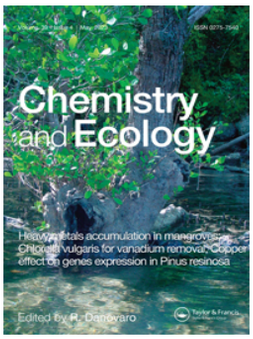

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NOTE

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Assessing acetamiprid and chlorpyrifos pesticide concentrations in water and sediments across macadamia orchard and communal area small reservoirs

Thendo Mutshekwa[a], Lutendo Mugwedi[a], Babra Moyo[b,c], Ntakadzeni E. Madala[b], Ryan J. Wasserman[d,e,f], Farai Dondofema[a] and Tatenda Dalu [f,g]

[a]Aquatic Systems Research Group, Department of Geography and Environmental Sciences, University of Venda, Thohoyandou, South Africa; [b]Department of Biochemistry and Microbiology, Faculty of Science, Engineering and Agriculture, University of Venda, Thohoyandou, South Africa; [c]Department of Food Science and Technology, Faculty of Science, Engineering and Agriculture, University of Venda, Thohoyandou, South Africa; [d]Department of Zoology and Entomology, Rhodes University, Makhanda, South Africa; [e]School of Science, Monash University Malaysia, Bandar Sunway, Malaysia; [f]South African Institute for Aquatic Biodiversity, Makhanda, South Africa; [g]School of Biology and Environmental Sciences, University of Mpumalanga, Nelspruit, South Africa

ABSTRACT

Pesticides are well known for their persistence in the environment their slow degradation and high toxicity. Aquatic environments, while not the target of many pesticide applications, often receive these chemicals from their catchments through runoff dynamics. Here, we assessed pesticide concentrations of acetamiprid and chlorpyrifos in water and sediment across macadamia orchard and communal area reservoirs in the Levubu area, South Africa, using liquid chromatography tandem mass spectrometry. Analysis of acetamiprid and chlorpyrifos associated with sediments in macadamia orchard reservoirs revealed mean pesticide concentrations of 14.48 µg L^{-1} and 5.67 µg L^{-1}, respectively, whereas, in communal area reservoirs both pesticides were not detected. Acetamiprid was not detected across reservoir water, whereas the mean pesticide concentration of chlorpyrifos of 6.51 µg L^{-1} (macadamia orchard) and 0.13 µg L^{-1} (communal area) were detected. Significant differences were observed for chlorpyrifos concentrations in water samples between macadamia orchard and communal area reservoirs, whereas acetamiprid and chlorpyrifos indicated non-significant differences in sediments. The results indicate that macadamia orchard reservoirs are highly contaminated by acetamiprid and chlorpyrifos. Consequently, these pesticides can alter water quality and ecosystem functioning by reducing species diversity, adjusting community structure, altering energy flow and nutrient recycling.

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CONTACT Thendo Mutshekwa thendzamuchekwa@gmail.com Aquatic Systems Research Group, Department of Geography and Environmental Sciences, University of Venda, Thohoyandou 0950, South Africa; Tatenda Dalu dalutatenda@yahoo.co.uk South African Institute for Aquatic Biodiversity, Makhanda6140, South Africa; School of Biology and Environmental Sciences, University of Mpumalanga, Nelspruit1200, South Africa

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Introduction

In the last few decades, pesticides have been used on an increasingly wider scale throughout the world [1]. Pesticides are highly associated with anthropogenic activities [2]. As indicated by Elhatip et al. [3], agricultural fields activities contribute increased pesticides contamination in water bodies than residential and/or communal areas activities. In agricultural fields, chemicals are used to control insects (pesticides) and weeds (herbicides) due to their effectiveness [4]. Regardless of their agricultural benefits, pesticides are often considered a serious threat to the environment because of their persistence [2,5]. These pesticides can cause profound changes to the quality of the environment [6]. This is due to their persistence which allows them to remain for years in the environment, as well as their toxicity. The widespread use of pesticides contaminates various aquatic ecosystems, including sediments, water, and biota [7,8]. These pollutants accumulate in aquatic organisms, directly from polluted environments (water, sediment) or indirectly via the food chain, with a potential risk to humans [9].

Pesticides are compounds in continuous evolution, characterised by their diversity, physico-chemical properties, and concentrations. Organophosphates (OPs) and neonicotinoids pesticides are very toxic and persistent in the environment and tend to accumulate in the living organisms. The OPs are a class of pesticides such as chlorpyrifos, several of which are highly toxic [10]. Until the twenty-first century, chlorpyrifos were among the most widely used pesticides available [11]. Neonicotinoids such as N-(6-chloro-3-pyridylmethyl)-N′-CYANO-N-, better known as acetamiprid, are now the most widely used pesticides in the world [12,13]. They act systemically, travelling through plant tissues and protecting all parts of the crop, and are widely applied as seed dressings [13]. These pesticides were introduced because of their reduced persistence in the environment relative to the organochlorine pesticides. Nevertheless, concerns about bioaccumulation, acute and chronic toxicity persist. Furthermore, the impact of pollution of both soil and water by such chemicals is often difficult to observe unless there is a gross accidental or intentional spill [14]. Therefore, the occurrence of these pesticides and their toxicity require an analytical technique for quantification [15].

Rapid increases in macadamia plantations and demand for macadamia nuts have resulted in increased usage of pesticides worldwide over the last decade [16]. South Africa is the largest macadamia producer globally (50,133 hectares under cultivation and 50,000 tonnes harvested annually), followed by Australia and the USA, with China and some South American and other African countries growing fast in production [17]. In South Africa, the industry is predominantly spread over the Mpumalanga (44%), KwaZulu-Natal (28%) and Limpopo (20%) provinces [17]. Due to low pesticide utilisation in communal areas, the reservoirs within these areas can serve as sites for comparison with macadamia orchard reservoirs of pesticide effects on biotic and ecosystem dynamics at local scales. With increased pesticide usage in the macadamia orchards, it is necessary to understand the occurrence of pesticides in reservoirs. For that, the knowledge of occurrence of the pesticides as sediment and surface water contaminants is imperative. Therefore, the aim of the study was to highlight the main aspect of pesticides in freshwater environment i.e. their occurrence, in the sediment and surface water among macadamia orchard and communal area reservoirs. However, pesticide levels require quantification as a first step in such comparative studies. As part of a larger study on pesticide dynamics in

agricultural landscapes, we used liquid chromatography–tandem mass spectrometry (LC-MS/MS) to determine concentrations of acetamiprid and chlorpyrifos in water and sediment of macadamia orchard and communal area reservoirs. Solid phase extraction (SPE), based on C_{18} cartridges, was used for the extraction of the compounds of interest. It was hypothesised that pesticide concentrations will vary between the two reservoir types and that macadamia orchard would contain increased concentrations of acetamiprid and chlorpyrifos in both water and sediment habitats due to its high use within the orchards compared to the communal areas.

Methods and materials

Study area

The samples were collected once on the 14th of November 2021 from macadamia orchard and communal area reservoirs in Limpopo province, South Africa. Two macadamia orchard reservoirs (Site 1, 23°06′31.6″S, 30°15′54.2″E; site 2, 23°06′54.5″S, 30°15′46.5″E) are located in the southern foothills of the Soutpansberg Mountain range, 20 km east of the town of Makhado (previously Louis Trichardt), were sampled. The reservoirs were selected due to the presence of large macadamia orchard plantations and excessive use of pesticides. Two communal area reservoirs were similarly sampled i.e. site 3, (22°56′43.0″S, 30° 23′01.9″E) was located in Phiphidi village, while site 4 (22°59′11″S, 30°36′16.19″E) was located between Tshikunda, Phiphidi and Duthuni villages. Both communal area reservoir sites are approximately 10 km from Thohoyandou, Limpopo province, South Africa, and

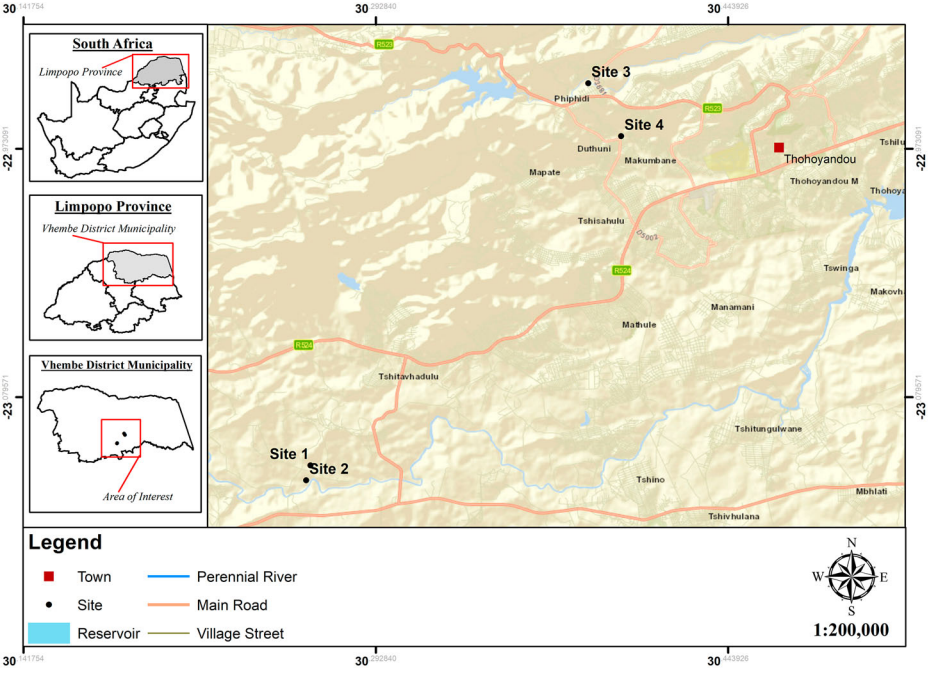

Figure 1. Location of the sample collection sites (Site 1 and 2 – macadamia orchards; Site 3 and 4 – communal area) in Vhembe District, Limpopo province of South Africa.

are mainly used for domestic water supply and irrigation (Figure 1). The distance from macadamia orchard reservoirs to communal reservoirs is ~ 21.67 km and communal areas are comprised of increased surrounding residence compared to communal orchards. At each reservoir, triplicate ($n = 3$) water and sediment samples were collected.

Apparatus

The SPE was performed with Cleanert S C_{18} (6 mL, 500 mg) cartridges (Stargate Scientific, South Africa). The chromatographic measurements were done using LC-MS/MS system (Shimadzu, Corporation, Kyoto, Japan) consisting of triple quadrupole mass spectrometer (LC-MS/MS-8045) equipped with turbo ion spray ionisation source in the positive ionisation mode. The multiple reaction monitoring (MRM) method was used for absolute quantification of the targeted pesticides The chromatographic separation of the compounds of interest was achieved on a Shim-pack Velox SP-C_{18} column (100 × 2.1 mm, 2.7 µm). A gradient elution using binary solvents i.e. phase A (1 mM ammonium formate) and phase B (acetonitrile) in 0.1% formic acid was used. The flow rate was 0.4 mL min^{-1} with the binary gradients: 1–2 min 5% B, 2–3 min 5% B, 3–4 min 95% B, 4–5 min 5% B, and 5–6 min 5% B. The column oven temperature was maintained at 55°C and the injection volume was 3 µL.

Reagents and chemicals

All pesticides were of pestanal grade standards. Acetamiprid and chlorpyrifos were obtained from Sigma-Aldrich, South Africa. Methanol (LC-MS grade, 99%) and dichloromethane (99%) were obtained from Sigma-Aldrich, South Africa. The individual stock solutions of the analytes were prepared by dissolving 10 mg of the standards in 10 mL methanol to obtain a concentration of 1 mg mL^{-1}. The working standard solutions of concentrations ranging from 0.1 to 500 µg L^{-1} were then prepared by proper dilution of the stock solutions with methanol. For SPE, Cleanert S C_{18} (6 mL, 500 mg) were supplied by Stargate Scientific (South Africa).

Sample collection and pre-treatment

Water sampling

Water variables pH, conductivity (µS cm^{-1}), total dissolved solids (mg L^{-1}), and temperature (°C) were measured on the day of sampling using a multiparameter handheld waterproof Cyber Scan 300 (EUTECH Instruments, Singapore). A total of 12, 1 L glass bottles were used during the collection of water samples (4 sites × 3 replicates). After collection, water samples were immediately placed on ice in a cooler box and transported to the laboratory. Upon arrival, collected water samples were filtered (vacuum of <5 cm Hg) through a 0.7 µm Whatman GF/F filter to remove particulate matter from the background matrix, preventing the SPE cartridge blockage. After filtration, water samples were stored in 1 L polyethylene bottles in the until ready for analysis.

Sediment sampling

Approximately 2 kg sediments samples were collected (depth 5–10 cm) using a plastic shovel from each reservoir (4 sites × 3 replicates), placed into polyethylene zip–lock

bags, and labelled according to sites. After collection, sediment samples were immediately transported to the laboratory in a cooler box, frozen at −20°C, lyophilised, grind with a pestle and mortar sieved through 125 µm mesh to obtain a homogeneous material, and stored at −20°C until extraction. This was done to increase the surface contact between the extraction solvent and sample [18].

Sample extraction

Sediment extraction

The sieved sediment was weighed, and 12 × 0.5 g sediments samples (n = 12, 4 sites × 3 replicates) were added to 35 mL of methanol and placed into a shaker for 12 h (overnight). After shaking, each sample was filtered (vacuum of <5 cm Hg) through a 0.7 µm Whatman GF/F filter into 50 mL centrifuge. For LC-MS/MS, the samples were further filtered using a syringe filter (0.22 µm) into 2 mL amber vials.

Water extraction

For water extraction, SPE based on Cleanert S C_{18} cartridges was utilised. Prior to extraction, water samples were removed from the refrigerator and allowed to reach ambient temperature. The SPE sorbents were first pre-conditioned with 10 mL dichloromethane, 10 mL methanol and 10 mL distilled water. Before the cartridges dried out, water samples (1 L) were passed through the SPE cartridges using a vacuum manifold that was maintained at constant pressure. Retained analytes were eluted with 5 mL methanol followed by 5 mL of acetonitrile following a procedure by Bonansea et al. [19]. The eluate was collected in 10 mL glass vials and filtered using a syringe filter (0.22 µm pore size) into 2 mL amber vials for LC-MS/MS analysis.

Statistical analysis

A two-way ANOVA was used to assess the differences in water variables (i.e. pH, conductivity, total dissolved solids and temperature) and pesticide concentrations (i.e. acetamiprid and chlorpyrifos) across sites, after testing for homogeneity of variances (Levene's test, $p > 0.05$) and normality of distribution (Shapiro–Wilk test, $p > 0.05$). Sites were used as explanatory variables, while water variables, and pesticide concentrations were the response variables. For this model, significant variables were further tested using the Tukey post-hoc tests performed via estimated marginal means. In all analyses, significance was inferred at $p < 0.05$ and all statistical analyses were performed using IBM SPSS version 28.0.0.0.

Results

Water variables

Across sites, a high mean temperature (28.9°C) was observed in the macadamia orchard reservoirs, whereas, high mean pH (7.08), conductivity (356.6 µS cm ^{1}) and total dissolved solids (179.9 mg L^{-1}) were observed in the communal area reservoirs (Figure 2). Overall, water variables differed significantly, i.e. pH (range: 6.3–7.1), conductivity (range: 213.3–

356.6 µS cm^{-1}), total dissolved solids (range: 127.7–179.9 mg L^{-1}) and temperature (range: 24.2–28.9°C). Significant differences were observed for pH ($p < 0.001$) across sites, whereas temperature ($p = 0.841$) conductivity ($p = 0.510$) and total dissolved oxygen ($p = 0.990$) indicated non-significant differences. Pairwise comparisons for pH indicated significant differences for sites 1 *vs* 2 ($p = 0.018$), sites 2 *vs* 4 ($p < 0.001$) and sites 3 *vs* 4 ($p = 0.021$).

Pesticide concentration in water and sediments

The residue analysis results of acetamiprid and chlorpyrifos associated with water and sediments in the macadamia orchard and communal area reservoirs are presented in Table 1. Acetamiprid and chlorpyrifos were found to be common in the macadamia orchard as compared to communal area reservoirs. In sediment samples from the macadamia orchard, the mean concentrations of acetamiprid and chlorpyrifos were 14.48 µg L^{-1} and 5.67 µg L^{-1}, respectively, whereas, in the communal area reservoirs both pesticides were not detected. Additionally, in water samples, acetamiprid was not detected across macadamia orchards and communal area reservoirs. In contrast, chlorpyrifos were detected with mean concentrations of 6.51 µg L^{-1} and 0.13 µg L^{-1} in the macadamia orchard and communal area reservoirs, respectively. Non-significant differences were observed for both acetamiprid ($F = 0.668$, $p = 0.595$) and chlorpyrifos ($F = 0.669$, $p = 0.594$) in sediment samples across sites. Moreover, in water samples, significant differences were observed chlorpyrifos ($F = 13.914$, $p = 0.002$) across sites. Pairwise multiple comparisons for chlorpyrifos in water samples highlighted differences for sites 1 *vs* 3 ($p = 0.005$), sites 1 *vs* 4 ($p = 0.004$), sites 2 *vs* 3 ($p = 0.017$), and sites 2 *vs* 4 ($p = 0.013$). The chlorpyrifos in macadamia and communal reservoir water was within the

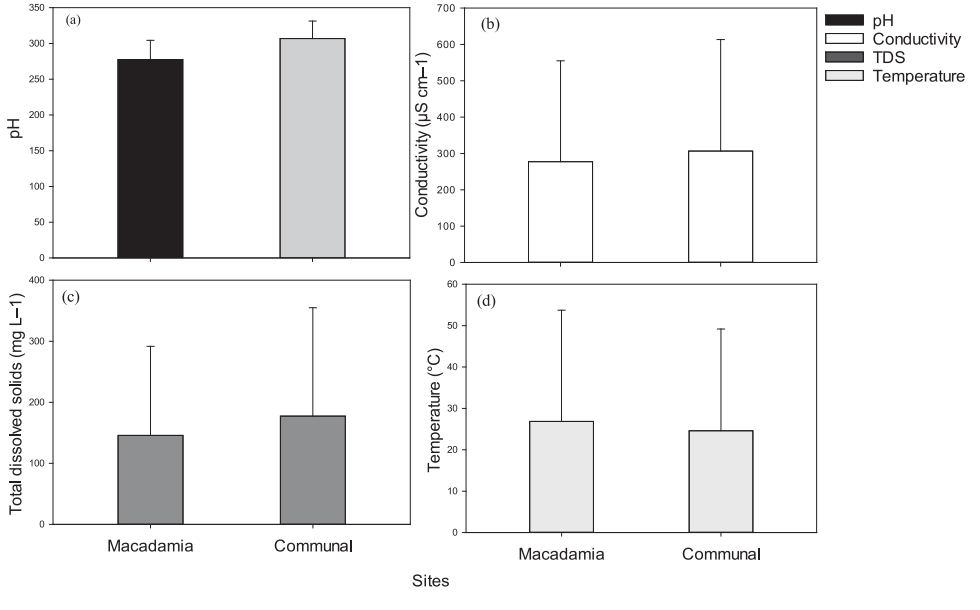

Figure 2. Mean (±standard deviation) water variables measured across macadamia orchard and communal area reservoirs during sampling event.

Table 1. Mean ± SD pesticide concentrations (μg L^{-1}) of acetamiprid and chlorpyrifos in water and sediments from the macadamia orchard and communal area reservoirs.

	Acetamiprid		Chlorpyrifos	
Sites	Sediment	Water	Sediment	Water
Macadamia	14.48 ± 9.72	n.d.	5.67 ± 3.59	6.51 ± 0.93
Communal	n.d.	n.d.	n.d.	0.13 ± 0.08

Note: n.d.: not detected.

recommended chlorpyrifos levels (0.03–100 μg L^{-1}) as indicated by Li and Fantke [20] for the European Union guidelines.

Discussions

To better comprehend the fate of pesticides in the aquatic environment together with their potential impact that they might pose to aquatic organisms, it is critical to know their concentrations in the water and sediments. Thus far, previous studies [21–23] have demonstrated that high pesticide concentrations occur in aquatic ecosystems associated with increased anthropogenic activities and that contaminants decline with decreasing anthropogenic activities. Similarly, the present study demonstrated that macadamia orchards drive increased pesticide concentrations in nearby reservoirs, compared to communal areas. The study also highlights that sediments accumulate increased pesticide concentrations compared to water. This is because most of the pesticides are deposited on the bottom of the water bodies forming sediment layers, whereas pesticides in the surface water are easily washed away, thus sediments act as a pollution sink [24,25]. However, sediments can also act as a pollution source, as retained contaminants can be bioaccumulated by sediment-dwelling organisms and subsequently pose a risk to higher trophic organisms through biomagnification among the food chain. Moreover, retained pollutants can be released at any time via re-suspension by natural processes or human actions.

This study showed high pesticide concentrations of chlorpyrifos and acetamiprid in sediments than in water. Furthermore, macadamia orchard reservoirs were associated with increased concentrations, whereas communal area reservoirs had the least concentrations. As stated by Halbach et al. [26], water and sediments-associated pesticide concentrations are often much higher than recorded and significantly higher in reservoirs surrounded by increased anthropogenetic activities. Moreover, acetamiprid was not detected in water samples across macadamia orchard and communal area reservoirs, whereas Chlorpyrifos was detected in the macadamia orchards (6.51 μg L^{-1}) and communal area reservoirs (0.13 μg L^{-1}). The increased sediment-associated pesticide concentrations in the macadamia orchard reservoirs are not surprising given the fact that sediments are an important sink for various pollutants which also play a significant role in the remobilisation of contaminants in aquatic systems under favourable conditions and in interactions between water and sediment [27]. Overall, the accumulation of these pesticides in sediments in the macadamia orchard reservoirs can pose a direct toxicological risk for organisms living and feeding on reservoir sediments due to chronic exposure [28]. The lower concentrations of both pesticides in the water samples might be attributed to the fact that the input of pesticides in water is a function of suspended particulate concentrations [29]. Although low, these concentrations can build up in the

water, get magnified through the food chain, and enter aquatic organisms that are hazardous for human consumption [30]. Chlorpyrifos, concentrations in water samples in the macadamia orchards were like those reported by Hossain et al. [31], and chlorpyrifos ranged from 3.27 to 9.31 μg L^{-1} in agricultural fields. However, several studies have recorded decreased chlorpyrifos concentrations. For instance, Singh et al. [30], recorded chlorpyrifos concentrations ranging from 0.01 to 0.04 μg L^{-1}, which corresponded with our findings in communal area reservoirs.

Like other ecological studies, this study had several limitations. For instance, in the current study, we collected samples once in triplicates in order to quantify sediments and water pesticide concentrations in the macadamia orchard and communal area reservoirs in water and sediments. Moreover, the samples were collected during rainy season. Nonetheless, the quantity of pesticides in agricultural fields is known to depend on climate or seasons and the abundance of pests within an area [32]. For instance, rainy seasons and high temperatures drive increased pest abundances, thus increasing the usage of pesticides and pesticide concentrations in nearby reservoirs [33]. As indicated by Nguyen et al. [34] and Nyantakyi et al. [35], increased pesticide concentrations during rainy seasons compared to other seasons may be due to higher runoffs with increased precipitation of suspended solids containing the pesticide residues in the run-off. The quantity of pests across various seasons may also contribute to the quantity of pesticides being used as pests are known to favour humid, rainy weather since they reproduce more frequently and become more active [36]. Consequently, future studies should seasonally quantify the concentrations of acetamiprid and chlorpyrifos in the macadamia orchard and communal area reservoirs to strengthen the understanding of these pesticides and their potential impact on aquatic organisms. However, our results from the preliminary foundation that will enable us to understand the occurrence, distribution and concentrations associated with macadamia orchard reservoirs within the tropical regions of the world.

Conclusions

From our findings, it can be concluded that reservoirs are continuously contaminated with pesticide runoff from the nearby macadamia orchards and/or agricultural fields. For instance, the present study showed that macadamia orchard reservoirs are highly contaminated by acetamiprid and chlorpyrifos pesticides. As detailed in the discussion, it is very much clear that concentrations of these pesticides varied in water and sediments across macadamia orchards and communal area reservoirs with macadamia orchards, indicating increased concentrations. The increased concentrations in the macadamia orchards are most likely due to the effective use of these pesticides during pest control for macadamia plantations. The contamination of macadamia orchard reservoirs by these pesticide residues from macadamia orchards thus poses a greater impact on the aquatic ecosystems. This may lead to deleterious effects on the aquatic organisms and the public dependent on the water supply from the contaminated reservoirs.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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Data availability statement

The datasets generated and/or analysed during the current study are not publicly available as they are part of a larger study that is currently ongoing but are available from the corresponding author on reasonable request.

Notes on contributors

Thendo Mutshekwa recently completed his PhD Environmental Sciences studies at the University of Venda and was awarded an NRF Postdoctoral Fellow.

Lutendo Mugwedi is a Senior Lecturer of Environmental Sciences at the University of Venda and Chair of the Vhembe Biosphere Reserve, South Africa.

Babra Moyo is Technical Officer and a PhD Chemistry candidate at the University of Venda, South Africa.

Ntakadzeni E. Madala is an Associate Professor of Biochemistry and currently Acting Deputy Dean Teaching and Learning, Faculty of Science, Engineering and Agriculture, University of Venda, South Africa.

Ryan J. Wasserman is an Associate Professor of Zoology at Rhodes University and also a Research Associate, South African Institute of Aquatic Biodiversity.

Farai Dondofema is a Chief Technician and Lecturer at the University of Venda.

Tatenda Dalu is a Senior Lecturer of Aquatic Ecology at University of Mpumalanga and also a Research Associate, South African Institute of Aquatic Biodiversity.

ORCID

Tatenda Dalu http://orcid.org/0000-0002-9019-7702

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