Seasonal Variation and Health Risk Assessment of Selected Pesticide Residues in Shallow Groundwater Water in Gokwe-Nemangwe, Zimbabwe

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Received: 5/03/2024 **Revised: 25/04/2024** **Accepted: 10/05/2024**

While pesticides application has caused improved agricultural yields, their use has raised concerns of potential harm to the health of humankind. This study focused to assess seasonal variability of health risk linked with pesticide residues to humans through shallow groundwater. To assess water quality, samples were collected from shallow groundwater sources once in each of the rain and dry spells of 2020 and analyzed for five pesticide residues including amitraz, dimethoate, omethoate, endosulfan and endosulfan sulphate. Liquid chromatography tied with tandem mass spectrometry was used to assess residues of pesticides in water samples. Health risk evaluation was achieved using the Human Health Risk Assessment model for children and adults on the residues through ingestion. All the pesticide residues tested were detected in the shallow groundwater samples in both spells. Endosulfan had the greatest concentration, with an average concentration of 0.009 mg/L varying from 0.005 mg/L to 0.012 mg/L, in the wet season. Dimethoate and omethoate highest mean concentration was 0.007 mg/L in the wet period, which exceeded the maximum allowable limit advised by the World Health Organization. The least concentration level was 0.006 mg/L for amitraz and endosulfan sulphate. Dimethoate and omethoate contributed to non-carcinogenic risks for children in both the wet and the dry seasons, calculated at the level of 3.5 and 2.5 respectively. The same pesticide residues were also a risk to adults in the wet season with a similar HQ value of 1.17. Pesticide residues contamination of groundwater is imminent and results in human health risk via ingestion. There is a need therefore to assess health risks through well-planned preventive measures, including risk assessment, thorough monitoring, and regulating shallow groundwater wells.

Keywords: Groundwater, Hazard quotient, Human Health Risk Assessment, Ingestion exposure, Pesticide residues, Toxicity, Water quality

https://dx.doi.org/10.4314/etsj.v15i1.8

INTRODUCTION

Pesticides are valuable innovations in agriculture hence widely used to control, eliminate, and assuage any pest or weeds (Mergia *et al*., 2021; Şimşek Uygun & Albek, 2022; Tudi *et al*., 2021). Furthermore, global population growth has increased the demand for agricultural products (Masindi & Foteinis, 2021), hence, heavy reliance on pesticides to intensify both harvest and quality products. Additionally, pesticides are also utilized in the public health sector to prevent and manage insect-borne illnesses like malaria (Zinszer & Talisuna, 2023). However, increased pesticides use coupled with indiscriminate handling have led to contamination of drinking water (Materu *et al*., 2021; Matowo *et al*., 2020). Individual exposure to low dose of residues of pesticides through polluted water may lead to their accumulation in human bodies as well as damaging vital functions of the human system (Eissa *et al*., 2021). Several pesticides were directly reported in body fluids (Afata *et al*., 2021; Filippi *et al*., 2021; Iqbal *et al*., 2020; Kuang *et al*., 2020; Laubscher *et al*., 2022; Norén *et al*., 2020; Qi *et al*., 2022; Witczak *et al*., 2021), consequently, causing chronic conditions including human reproductive disorders (Interdonato *et al*., 2023; Silva *et al*., 2023); cancers (Habeeb *et al*., 2022; New-Aaron *et al*., 2021; Panis *et al*., 2022; Perera-Rios et al., 2022; Shankar et al., 2019); endocrine disruption (Interdonato et al., 2023; Stephens *et al*., 2022); autism (Biosca-Brull *et al*., 2021; von Ehrenstein *et al*., 2019), developmental disorders (Addissie *et al*., 2020), neurological disorders (Laubscher *et al*., 2022; Vellingiri *et al*., 2022).

Water is needed for various functions in the body, and its consumption exposes humans to pesticides (Pathak *et al*., 2022). Shallow groundwater wells are some of the sources of drinking water to rural smallholder farmers. Unfortunately, such water sources are vulnerable to pesticide pollution from several processes including spray drift, percolation, atmospheric deposition, overland and drain flows (Bexfield *et al*., 2021; Sjerps *et al*., 2019). Contamination is exacerbated through pesticide malpractices including washing spray containers, reuse of pesticide waste containers to fetch water, and having open wells just in the fields where spraying occurs (Basopo & Muzvidziwa, 2020; Demi & Sicchia, 2021).

Furthermore, meteorological factors including precipitation and wind direction, water solubility and farming management practices also influence the prevalence of pesticide residues in shallow groundwater (Bexfield *et al*., 2021; Tudi *et al*., 2021). Thus, shallow groundwater sources have been reported to have more pesticide residues contamination compared to deep wells sources (Bexfield *et al*., 2021). Likewise, the residues of pesticides were detected in high concentrations in the shallow subsurface water during the rainy spell than in the dry spell (Materu *et al*., 2021; Merga *et al*., 2021). This is because wet season brings increased rainfall, which can lead to mobilization and transport of pesticide residues from agricultural fields into shallow groundwater, thus increasing pollution (Bexfield *et al*., 2021; Materu *et al*., 2021). Movement is heighted where soils are more permeable (Bexfield *et al*., 2021). Consequently, farmers who rely on shallow groundwater are likely to experience increased exposure to pesticide residues through consumption of the contaminated groundwater. On the other hand, during the dry season, shallow groundwater may experience reduced dilution capacity due to limited water (Tudi *et al*., 2021). Therefore, pesticide residues that have accumulated in the groundwater over time may become concentrated.

While accumulated within the groundwater some pesticide residues undergo degradation, thereby producing new compounds which may not only be more persistent than the parent pesticides (Chidya *et al*., 2022; Syafrudin *et al*., 2021), but more toxic. For instance, Mitrović *et al*., (2019), and Guo *et al*. (2021), described increased toxicity of omethoate compared to that of dimethoate in separate studies. Earlier on, Gao *et al*. (2017), had reported greater persistence of amitraz degradation products than the parent compound, leading to long term exposure to low doses (Pathak *et al*., 2022). Despite health challenges associated with pesticide compounds and their degradation products, more continue to be used in farmlands thereby contaminating groundwater sources worldwide (Berni *et al*., 2021; Bexfield *et al*., 2021; Duttagupta *et al*., 2020; Oyekunle *et al*., 2022). For instance, dimethoate was detected in groundwater in different localities, 0.09 µg/L in Al Kharj, Saudi Arabia (El Alfy & Faraj, 2017); and 0.177 µg/L in Niayes-Dakar, Senegal (Diop *et al*., 2019). Similarly, Twinomucunguzi *et al*., (2021), reported several pesticide residues in both surface and groundwater samples in Uganda. These findings provide evidence of water contamination by pesticide compounds.

Analysis of residues of pesticides in water is a key tool for monitoring the levels of human exposure to the residues and further determine health risk. Given this, several studies worldwide notably (Affum *et al*., 2018; Berni *et al*., 2021; Derbalah *et al*., 2019; Oyekunle *et al*., 2022), employed hazards quotient approaches to estimate pesticide residue risks. Proof of water pollution has been reported in Zimbabwe (Basopo & Muzvidziwa, 2020). Therefore, health risk could be high since consumption of shallow groundwater assumed to be potentially polluted by residues of pesticides occurs. However, there is no information on health risk based on exposure of humans to pesticides through shallow groundwater consumption. This study, therefore, provides baseline information on pollution levels of pesticides in shallow groundwater in Ward 11 of Gokwe-Nemangwe, and further assesses health risk for children, and adults due to the pesticide residues. The findings of the study provide useful information to public health personnel to promote environmental contamination management and find solutions to mitigate the negative consequences of pesticide residues on human health.

MATERIALS AND METHODS

Study Area

Gokwe-Nemangwe is situated in North-West Zimbabwe, with a population estimate of 11 760, of which 5 340 are children (ZIMSTAT, 2021). The area is within region III agro-ecological zone with geographical co-ordinates lying between latitudes 18° 11' 00"S and 18° 12' 17" E longitudes, respectively (Mubvekeri et al., 2014). The area experiences a warm and temperate climate with an average annual temperature of 21.6°C, suitable for cotton production (ZIMSTAT, 2021). Whilst Zimbabwe receives an average annual precipitation of 666.65 mm, Gokwe-Nemangwe being semi-arid to arid conditions receives a maximum of 268.85 mm of rainfall, annually between October and February (ZIMSTAT, 2021). The dry period ranges from May to September with July being the driest month experiencing almost zero precipitation. The average amount of rainfall in this area influences the growing of cotton. The most prevalent activity in the area is rain-fed agricultural, growing cotton as one of the main crops. The cash crop contributes substantially to the area's economy. For easy access to drinking water, and irrigation during summer, the smallholder farmers hand-dig shallow groundwater wells 0.2 to 3 m, in field or along rivers Gwavi, Tare and Svisvi. Due to volatilization, pesticide residues are carried into the groundwater and cause contamination. The Gokwe-Nemangwe area is shown in Figure 1.

Chemicals and Reagents

All the reagents were of analytical reagent grade and used without further purification. Methanol, acetonitrile, methanoic acid, ammonium formate and ultrapure quality water were all of LC-MS high quality analysis, obtained from Sigma-Aldrich (Bulawayo-Zimbabwe). The pesticides amitraz, dimethoate, omethoate, endosulfan and endosulfan sulphate were pure standards of 99 % purity procured from Sigma Aldrich Chemical Company.

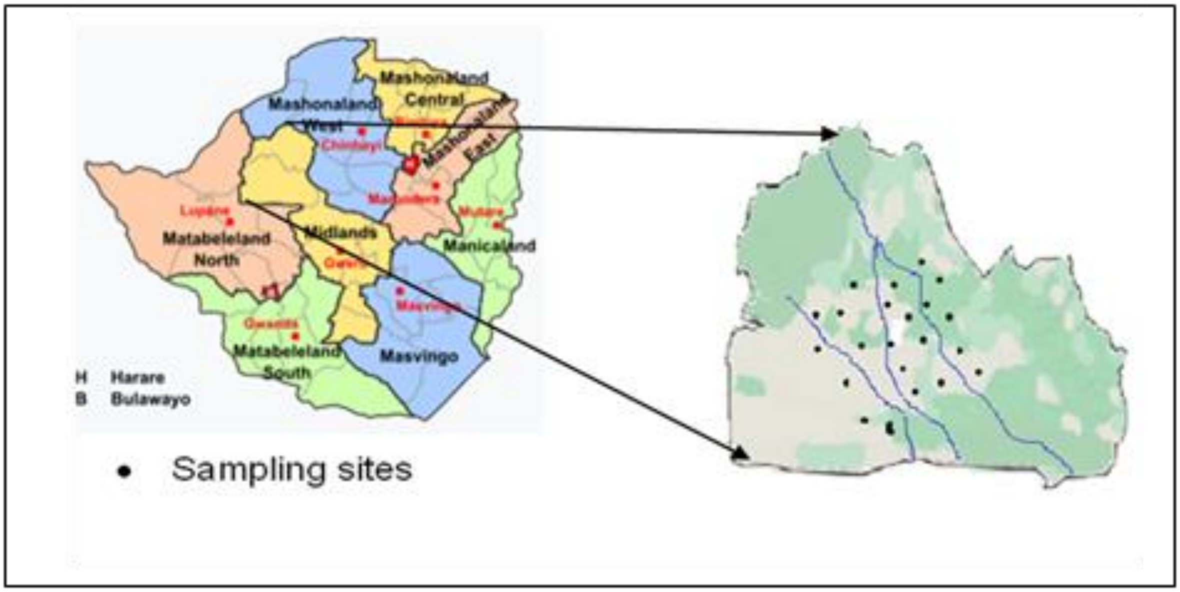

Figure 1: Zimbabwe showing the location of Gokwe-Nemangwe and Sampling Sites

Sample Collection and Storage

Shallow subsurface water samples were collected using a bailer at half the water depth for wells below a metre deep, and at 30 cm deep for wells deeper than a metre. Samples were collected in duplicates in clean labware containers twice, once in the rainy spell (February) and in the dry spell (September). A total of 62 samples were collected. All samples were transported in cooler boxes to the laboratory where they were kept at 4 °C awaiting further investigative procedures. Water parameters, comprising temperature, and pH, were measured at each collection point, using handheld instruments. Average pH values of 7.22 and 7.71 and temperature of 21℃ and 24 ℃ respectively in the wet and dry seasons were recorded.

Stock Solution Preparation

Stock solutions of five target pesticides (amitraz, dimethoate, omethoate, endosulfan and endosulfan sulphate) were prepared by dissolving 10 mg of solid standards pesticides in 10 mL of acetonitrile plus 0.1% methanoic acid to achieve solubility of the poorly soluble pesticide residues. For calibration curve, different concentrations (10, 20, 50, 100, 500, 1000, and 2000 µg/L.) were made ready with suitable dilution of the stock solution and kept at 4 °C in darkness.

Sample Preparation and Separation

Sample preparation was achieved by pipetting 10 mL of water into 50 mL centrifuge tubes, followed by addition of sodium chloride solution until saturation, then vortexed for I minute. Further, acetonitrile was added with vortexing, followed by centrifugation at 4000 rpm for 10 minutes at room temperature. An LC–MS/MS detector was used to separate the mixture, on a Synergi Fusion-RP-100 Å Phenomenex analytical column, (50 x 2.0 mm, 2.5 µm particle size) and precolumn Security Guard Phenomenex Fusion-RP cartridges with (4 x 2.0 mm, 2.5 µm particle size), cartridges. Mobile phase ‘A’ comprised de-ionized Water/Methyl alcohol in the ratio (90:10, v/v), plus 5 mM ammonium formate, and mobile phase ‘B’ was Methyl alcohol/deionized water (90:10, v/v) ratio, plus 5 mM ammonium formate. The moveable phase had a flow rate of 0.4 mL/min over 11 minutes, with an additional 2 min equilibration prior to each run. The chromatographic column temperature was controlled at 25 °C. The sample was injected in a volume of 10 µL. The eluate was gathered, passed through a filter, and directly introduced into the LC-MS/MS systems (Pietrzak *et al*., 2019).

Mass Spectrometry Evaluation and Operational Conditions

The LC-MS investigation was operated on a QTRAP ® 5500 LC-MS/MS system with Turbo V ^{TM} source, in positive polarity with an electron multiplier voltage set at 5500 V, and the Multiple Reaction Monitoring (MRM) mode operating a triple quadrupole MS/MS. Source ionization temperature was set to 400°C, curtain gas 30 psi, ion source gas I (GS1 nebulizer gas) was 60 psi, while source gas 2 (GS2 auxiliary gas) was 60 psi. The MRM detection window was 120s, while the target scan time was 0.5 s.

Validation of the Method

Parameters measured for validation included sensitivity, accuracy, linearity, selectivity, and precision (Pietrzak *et al*., 2019). Calibration curves were obtained by spiking the pesticide analytes in the blank matrix at concentrations varying from 10 to 2000 µg/L comprising at least six calibration levels. Three replicates for each concentration level were prepared. Accuracy and precision were assessed at three concentration levels 10, 100, and 2000 µg/L in triplicates. Limit of quantification (LOQ) was confirmed as the smallest concentration with a signal/noise (S/N) ratio of at least 10 concentrations producing a peak with (S/N ≥ 10). Selectivity was evaluated through analyzation of sequential reagent blank samples, evaluating corresponding responses in the retention times of the analytes.

Assessment Health Risks to Humans

A model for assessing health risks was drawn from the World Health Organization (World Health Organization, 2017), to approximate non-cancer-causing risk using the relationships following:

$$\text{CDI} = \frac{Cw \ x \ IR \ x \ EF \ x \ ED}{BW \ x \ AT} \qquad \text{[Equation 1]}$$

where CDI = chronic daily intake in mg/kg/d), Cw is pesticide residue concentration in the shallow groundwater in mg/L, IR is groundwater ingestion rate (L/day/person) (adult, 2 L and children, 1 L; EF is frequency of exposure (365 days/year); ED is contact duration (year) (for children is 6 years, for adults 70 years), BW is the weight of adult body (adult 60 Kg and children 10 Kg), AT = regular lifespan (for children: AT = 2190 days, for grown persons: AT = 25550 days), AT is the average lifetime for non-carcinogen exposure (ED × 365 days/year). An estimation of non-cancer-causing risk, hazard quotient (HQ) was estimated by use of the equation given below:

$$\text{HQ} = \frac{CDI}{RfD} \qquad \text{[Equation 2]}$$

where RfD is the reference dose of the pesticide residue through oral exposure route (mg/kg/day). The values of RfD for the pesticide residues were obtained from the United States of America Protection Agency, Integrated Risk Information System (United States Environmental Protection Agency, 2022). A risk is posed if the HQ is greater than 1.

Statistical Analysis

The general distribution of residual pesticide concentration in water samples was analysed using descriptive statistics. A student's t-test was utilized to compare the means of residues of pesticide levels in shallow subsurface water between the two seasons. Within this investigation, p value < 0.05 was considered statistically significant. Health risk was determined using the risk assessment model equations.

Validation

Linearity was acceptable with the association coefficient value, r > 0.9985 for all substances obtained from calibration curves matched to the matrix. There were no interference peaks detected on blank samples. LOQs were established for the residues of pesticides at 0.01 mg/l. Recovery was in the range of 77.0 to 116%, at all studied concentrations, the relative standard deviation (RSD%) was within the acceptable range ≤ 20%.

RESULTS AND DISCUSSION

Seasonal Variation of Pesticide Residues in Shallow Groundwater Samples

Table 1 shows differences of pesticide residue levels in shallow groundwater between the rainy and dry spells. Levels of pesticide residues in the rainy spell were significantly above those of dry spell samples. Endosulfan had the highest concentration level of 0.009 mg/L in the wet season. In the dry spell levels of pesticide residues were below the detection limit.

Table 1: Seasonal fluctuations of pesticide residues in shallow groundwater samples

Pesticide residue	Mean concentration in (mg/L)			
	Wet Season	Dry Season	t-value	p-value
Amitraz	0.006	0.005	2.949	0.003*
Dimethoate	0.007	0.005	4.340	7.45E-05*
Omethoate	0.007	0.005	4.046	0.0001*
Endosulfan	0.009	0.005	7.327	1.83
Endosulfan sulphate	0.006	0.005	2.948	0.003*

*Denotes statistically significant ($p < 0.05$)

Higher concentration levels of residues of pesticides described in the rainy spell reflect heightened runoffs from agricultural fields with increased rainfall. Solid particles that are suspended in water containing pesticide residues in the runoff upsurge with increased precipitation amounts (Tudi et al., 2021). In Akkar Plain, Northern Lebanon, Chaza *et al*., (2018), also reported increased levels of residues of pesticide in groundwater in the rainy spell. Similarly, Sishu *et al*., (2022), reported dimethoate concentration of below detection limit in shallow subsurface water during both the rainy spell and dry spell as in Table 2. Furthermore, the short half-life of dimethoate and amitraz justifies why they were detected in shallow subsurface water in the wet spell than in the dry spell (Anićijević *et al*., 2022; Sishu *et al*., 2022). Occurrence of pesticide residues in shallow groundwater in this study, even in small quantities may thus be a cause for concern as this leads to increased health risk to the consumers (Bexfield *et al*., 2021). Prolonged exposure to pesticides in drinking water can lead to various health issues, including increased risk of cancer, reproductive problems, and neurological effects (Habeeb *et al*., 2022; Laubscher *et al*., 2022; New-Aaron *et al*., 2021; Vellingiri *et al*., 2022). Currently the country has a challenge of heighted chronic disease incidence (Das, 2021), exposure to carcinogenic pesticide residue could be contributing to this. The findings underscore the importance of monitoring and regulating pesticides used to protect human health.

Large-scale agricultural activities in the wet spell might also have led to higher levels of residues of pesticides in the water. This is because with cotton growing large amounts of pesticides are used as the crop yield is extremely affected by pest attacks (Zinyemba *et al*., 2020). Similarly, Chaza *et al*., (2018), detected large amounts of organochlorines and organophosphates in groundwater at concentrations 58.9, 44.6, and 5.6 µg/L, respectively, in Akkar, northern Lebanon and they were associated with large-scale agriculture activities.

In addition to intensify use and increased runoffs, current use might have also led to the detection of higher levels of residues of pesticide in the wet spell compared to dry spell. Largely, the main origin of residues of pesticides to shallow groundwater wells is agrarian runoffs and drift from application of pesticides is through spraying (Berni *et al*., 2021; Tudi *et al*., 2021). Therefore, heightened pesticides applications in the wet season along with activities of farming may result in higher pesticide residue levels in the shallow groundwater sources. Studies comparing pesticide residues in groundwater systems between wet and dry season also reported higher pesticide residue concentration levels in the wet season (Merga *et al*., 2021; Sishu *et al*., 2022; Twinomucunguzi *et al*., 2021), Table 2.

Table 2: Seasonal Pesticide Residue Levels of Previously Reported in Literature

Pesticides residue detected	Analytical technique(s) used for detection	Season of detection and concentration (µg/L)		References
		Wet	Dry	
Amitraz	LC-MS/MS	<0.0066	<0.0066	(Twinomucunguzi *et al*., 2021)
Endosulfan sulphate	LC-MS/MS	<0.0037	<0.0037	(Twinomucunguzi *et al*., 2021)
Dimethoate	GC-MS	0.63	0.54	(Merga *et al*., 2021)
Endosulfan	GC-MS	1.11	0.76	(Merga *et al*., 2021)
Endosulfan	GC	>0.1	>0.1	(Sishu *et al*., 2022)
Dimethoate	GC	<LOD	<LOD	(Sishu *et al*., 2022)

These authors also suggested intensified pesticides use being associated with groundwater pollution. Furthermore, Calista *et al*. (2022), and Zikankuba *et al*. (2019), asserted that increased pesticide uses in the farming season coupled with malpractices in pesticide application add to the high contamination burden in the wet season. Malpractices may include use of inappropriate dosage, poor disposal of waste containers and residual pesticides, washing of pesticide containers at water sources, accidental spills, use of counterfeit pesticides and use of a combination of pesticides in a single spray (Basopo & Muzvidziwa, 2020; Kearns, 2020; Materu *et al*., 2021). Washing of pesticide containers could have contributed to the detection of the poorly adsorbed and fast degrading pesticide residues including amitraz and dimethoate, in higher concentrations levels in the wet season (Anićijević *et al*., 2022). The presence of the pesticide residues in the shallow groundwater leads to their consumption thereby contributing to health risk.

Groundwater contamination has been ubiquitously reported elsewhere. Correspondingly, 24 µg/L dimethoate levels were reported in groundwater in California (Van Scoy *et al*., 2016). Similarly, in Sub-Saharan Africa. Affum *et al*., (2018), reported contamination of groundwater by both banned and current use pesticides in Ankobra Basin, Ghana. In Nigeria, Ile-Ife, Osun State, organochlorines heptachlor (14.60 µg/L) and methoxychlor (12.60 µg/L) residues of pesticides were reported in groundwater (Oyekunle *et al*., 2022). Likewise, Berni *et al*. (2021), reported the occurrence of chlorinated residues of pesticides in groundwater of Saïss plains, in Morocco. These findings confirm groundwater contamination by residues of pesticides, though not seasonally specified.

Comparatively, dimethoate and omethoate concentration levels in this study, shallow groundwater is not safe for human consumption in the wet season, as levels are above the maximum residue levels (MRLs) permitted by the World Health Organization (World Health Organization, 2017). The findings, thus, have direct relevance particularly in public health, as they address the potential exposure of individuals in Gokwe-Nemangwe to pesticides through drinking water. Furthermore, these findings could have unique implications for regulatory and policy measures related to pesticide use and water quality standards as well as informing decision-making processes aimed at protecting water resources and public health. Likewise, the findings of this study warrant interdisciplinary collaboration involving collaborative working between environmental scientists, public health experts, water resource management professionals, and regulatory authorities. Such interdisciplinary approach is crucial for interaction between pesticides, groundwater, and human health. Differences in concentrations of pesticides detected in groundwater may vary from place to place due to specific geographic location and contextual factors. Different regions may have varying pesticide use patterns, hydrogeological conditions, and water management practices, leading to unique findings and implications for each location.

Health Risk Assessment

Tables 2 and 3 provide a summary of health risk assessments for humans due to pesticide residues in the shallow subsurface water samples upon drinking by children and adults for the wet and dry spells correspondingly. The health risks were evaluated in terms of non-cancer-causing health hazards for amitraz, dimethoate, omethoate, endosulfan and endosulfan sulfate.

Table 3: Non-carcinogenic risk (HQ) for the pesticide residues in groundwater during the wet season

Pesticide residue	CDI		RfD	HQ	
	Children	Adults		Children	Adults
Amitraz	6.0×10^{-4}	2.0×10^{-4}	0.0025	0.24	0.08
Dimethoate	7.0×10^{-4}	2.0×10^{-4}	0.0002	3.5	1.17
Omethoate	7.0×10^{-4}	2.0×10^{-4}	0.0002	3.5	1.17
Endosulfan	9.0×10^{-4}	3.0×10^{-4}	0.0060	0.15	0.05
E/sulphate	6.0×10^{-4}	2.0×10^{-4}	0.0060	0.1	0.03

The non-cancer-causing health risks were projected by hazard quotients (HQs) linked to the intake of the shallow subsurface waters. In children, HQs larger than 1 were dimethoate and omethoate; 3.5 wet spell and 2.5 in the dry spell respectively. In adults, HQs of dimethoate and omethoate were 1.17 in the wet season and other pesticide residues indicated insignificant health risk in both wet and dry seasons.

Hazard quotient above 1 is an indicator that there are non-carcinogenic health risks linked with the consumption of the shallow groundwater (United States Environmental Protection Agency, 2022; World Health Organization, 2021).

Table 4: Non-carcinogenic risk (HQ) for the pesticide residues in groundwater during the dry season

Pesticide residue	Mean Conc. mg/L	CDI		RfD	HQ	
		Children	Adults		Children	Adults
Amitraz	0.0050	5.0×10^{-4}	1.67×10^{-4}	0.0025	0.2	0.07
Dimethoate	0.0050	5.0×10^{-4}	1.67×10^{-4}	0.0002	2.5	0.83
Omethoate	0.0050	5.0×10^{-4}	1.67×10^{-4}	0.0002	2.5	0.83
Endosulfan	0.0050	5.0×10^{-4}	1.67×10^{-4}	0.0060	0.08	0.03
E/sulphate	0.0050	5.0×10^{-4}	1.67×10^{-4}	0.0060	0.08	0.03

Comparatively greater HQs detected in children as contrastive to adults are consistent with the assertion that children are the more vulnerable population to the analysed environmental contaminants (Etzel, 2020).

HQs for the children were higher in the rainy spell in comparison to the dry spell due to increased exposure to harmful chemicals. As alluded to earlier, increased rainfall increases runoff with pesticides residues to groundwater sources thereby increasing exposure through ingestion. Similarly, Kruć-Fijałkowska *et al*. (2022), categorized the wet season as a period of amplified exposure of water to contamination, due to increase rainfall. Furthermore, the wet season coincides with increased pesticide application to control pests and diseases (Merga *et al*., 2021). This can result in higher levels of pesticide residues in shallow groundwater wells and consequently, increasing the non-cancer-causing risks linked with pesticide residue exposure as observed in the study (Materu *et al*., 2021).

While low concentration readings of some residues of pesticides in the shallow subsurface water did not give rise to HQs above I, prolonged exposure to low doses, however, may likely trigger the on-set of chronic health effects. Organochlorine pesticide residues including endosulfan and endosulfan sulphate are classified as carcinogens, thus long-term exposure to their low doses may lead to bioaccumulation in body tissues (Afata *et al*., 2021; Filippi *et al*., 2021; Iqbal *et al*., 2020; Kuang *et al*., 2020; Laubscher *et al*., 2022; Norén *et al*., 2020; Qi *et al*., 2022; Witczak *et al*., 2021), eventually inducing carcinogenicity (Habeeb *et al*., 2022; New-Aaron *et al*., 2021; Panis *et al*., 2022; Perera-Rios *et al*., 2022; Shankar *et al*., 2019), and other conditions (Interdonato *et al*., 2023; Silva *et al*., 2023; Stephens *et al*., 2022; Addissie *et al*., 2020; Biosca-Brull *et al*., 2021; Laubscher *et al*., 2022; von Ehrenstein *et al*., 2019). Therefore, more attention needs to be given to the groundwater taken in by both adults and children to prevent such health risk. Furthermore, more health risk studies should be conducted to inform public health officials.

The HQs for the adults drinking contaminated shallow groundwater with dimethoate and omethoate were above one (1) in the wet season. However, in the dry season the HQ values were below 1 for all pesticide residues in both the rainy and the dry spells. The findings are consistent with the observations of Affum *et al*. (2018) who had earlier assessed the risk for both five banned and nine current-use pesticides and reported values of HQ lower than 1 in all cases. However, health risk to children due to dimethoate and omethoate were observed in both seasons. The findings in this study agree with the findings of previous studies. For instance, Zhang *et al*. (2021), reported a non-carcinogenic risk of omethoate with an HQ of greater than 1. Likewise, Huang *et al*. (2019), reported that dimethoate could pose risk to infants and children. Similarly, Liu *et al*. (2015), observed a high dimethoate non-carcinogenic risk of more than 1, with specific HQ values up-surging from 1.995 to 5.094 between 2011 and 2013.

Comparatively, high HQs values reported for children in this study as differing to adults were congruous with the claim that children are more susceptible than adults to the investigated ecological pollutants. This is because children ingest proportionately more water per unit size than adults (Hauptman & Woolf, 2017). Furthermore, the risk posed by the pesticide residues maybe exacerbated by children's fewer natural defences (Shah, 2021), and "vulnerability at certain windows" during their development and growth when their target organs may be more liable than those of adults indicating possible adverse health effects (Huang et al., 2019). As a result, exposure to pesticide residues at certain windows in their development may result in autism (Biosca-Brull *et al*., 2021), and other conditions. Therefore, if this situation continues unchanged, especially on the concentrations of dimethoate and omethoate in shallow groundwater sources, children are perpetually at risk (Cortés-Iza & Rodríguez, 2018). Toxicity of dimethoate and omethoate is manifested through inhibition of the enzyme acetylcholinesterase through phosphorylation of the esterase site causing subsequent accumulation of acetylcholine (Caragea *et al*., 2018; Cortés-Iza & Rodríguez, 2018). In turn, this has caused dimethoate and omethoate to be correlated with adverse reproductive and neurodevelopmental outcomes (Pascale & Laborde, 2020). Various studies revealed that these pesticide residues have endocrine-disrupting impacts (Wee & Aris, 2017), cytotoxic effects (Cortés-Iza & Rodríguez, 2018), mutagenic (Caragea *et al*., 2018), and immunosuppressive impressions (Rajak *et al*., 2021). Some of these health challenges are therefore likely to be induced in the children of Gokwe-Nemangwe since the risk observed was above 1. Even though toxic, both pesticide residues are not bio-accumulative in the body, as they are readily broken down to compounds that are removed through urine (Caragea *et al*., 2018).

CONCLUSION

This study has revealed shallow subsurface water contamination by the selected residues of pesticides in Gokwe-Nemangwe. Furthermore, the pollution was higher in the wet spell than in the dry spell. Comparing the residual concentration of the studied pesticides with the World Health Organization MRLs, the residual level of dimethoate in the water was above its respective MRL for drinking water. Analysis of health risk assessment showed that dimethoate and omethoate had non-carcinogenic risk for both children and adults in the wet spell. Therefore, continuous monitoring of the shallow groundwater is needed to prevent the smallholder farmers and their families from being exposed to harmful effects of pesticide residues both now and the nearest future.

Conflicts of Interests

The authors have not declared any conflict of interests.

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