
Research Article

The effects of herbicide application on the properties of agricultural soil in Algeria

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Article history:

Received 28 May 2024

Revised 18 June 2024

Accepted 19 June 2024

Published 09 August 2024

Keywords:

Biological control

Clay-loam soil

Environmental impact

Herbicides

Liquid chromatography

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Abstract

Phytosanitary products, particularly herbicides, are essential for weed control in agriculture. This study examined the concentration and persistence of Pinoxaden residues in different soil textures. Seventy-two soil samples from two farms in Tiaret, Algeria, were analyzed using liquid chromatography (HPLC) to measure herbicide residues. The analysis used a mobile phase of acetonitrile and methanol (50/50, V/V) with a retention time of 2 minutes. Results indicated significant differences in residue persistence based on soil texture. Clay-loam soils showed higher residue persistence, averaging $6.01 \times 10^{-4} \pm 8.7 \times 10^{-5} \mu\text{g/g}$, while sandy soils had lower persistence, averaging $6.4 \times 10^{-5} \pm 5.9 \times 10^{-6} \mu\text{g/g}$. This underscores the impact of soil characteristics on herbicide behavior and the need for tailored management strategies. Despite herbicides' benefits, their environmental impacts are concerning. Persistent residues can contaminate soil and harm ecosystems. Raising awareness among stakeholders about these risks is essential. The study recommends sustainable alternatives, such as biological control methods, to reduce dependency on chemical herbicides. Biological controls offer eco-friendly solutions, promoting ecosystem balance and reducing agriculture's ecological footprint. Implementing crop rotation and other integrated pest management (IPM) strategies can enhance weed control effectiveness while decreasing reliance on chemical herbicides. These practices mitigate environmental risks and improve soil health and agricultural productivity. In conclusion, while herbicides are indispensable in modern agriculture, responsible use and management are crucial for environmental sustainability and the long-term viability of agricultural systems. By adopting sustainable practices and innovative technologies, it is possible to balance agricultural productivity with environmental protection.

How to cite:

Meliani, K., Oulbachir, K., Zemour, H., & Ardjane, T. E. A. (2024). The effects of herbicide application on the properties of agricultural soil in Algeria. *Journal of Agriculture and Applied Biology*, 5(2): 154 - 163. doi: 10.11594/jaab.05.02.02

1. Introduction

The application of phytosanitary products in agricultural activities is currently essential to control a large number of harmful agents and improve crop yields (Suteu et al. 2020). However, the abusive use of such products leads to negative effects on soil quality, microbial community structure, and nutrient turnover rates (Wainwright, 1978; Subhani, El-Ghamry, Changyong, & Jianming, 2000; Chowdhury, Pradhan, Saha, & Sanyal, 2008; Jacobsen & Hjelmsø, 2014). Pesticides comprise organic and inorganic compounds from various chemical classes, contributing significantly to agricultural yield enhancement (Masia, Vásquez, Campo & Picó, 2014). The endeavors concerning sustaining agricultural soil are imperative tasks (Hegazy et al., 2014; Abo-Habaga et al., 2018; Abo-Habaga et al., 2022). Among them, herbicides are available in liquid, granular, and fumigation forms, with liquid formulations commonly used by farmers (Zimdahl, 2018). Pinoxaden, a selective postemergence herbicide introduced by Syngenta Crop Protection AG, belongs to the phenylpyrazoline chemical group and is marketed globally under the trade name AXIAL (Tang et al., 2014).

Cereal crops dominate agricultural practices in Algeria (Bouchafaa & Djeddour-Djaballah, 2022), with approximately 480 phytosanitary products registered and marketed in the country in 2012 (Ayad-Mokhtari, 2012). Soil and water, as key reservoirs of pollution, require thorough consideration by researchers to manage and control environmental quality effectively (Kvicalova et al. 2012). Various environmental organizations, such as the European Union, have established regulations and standards for residue use globally (Agathokleous, 2022).

Currently, several methods and techniques, including gas chromatography (GC), mass spectrometry (MS), and high-performance liquid chromatography (HPLC), are employed for pesticide residue determination (Bai et al. 2013; Ranz, Eberl, Maier & Lankmayr, 2008). This study aims to determine the quantity and persistence of pinoxaden in different soil types in agricultural lands in Tiaret, western Algeria, using the liquid phase chromatography method (HPLC).

2. Materials and methods

2.1 Location of the study area

The study area encompassed two pilot farms, Sidi Abdelkrime and Chaouchaoua, located in the Tiaret region at an altitude of 1,080 m. Situated in a region characterized by diverse relief and influenced by significant air masses, the area experiences varied climatic conditions (Negadi et al. 2018). Figure 1 illustrates the geographic positioning of these two farms within the Tiaret region.

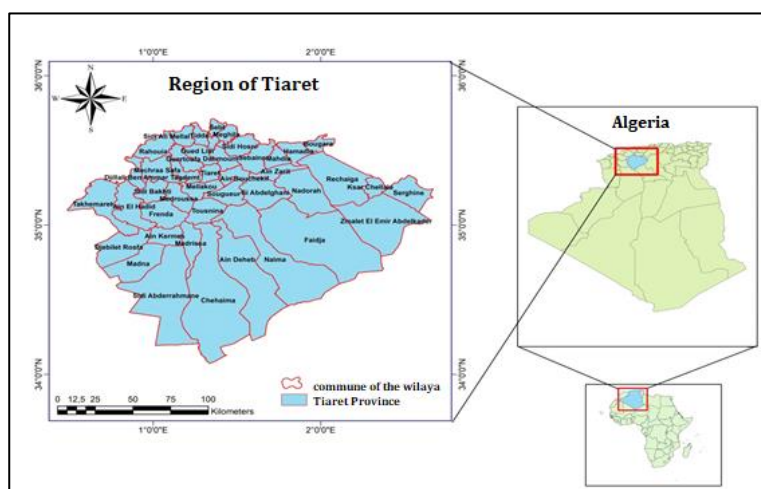


Figure 1. Presentation of the study area Tiaret region, Western Algeria (Zemour, 2022)

2.2 Pinoxaden herbicide standard

In this study, we employed a commercial herbicide formulation containing pinoxaden ($C_{23}H_{32}N_2O_4$), produced by Syngenta Switzerland. This formulation comprises a combination of pinoxaden and clodinafop-propargyl in an emulsion form. Pinoxaden, a selective postemergence herbicide, and clodinafop-propargyl, another herbicidal compound, are key active ingredients utilized in weed management practices. The emulsion form of the herbicide formulation ensures efficient application and distribution, facilitating targeted weed control within agricultural settings. By utilizing this commercial product, we aimed to assess the efficacy and persistence of pinoxaden residues in different soil textures within the agricultural lands of Tiaret, western Algeria.

2.3 Sample collection and preparation

Firstly, soil samples were collected from a depth of 0 to 15 cm using a two-stage helical auger on two separate occasions: the first day and 105 days after herbicide application. These samples were carefully placed in aluminum foil and stored at 4°C until analysis. Subsequently, the samples underwent drying at room temperature in a well-ventilated cupboard to prevent contamination. Finally, they were ground and sieved using a 2 mm diameter sieve.

2.4 Extraction procedures ample collection and preparation

In this study, the method of [Fatoki and Awofolu \(2003\)](#) was adopted with slight modifications. 20 g of homogenized samples were extracted using the Soxhlet apparatus. The extract solution was filtered through a flask and concentrated to remove acetone at 40 °C by a rotary evaporator.

2.5 Extraction procedures ample collection and preparation

The determination and dosage of the herbicide penoxaden was carried out by a liquid chromatograph (HPLC, Shimadzu SPD-10Avp). The mobile phase consisted of HPLC-grade acetonitrile and methanol. The gradient elution was carried out using different volume of acetonitrile and methanol respectively (20:80, 50:50 and 80:20) for 6, 2 and 7 min. The flow rate was 0.7 ml/min. The quantity injected was 20 µl. The measurement was undertaken at 280 nm.

3. Results and discussion

3.1 Physico-chemical characterization of the soil

According to the physicochemical analysis of the soil samples, the results obtained showed a diversity of soil texture (loamy-sandy, clay-loamy, clayey, clayey-sandy and sandy-loamy) with organic matter contents and pH varied widely ([Table 1](#)) shows these results.

Table 1. The average texture of the studied samples

	Soil texture	Loamy	Sandy	Clayey- loamy	Clayey	Clayey- loamy-sandy	Clayey- Sandy	Sandy- loam	
Physical parameter	pH	A	7.22	7.75	7.68	0	0	7.96	7.98
		B	0	7.76	7.79	7.81	7.82	0	7.97
	Electrical conductivity us0cm 105	A	365	442	415	0	0	341	291
		B	0	346	329	313	362	0	298

Continued Table 1

	Soil texture		Loamy	Sandy	Clayey-loamy	Clayey	Clayey-loamy-sandy	Clayey-Sandy	Sandy-loam
Chemical parameter	Assimilable phosphorus ppm	A	259.44	238.52	41.67	0	0	129.63	271.3
		B	0	97.22	2255.63	83.33	50.93	0	32.41
	Organic material %	A	0.58	0.52	0.55	0	0	0.62	0.39
		B	0	0.41	0.57	0.7	0.54	0	0.64
	Total limestone %	A	22.71	51.86	6	0	0	15.86	21
		B	0	2.57	2.14	1.71	2.14	0	37.71
	Active limestone %	A	7.18	9.18	2.15	0	0	4.88	7.15
		B	0	0	0	0	0	0	8.75
	CEC meq/100g of soil	A	20.75	17.05	20.75	0	0	7	9.68
		B	0	20	19.75	18.55	11.58	0	4.05

Based on Table 1, The soil samples collected for analysis exhibited various textures, including loamy, sandy, clayey-loamy, clayey, clayey-loamy-sandy, clayey-sandy, and sandy-loam. Each texture was characterized by different physical and chemical parameters, providing insights into soil composition and fertility. For physical parameters, pH levels ranged from 7.22 to 7.98 across the different soil textures, with sandy-loam soil showing the highest pH at 7.98. Electrical conductivity ($\mu\text{S}/\text{cm}$) varied from 291 to 442, with sandy soil exhibiting the lowest conductivity at 291 $\mu\text{S}/\text{cm}$ and loamy soil recording the highest at 442 $\mu\text{S}/\text{cm}$. Assimilable phosphorus content (ppm) ranged from 32.41 to 2255.63, with the clayey-loamy soil containing the highest concentration at 2255.63 ppm and sandy soil displaying the lowest at 32.41 ppm.

In terms of chemical parameters, organic material content (%) varied from 0.39 to 0.64, with sandy-loam soil having the highest organic material content at 0.64% and sandy soil showing the lowest at 0.39%. Total limestone content (%) ranged from 1.71 to 51.86, with clayey soil exhibiting the lowest limestone content at 1.71% and sandy soil recording the highest at 51.86%. Active limestone content (%) varied from 0 to 9.18, with clayey-loamy soil displaying the highest active limestone content at 9.18% and sandy soil showing no active limestone content.

Furthermore, cation exchange capacity (CEC) in meq/100g of soil ranged from 4.05 to 20.75, with sandy soil exhibiting the lowest CEC at 4.05 meq/100g and loamy soil recording the highest at 20.75 meq/100g. These parameters collectively provide valuable information about soil fertility, nutrient availability, and overall soil health across different soil textures in the study area.

3.2 HPLC analysis and determination of pinoxaden retention time

In Figure 03, the chromatogram displayed a prominent peak corresponding to the Pinoxaden Standard, with a retention time of 2.094 minutes. This peak represents the characteristic height associated with Pinoxaden, a key herbicidal compound under investigation in this study. Interestingly, previous research has reported a different retention time for the peak, specifically at 6.37 minutes, when employing an ultrasonic extractor (Shehzad & Shah, 2013). This discrepancy underscores the influence of extraction methods and chromatographic conditions on the retention time of analytes, highlighting the importance of methodological considerations in analytical studies.

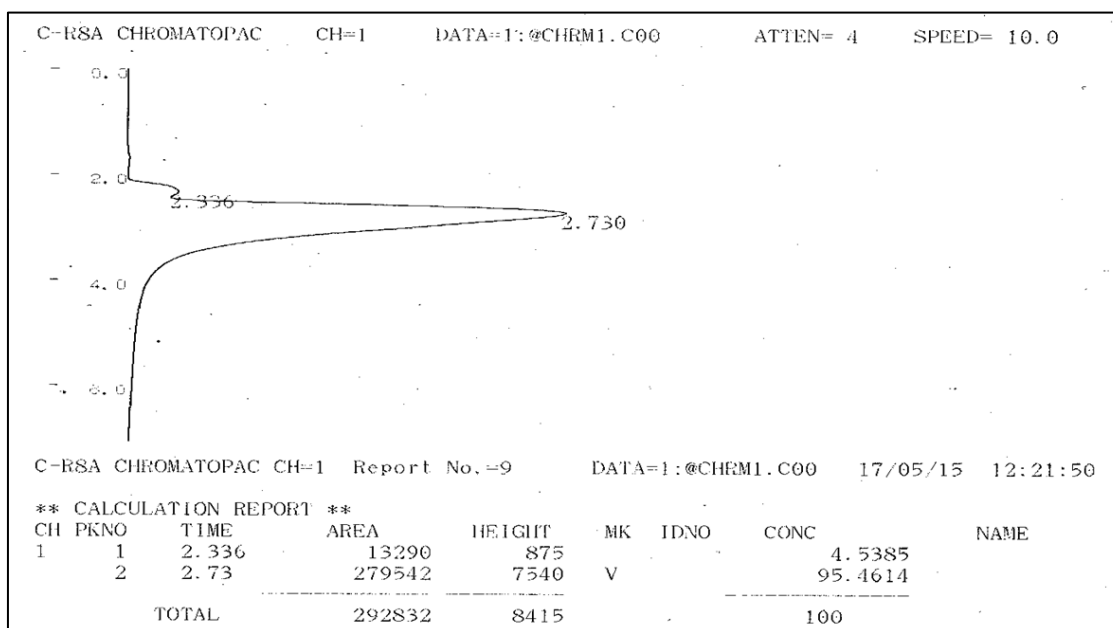


Figure 2. The height peak of the standard pinoxaden

3.3 Dissipation concentration and persistence of pinoxaden

The dissipation and persistence concentrations of the herbicide recorded in the study area are expressed in $\mu\text{g/g}$ (microgram for gram of soil).

3.3.1 Dissipation after application of pinoxaden in Sidi Abdelkrime

The analysis revealed that the average mass concentrations ranged from $(1.35 \times 10^{-2}) \mu\text{g/g}$ to $(1.818 \times 10^{-2}) \mu\text{g/g}$ for clay-silty and sandy soils, respectively (Figure 3). This variation in pesticide dissipation is influenced by climatic factors such as precipitation and soil characteristics including texture, pH, and organic matter content (MO). Singh and Kulshrestha (2006) reported that high pH levels can significantly enhance the infiltration rate of plant protection products and facilitate deeper mobility of herbicides like triasulfuron. Additionally, microbial activity and abiotic factors play crucial roles in extending the persistence of herbicides.

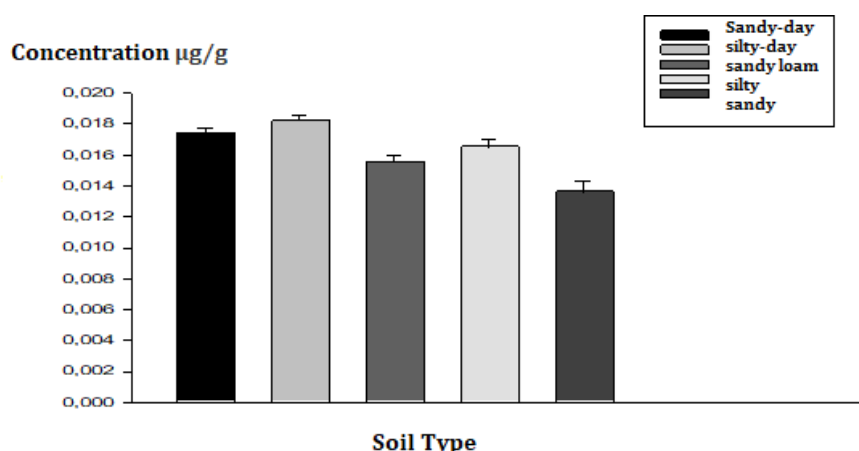


Figure 3. Pinoxaden dissipation concentrations in Sidi Abdelkrime ($\mu\text{g/g}$)

3.3.2. Persistence of pinoxaden residues in the sidi abdelkrime area after the harvest

The obtained results highlighted the highest residue concentrations for clay-loam texture with an average of $4.64 \cdot 10^{-4} \pm 3.45 \cdot 10^{-5} \mu\text{g/g}$ (Figure 4). These soils are characterized by a very low porosity rate, which allows the adsorption of molecules on the soil particles, by a small quantity of organic matter, which is negatively influenced by the presence of soil microorganisms that work on the transformation of organic compounds. The pollution by several elements (NCu and ATZ) produces a significant deceleration in the dispersion of pesticides, due to the interactions of the ATZ-NCu mixture with the particulate fraction of the soil (Paradaa et al. 2019).

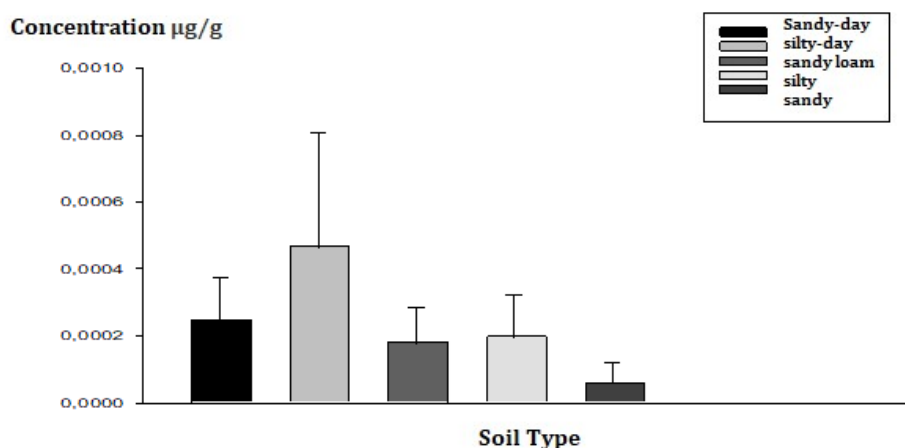


Figure 4. Persistence concentrations of pinoxaden in Sidi Abdelkrime area ($\mu\text{g/g}$)

The chemical composition of the soil has an effect on the persistence of active molecules (Yaduraju, 1994). Additionally, the high amount of organic matter in a soil, allows microorganisms with a higher quantity to maintain their microbial activity in terms of decomposition of herbicides. However, it also promotes the adsorption process of active materials, which stops the transformation process. The degradation of phytosanitary products by microbial activity depends on the texture of the soil. Indeed, a high rate of porosity facilitates access of microorganisms which improves the degradation of pesticides.

3.3.3 Dissipation of pinoxaden after application in Chaouchaoua

The result showed that the highest value of the mass concentrations of the herbicide has been recorded in clayey soil ($1.81 \cdot 10^{-2} \mu\text{g/g}$), while sandy soil registered the lowest mass concentrations with value of around of $1.66 \cdot 10^{-2} \mu\text{g/g}$ (Figure 5).

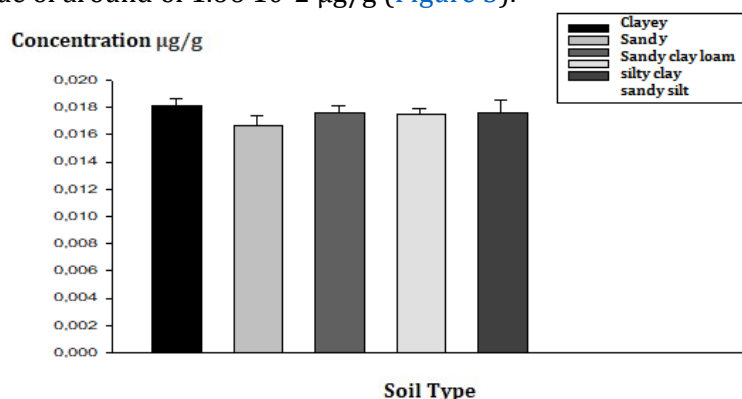


Figure 5. Dissipation concentrations of pinoxaden in Chaouchaoua ($\mu\text{g/g}$)

The presence of clay in the soil has been shown to decrease pesticide levels (Jacobsen et al., 2008). Studies have demonstrated that the degradation of pesticides, such as atrazine, by microorganisms varies depending on soil type and the clay content within the matrix (Besse-Hoggan et al., 2009). Conversely, sandy soils exhibit higher rates of aeration, which promote the volatilization of herbicides. Upon application to the soil, phytosanitary products undergo various reactions that contribute to their dissipation (Hussain et al., 2013). The texture and composition of the soil directly influence the transformation of pesticides.

3.3.4 Persistence of pinoxaden residues after harvest in the Chaouchaou area.

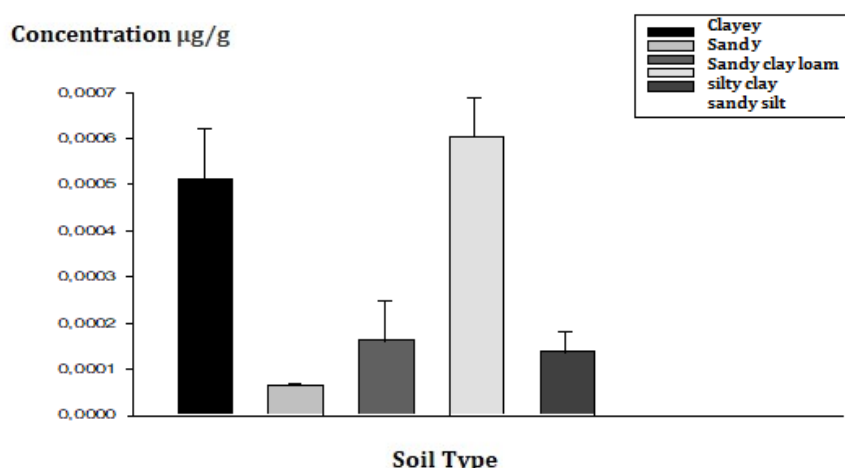


Figure 6. Persistence concentrations of pinoxaden in Chaouchaou (µg/g).

The analysis of the results (Figure 6) reveals a heterogeneous distribution of herbicide residue mass concentrations across different soil types. Specifically, clay-silt soils exhibit significantly higher mass concentrations of residues, with an average of $(6.01 \times 10^{-4} \pm 8.77 \times 10^{-5}) \mu\text{g/g}$. These findings are consistent with previous studies by Marín-Benito et al. (2018) and Tasli et al. (1996), indicating the robustness of the results.

Conversely, sandy soils display lower mass concentrations, averaging $(6.43 \times 10^{-5} \pm 5.9 \times 10^{-6}) \mu\text{g/g}$. This soil type facilitates the release of volatile substances and exhibits weak adsorption on soil particles, as reported by Jablonowski et al. (2010), Jablonowski, Schäffer, and Buraue (2010), and Jablonowski, Modler, Schaeffer, and Buraue (2008). The availability of pesticides is influenced by the bioavailability of active molecules and microbial activities' capacity to transform them.

4. Conclusion

The utilization of Soxhlet or ultrasonic extraction techniques combined with HPLC for determining pesticide residues represents an optimal approach for evaluating soil pollution. In the study area, traces of pinoxaden molecules were detected in soil samples post-harvest, with contamination levels varying by soil structure and texture. Clay-silty soils showed high persistence of herbicide residues, while sandy soils showed lower persistence. These results highlight the importance of understanding pesticide dynamics in agricultural ecosystems to identify potential risks to human health and environmental integrity. Future research should focus on long-term impacts of pesticide use, enhancing strategies to mitigate risks and safeguard public health and environmental quality. Despite a comprehensive approach, several limitations were present in this study. The geographic limitation to Tiaret, western Algeria, may limit generalizability to other regions. The temporal scope included only two time points, which could be expanded with more

frequent sampling. The study included various soil textures but did not cover all soil types found in agriculture. Focusing exclusively on Pinoxaden limits applicability to other herbicides. While HPLC is reliable, including other analytical techniques could cross-verify results. The study also did not extensively examine biological impacts on soil organisms or provide a detailed human health risk assessment. Addressing these limitations in future research will improve understanding of herbicide behavior and impacts, leading to better management practices and policies for environmental sustainability and public health protection.

Acknowledgement

The authors express their gratitude to all the personnel of the laboratories within the Department of Nature and Life Sciences at Tiaret University (Algeria). Their assistance and support throughout this study were invaluable and greatly appreciated.

Author's declaration and contribution

The authors certify that they have no conflicts of interest. Author contributions across all phases of this research article were diverse and crucial, spanning from idea inception and methodological refinement to data collection, analysis, manuscript drafting, critical review, project supervision, and highlighting a comprehensive collaborative effort.

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