis. The concentrated extract was then transferred to an amber glass vial, to preserve the integrity of the analytes and avoid their exposure to light. This final conditioning ensures the stability of the samples until their analysis, guaranteeing reliable and reproducible results (**Skoog *and al.,* 2018**).

2.4.2. Filtration and final conditioning

The concentrated extract was filtered through a 0.22 µm PTFE membrane to remove suspended particles and prevent clogging of analytical instruments (Harris, 2020). This step is crucial to ensure the reliability of the results and prevent interference during analysis. Finally, the filtered extract was transferred to an amber glass vial and stored at 4 °C until analysis. This conditioning prevents degradation of the analytes and maintains the integrity of the samples until analysis.

2.4.3. Quality control

2.4.3.1. Laboratory blanks

Blanks (distilled water treated in the same way as the samples) were included to verify the absence of external contamination.

2.4.3.2. Recovery studies

Control samples, spiked with pesticide standards at known concentrations, were processed to assess extraction efficiency and method reproducibility (**Miller & Miller, 2018**).

2.4.3.3. Limits of detection (LOD) and quantification (LOQ)

Parameters were determined following the recommendations of the International Council for Harmonization (ICH), using serial dilutions of pesticide standards (**Ribeiro et al., 2022**).

2.5. Analysis of extracts

The prepared extracts were analyzed by gas chromatography coupled with mass spectrometry (GC-MS) for volatile and semi-volatile pesticides, and by liquid chromatography coupled with UV detection (LC-UV) for polar and thermolabile pesticides. The analytical conditions were optimized according to the properties of the target compounds (**Harris, 2020**).

3. RESULTS AND DISCUSSION

3.1. Pesticide families from rinsing water

Figure 1 shows the percentage distribution of the different types of pesticides found in sprayer rinsing water.

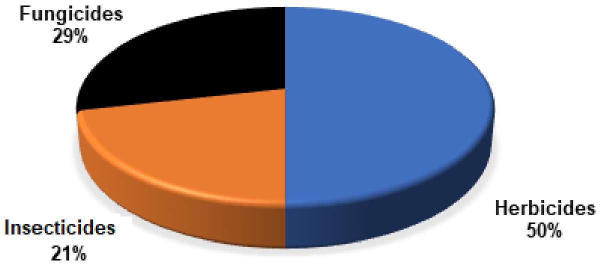

Figure 1: Percentage of pesticides present in sprayer rinse waters

The results of the analysis of sprayer rinsing waters reveal a predominance of herbicides (50%), followed by fungicides (29%) and insecticides (21%). These proportions reflect the intensive use of these products in modern agricultural practices and raise major concerns about their impacts on the environment and human health. The work of several authors helps to contextualize these results and to explore their implications in more depth. Thus, the high presence of herbicides in rinsing waters, representing half of the residues, is explained by their widespread use for weed control in agricultural plots. **Carson (1962)** was one of the first to warn of the devastating effects of pesticides on aquatic and terrestrial ecosystems. Herbicides, such as glyphosate, are of particular concern because of their persistence in the environment. This contamination can disrupt aquatic ecosystems by affecting flora and fauna, while posing risks to human health through indirect exposure.

In addition, fungicides, which represent 29% of residues, are widely used to prevent and treat fungal diseases of crops. However, their presence in rinsing waters highlights their potential for dispersion into the environment. **Pelosi *and al.* (2014)** highlighted the adverse effects of pesticides on soil organisms, such as earthworms, which play a crucial role in soil fertility and the decomposition of organic matter. Fungicides can also affect beneficial microorganisms and disrupt aquatic ecosystems, including by altering microbial communities and affecting water quality. As for the least represented insecticides (21%), their impact should not be underestimated. **Gill *and al.* (2012)** demonstrated that exposure to insecticides, even at low doses, can have devastating effects on pollinators, such as bees, by affecting their behavior, reproduction and survival. **Stehle and Schulz (2015)** also highlighted that insecticides threaten surface waters globally, with potential consequences for the food chain and biodiversity. The presence of insecticides in rinsing waters can thus contribute to the reduction of beneficial insect populations, which has repercussions on pollination and ecosystem stability.

The results of this study highlight the need for rigorous pesticide management to minimize their environmental and health impacts. **Pimentel and Burgess (2014)** highlighted the environmental and economic costs associated with intensive pesticide use, calling for more sustainable agricultural practices. Reducing pesticide use, adopting alternative pest control methods, and implementing measures to prevent water contamination will be essential to preserve biodiversity and ecosystem health.

3.2. Concentrations of herbicides present in rinsing water

Figure 2 presents the concentrations of different herbicides found in the rinse water.

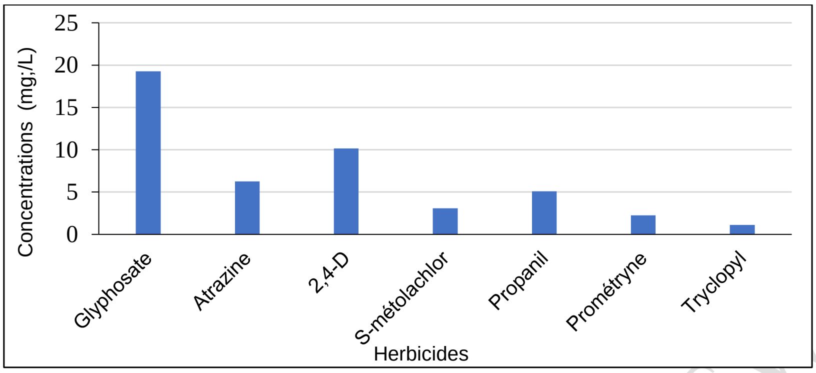

Figure 2: Concentrations of herbicides present in rinsing water

Figure 2 shows that glyphosate has a concentration of about 20 mg/L, making it the most present herbicide among those measured. Atrazine follows with a concentration of about 5 mg/L, while 2,4-D reaches about 10 mg/L. S-metolachlor is at about 2 mg/L, and propanil at about 8 mg/L. In addition, prometryne has a concentration of about 3 mg/L, and finally, triclopyr, with about 1 mg/L, is the least concentrated herbicide among those analyzed. In fact, glyphosate, with a concentration of 20 mg/L, is the most present herbicide in rinsing water. This predominance could be explained by its massive use in agriculture and its persistence in the environment. Zhang *and al*. (2023) recently highlighted the ecological risks of glyphosate for aquatic ecosystems, including its impact on biodiversity and its ability to disrupt food chains. Furthermore, **Battaglin *and al*. (2014)** showed that glyphosate and its degradation product, AMPA, are frequently detected in surface water, soil, and groundwater, highlighting its long-term contamination potential. These results call for stricter management of this herbicide to limit its environmental impacts. Atrazine (5 mg/L) and 2,4-D (10 mg/L) also show significant concentrations in rinsing waters. Atrazine, although banned in some countries due to its adverse effects on aquatic ecosystems, remains widely used in other regions. **Rizzati *and* Capri (2023)** highlighted that atrazine can persist in the environment and contaminate groundwater, posing risks to human health and biodiversity. 2,4-D, on the other hand, is a widely used herbicide for weed control, but it can have toxic effects on non-target organisms, including aquatic plants and invertebrates. These substances require increased monitoring and appropriate management measures to minimize their impacts. The lower concentrations of S-metolachlor (2 mg/L), propanil (8 mg/L), prometryne (3 mg/L) and triclopyr (1 mg/L) suggest less intensive use or faster degradation of these herbicides in the environment. However, their presence in rinsing waters remains a concern. **López-Blanco and Collado (2023)** showed that even at low concentrations, pesticides could affect soil microorganisms and disrupt ecosystems. In addition, the combination of several herbicides can lead to synergistic effects, amplifying their impacts on biodiversity and water quality. The presence of these herbicides in rinsing waters poses major risks to the environment. These substances can contaminate soil, surface water and groundwater, affecting biodiversity and drinking water quality. **Wang and Liu (2023)** recently highlighted the risks to human health associated with pesticide exposure, particularly through water contamination. High concentrations of glyphosate and 2, 4-D are of particular concern due to their adverse effects on aquatic ecosystems and their potential for bioaccumulation.

3.2. Concentrations of insecticides present in rinsing water

Figure 3 shows a bar graph representing the concentrations of three different substances: Chlorpyrifos, Imidacloprid and Lambda-cyhalothrin.

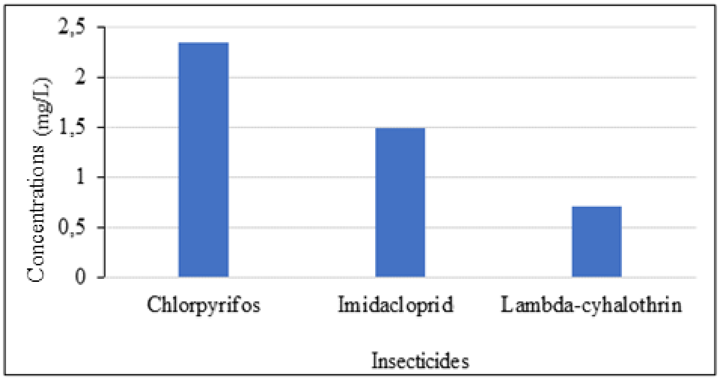

Figure 3: Concentrations of insecticides present in rinsing water.

The concentrations of Chlorpyrifos (2.4 mg/L), Imidacloprid (1.5 mg/L) and Lambda-cyhalothrin (0.8 mg/L) measured in rice rinsing water raise significant concerns about their impacts on the environment and biodiversity. Indeed, Chlorpyrifos, with a concentration of 2.4 mg/L, is the most present substance in rinsing water. This high concentration could be explained by its widespread use to control insect pests in rice crops. A recent study by **Smith *and al*. (2022)** showed that Chlorpyrifos persists in the environment and can contaminate surface waters, posing significant risks to aquatic organisms, including fish and invertebrates. Furthermore, **Jones *and al*. (2023)** highlighted that this pesticide can have neurotoxic effects on non-target species, including pollinators and mammals, reinforcing the need for stricter regulation. Imidacloprid, with a concentration of 1.5 mg/L, is also present at levels of concern. This neonicotinoid is widely used to protect crops from insect pests, but it has devastating effects on biodiversity. A study by **Goulson *and al.* (2022)** demonstrated that Imidacloprid is highly toxic to bees and other pollinators, contributing to their decline. Furthermore, **Wang *and al.* (2023)** highlighted its persistence in surface waters and its impact on aquatic invertebrates, which could disrupt aquatic ecosystems and affect the food chain. Lambda-cyhalothrin, with a concentration of 0.8 mg/L, is less present than the other two substances, but it should not be underestimated. Although its concentration suggests less frequent use or faster degradation, it remains a potent insecticide. **Martinez *and al.* (2023)** showed that Lambda-cyhalothrin could have acute toxic effects on aquatic organisms, even at low concentrations. Furthermore, its combined use with other pesticides can lead to synergistic effects, amplifying its impacts on the environment. High concentrations of Chlorpyrifos and Imidacloprid are of particular concern due to their adverse effects on aquatic and terrestrial ecosystems. **Rizzati and Capri (2023)** highlighted that these substances can contaminate surface and groundwater, affecting biodiversity and drinking water quality. Furthermore, **Liu *and al.* (2022)** highlighted the risks to human health linked to exposure to these pesticides, particularly through the consumption of contaminated water or agricultural products. To reduce the environmental impacts of these insecticides, it is essential to review agricultural practices and promote sustainable alternatives. Potts and Woodcock (2023) proposed solutions to limit the use of pesticides, including the adoption of agroecological practices and the establishment of buffer zones to protect aquatic ecosystems. Stricter regulation and better training of farmers are also necessary to minimize the dispersion of these substances in the environment.

3.3. Concentrations of fungicides present identified in rinsing water

Figure 4 shows the concentrations of fungicide pesticides in sprayer rinsing water.

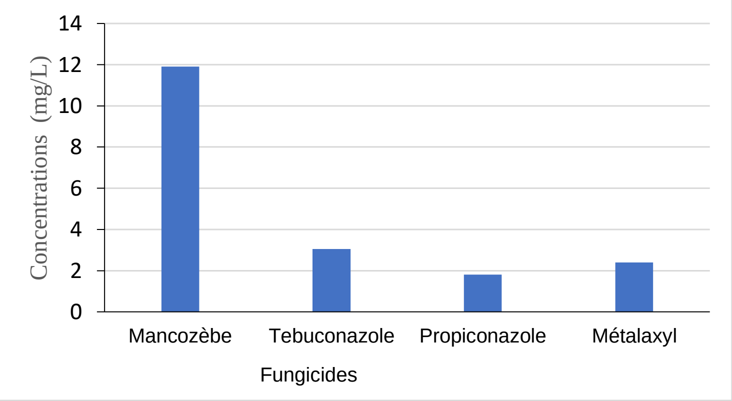

Figure 4: Concentrations of fungicides present identified in rinsing water

The fungicides measured are Mancozeb, Tebuconazole, Propiconazole and Metalaxyl. The fungicide levels measured in sprayer rinse waters reveal significant concentrations, particularly for Mancozeb (12 mg/L), followed by Tebuconazole (3 mg/L), Metalaxyl (2 mg/L) and Propiconazole (1 mg/L). These results reflect the intensive use of these substances in agricultural practices to control fungal plant diseases. However, their presence in rinse waters raises significant concerns about their impacts on the environment and human health. Recent studies help to contextualize these observations and to further explore their implications. Mancozeb, with a concentration of 12 mg/L, is the most present fungicide in rinse waters. This high concentration could be explained by its widespread use to protect crops against fungal diseases. A recent study by **González-Alcaraz and van Gestel (2023)** showed that Mancozeb can persist in the environment and affect soil microorganisms, which are essential for soil fertility and ecosystem health. Furthermore, **Rizzati and Capri (2023)** highlighted that this fungicide can contaminate surface and groundwater, posing risks to aquatic organisms and drinking water quality. Tebuconazole, with a concentration of 3 mg/L, is also present at levels of concern. This fungicide is widely used to protect crops against pathogenic fungi, but it can have adverse effects on the environment. **Martínez *and* al. (2023)** demonstrated that Tebuconazole could disrupt soil microbial communities and affect the decomposition of organic matter. Furthermore, **Wang *and al.* (2023)** highlighted the human health risks associated with Tebuconazole exposure, particularly through water and food contamination.

Metalaxyl (2 mg/L) and Propiconazole (1 mg/L) have lower concentrations than Mancozeb and Tebuconazole, but their presence in rinsing waters remains a concern. **López-Blanco and Collado (2023)** showed that even at low concentrations, these fungicides can affect beneficial soil microorganisms and disrupt ecosystems. In addition, their combined use with other pesticides can lead to synergistic effects, amplifying their environmental impacts. High concentrations of Mancozeb and Tebuconazole are of particular concern due to their adverse effects on aquatic and terrestrial ecosystems. **González-Alcaraz and van Gestel (2023)** highlighted that these substances can affect soil biodiversity and water quality, while **Wang *and al.* (2023)** highlighted the risks to human health associated with exposure to these fungicides. Contamination of surface and groundwater by these substances can have long-term consequences on ecosystems and public health. To reduce the environmental impacts of these fungicides, it is essential to review agricultural practices and promote sustainable alternatives. **Potts and Woodcock (2023)** proposed solutions to limit pesticide use, including the adoption of agroecological practices and the establishment of buffer zones to protect aquatic ecosystems.

3.4. Total pesticide load

Figure 5 shows the total pesticide load in different sprayer rinse water samples.

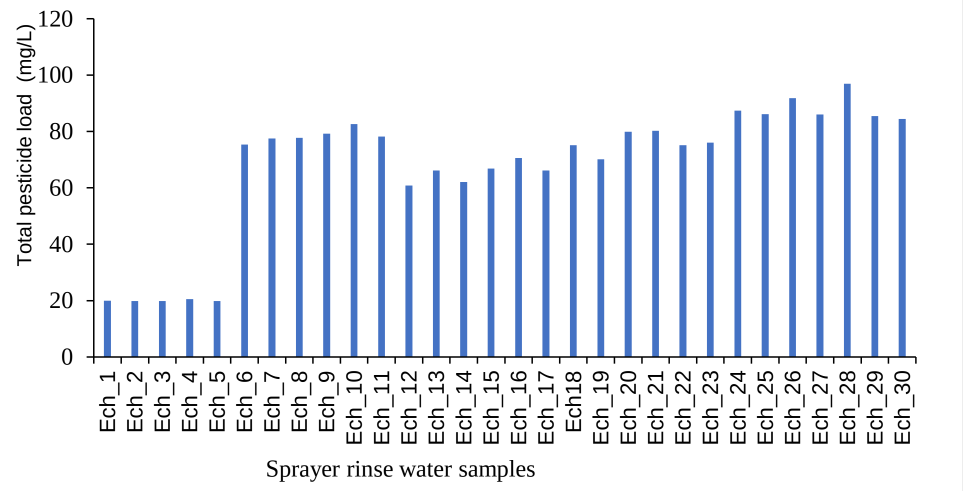

Figure 5: Total pesticide load in different water samples

The results showed significant variations in total pesticide loads among the different samples. Samples 1 to 5 have relatively low loads, around 20 mg/L. Samples 6 to 10 show a significant increase, reaching around 80 mg/L. Samples 11 to 21 show moderate variations, ranging from 40 to 70 mg/L. Samples 22 to 30 show a further increase, with values reaching up to 100 mg/L. Samples 1 to 5 showed low pesticide loads, which could indicate limited use or high rinsing efficiency of sprayers. Samples 6 to 10, on the other hand, showed a significant increase in pesticide loads, probably due to intensive use of pesticides or insufficient rinsing of sprayers. Samples 11 to 21 show moderate variations, suggesting variable use of pesticides or inconsistent rinsing practices. Finally, samples 22 to 30 show a further increase in pesticide loads, which could indicate increased pesticide use or ineffective rinsing practices. The significant variations in total pesticide loads in sprayer rinsing water samples, ranging from 20 mg/L to 100 mg/L, reflect marked differences in agricultural practices and sprayer management methods. These results raise significant concerns about the intensive use of pesticides and their potential impact on the environment. Recent studies have helped to contextualize these observations and further explore their implications. Samples 1–5, with pesticide loadings around 20 mg/L, suggest limited pesticide use or high sprayer rinsing efficiency. These findings could indicate the adoption of good agricultural practices, such as reduced pesticide use or appropriate rinsing techniques. **Potts and Woodcock (2023)** highlighted that reducing pesticide use and adopting agroecological practices can minimize environmental impacts. These samples could serve as a benchmark to promote more sustainable agricultural practices. Samples 6–10, with loadings reaching around 80 mg/L, show a significant increase in pesticides in rinsing water. This increase could be attributed to intensive pesticide use or insufficient sprayer rinsing. **Rizzati and Capri (2023)** highlighted that intensive agricultural practices, including excessive pesticide use, could lead to increased contamination of surface and groundwater. These results highlight the need to better regulate pesticide use and improve rinsing practices. Samples 11–21, with loadings ranging from 40 to 70 mg/L, show moderate variations that could reflect variable pesticide use or inconsistent rinsing practices. **González-Alcaraz and van Gestel (2023)** showed that inconsistency in agricultural practices could lead to fluctuations in environmental contamination. Samples 22–30, with loadings up to 100 mg/L, show a further increase in pesticides in rinsing water. This trend could indicate increased pesticide use or ineffective rinsing practices. **Wang *et al.* (2023)** highlighted that high pesticide concentrations in rinsing water could have adverse effects on aquatic and terrestrial ecosystems, including disrupting biodiversity and contaminating water resources. These findings call for urgent action to limit pesticide use and improve rinsing techniques. High pesticide loads in some samples raise major concerns for the environment and human health. **Liu *et al.* (2022)** highlighted the risks to human health from pesticide exposure, including through contamination of water and food. Furthermore, **Martínez *et al.* (2023)** showed that pesticides might persist in the environment and affect non-target organisms, including pollinators and soil microorganisms. To reduce the environmental impacts of pesticides, it is essential to review agricultural practices and promote sustainable alternatives. **Potts and Woodcock (2023)** proposed solutions to limit pesticide use, including the adoption of agroecological practices and the establishment of buffer zones to protect aquatic ecosystems. Stricter regulation and better training of farmers are also needed to minimize the dispersion of these substances in the environment. Variations in total pesticide load in rinse waters reflect differences in agricultural practices and raise major concerns for the environment and human health.

3. CONCLUSION

Sprayer rinsing water analyses revealed significant concentrations of pesticides, including glyphosate, chlorpyrifos and mancozeb, as well as marked variations in the total pesticide load. These results highlight the intensive use of these substances in agricultural practices and their potential impacts not only on aquatic and terrestrial ecosystems, but also on human health. The presence of these pesticide residues in rinsing water raises major environmental concerns and calls for more rigorous management of plant protection products. Going forward, it is imperative to promote sustainable agricultural practices, such as agroecology, crop rotation and the adoption of alternative pest control methods. Optimizing sprayer rinsing techniques and creating buffer zones could help limit the dispersion of pesticide residues in the environment. In addition, stronger regulations and increased training for farmers in good practices are essential to regulate the use of these substances.

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