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ASSESSMENT OF HERBICIDES UPTAKE BY SOIL AND TRANSLOCATION IN TO DIFFERENT MAIZE SEGMENTS

SANDISIWE GLADNESS ZONDO[1], PRECIOUS MAHLAMBI[2*]

[1]KwaZulu-Natal Department of Agriculture and Rural Development, Hilton, South Africa
[2]University of KwaZulu-Natal, Scottsville, Pietermaritzburg, South Africa

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Increased agricultural operations result in increased usage of various pesticides to safeguard crops, however, this is done without paying attention to the effects of the amounting potential harm to both humans and the environment. In this present study, a structured study was conducted on the uptake of *atrazine, mesotrione, 2,4-dichlorophenoxyacetic acid (2.4-D),* and *glyphosate* herbicides from contaminated soil and translocation into different maize segments. It was observed that *2.4-D* was least absorbed by the soil, however, all the studied herbicide showed high absorption in the leafy segment of the maize plant due to the high polarity of the leaf cuticle. *Glyphosate* showed a high absorption rate in soil, roots, stalk, and leaves while *mesotrione* was highly absorbed in corn and tassels in all treatments. The absorption rate of the herbicide increased with increasing growth days. The higher treatment concentration (0.75 µg/L) showed elevated accumulation with the highest concentration (1.0 µg/L) observed for *glyphosate* in leaves after 140 days and high *mesotrione* in corn (0.51 µg/L) and tassel (0.42 µg/L) observed after 120 days. The PTI values of all treatments were >1 however, the HI data were below 100% indicating minimal possible health risk linked to the intake of these crops by both adults and children.

Key words: pesticides, toxicity index, health risk assessment, maize, GC-FID

The cropping system that sustains agricultural fields without reducing soil fertility and controlling pests, weeds, and disease problems is essential for agricultural practices. The increasing population globally increases the demand for agricultural production and to meet these increasing demands, the cropping system must improve crop yields on both commercial farms, and small scale farms and maintain them. However, uncontrollable weed growth is a hindering factor, and also mechanical control is difficult and time-consuming with machinery as well as laborious by hand (Monteiro & Santos 2022). Consequently, the usage of chemical weed controllers has received great interest in the agricultural sector due to the minimal cultivation of crops. This, in turn, reduces soil erosion, the power necessary to work agricultural soil and improves microbial biomass, soil structure, and organic matter maintenance in the agricultural soils (Hellerstein & Vilorio 2019).

The application of herbicide in the agricultural field is during pre-planting, pre-emergence, and initial and late post-emergence (Hossain *et al*. 2019). Maize is a herbicide tolerant crop and the use of herbicide has intensified in maize production. Herbicide are applied to the soil, absorbed by the maize roots, and translocate to the stalk, leaves, tassel as well as maize cob. Tassel produces pollen, which is

Sandisiwe Gladness Zondo, KwaZulu-Natal Department of Agriculture and Rural Development, PBag X6005, Hilton, 3245, South Africa
Precious Mahlambi (*Corresponding author), Department of Chemistry, University of KwaZulu Natal, PBag X01, Scottsville, Pietermaritzburg, 3209, South Africa. E-mail: Mahlambip@ukzn.ac.za

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transported to the silk for the production of maize seed, in the leaves is where photosynthesis occurs which produces for the maize plant while the stem is where the cob grows. Therefore, the contamination of any of these matrices by pesticides may result in the contamination of the maize cob and thus be consumed by humans. It is believed that herbicides have a threatening effect on humans due to their non-biodegradable nature in the soil (Gill & Garg 2014). It is, therefore, important to monitor the uptake of herbicides by agricultural matrices to ensure that the concentration in the final product is within the levels that cannot cause harm to human health after consumption.

The absorption and uptake of organic compounds from the soil by crop roots are a crucial pathway for them to accumulate chemicals. In general, the availability of an organic compound in soil and its ability to diffuse over the root surface depends on its availability in the growing media (Wang *et al*. 2021). The bioavailability of chemicals in soil is primarily absorbed by soil structures followed by uptake and storage in plant roots, then translocated to aboveground tissues through plant transpiration. Many factors govern the influence of the uptake and transport of organic chemicals in soil, including cultivation conditions, plant species soil type, and the physicochemical characteristics of compounds (Li *et al*. 2019). However, under the same experimental conditions, physicochemical factors such as the molecular weight, octanol/water partition coefficient (log K_{ow}), and water solubility influence the absorption and translocation capabilities of compounds of the same plant. Li *et al*. (2021) studied the uptake, translocation, and subcellular distribution of *triadimefon, tebuconazole*, and *epoxiconazole* pesticides in rice. The findings showed that rice roots could take up the three triazole pesticides, although their distribution in plant tissues differed. In rice roots, the three pesticides accumulated in the following order: *epoxiconazole* (4.26 µg/L) > *tebuconazole* (2.63 µg/L) > *triadimefon* (1.37 µg/L), but in rice shoots, the order was reversed: *triadimefon* (0.48 µg/L) > *tebuconazole* (0.40 µg/L)>*epoxiconazole* (0.21 µg/L).

The assessment of herbicide residues in soil and other agricultural matrices has been conducted using microwave-assisted extraction (MAE) method (Kalogiouri *et al.* 2021; Feng *et al*. 2022). The advantage of this approach is the ability to extract analytes from different matrixes using lesser solvent and extraction duration (Sharma & Zalpouri 2022). Its simplified operation procedure converts electromagnetic waves absorbed by solid materials into thermal energy. The cell then magnifies as pressure is applied to the solid cell wall, the cell ruptures as pressure rises, and the organic residues in the solid cell leach into the organic solvent. The most popular chromatographic technique is gas chromatography (GC), which primarily separates substances based on their volatilities. Polar, non-polar, volatile, and readily vaporized substances can be studied using the GC technique. Pesticide characterization using GC is frequently coupled with particular detectors such as an electron capture detector (ECD), a flame photometric detector (FPD), a nitrogen phosphorus detector (NPD), and a flame ionization detector (FID) (Karapınar 2021). In this study, the most used herbicides (a*trazine, 2,4-D, glyphosate,* and *mesotrione*) in maize production in the KwaZulu-Natal Department of Agriculture were studied. The MAE technique was used to extract the herbicide from the sample matrix to study their uptake and translocation into different maize parts (roots, stalk, tassel, leaves, and maize cob). The extracted herbicides were then characterized with a gas chromatography-flame ionization detector. To the best of our knowledge, this study was conducted for the first time.

MATERIAL AND METHODS

Chemicals and materials

Analytical grade acetone (70%), n-hexane (95%), dichloromethane (99%) were sourced from Sigma-Aldrich (Steinheim, Germany). The deionized water was produced using Aqua Max Basic 360 Series water purification system (Trilab, Durban, SA).

Maize plantation

The 0.25 g/L, 0.50 g/L, and 0.75 g/L (w/v) treatment solutions of *glyphosate, 2,4-D, atrazine,* and *mesotrione* herbicides were prepared in water. Experiments plots were designed as a randomized block, in the experimental field, 12 plots were prepared by 6 m^2 each for the three replicates of

each of the four treatments including the control. Three prepared treatments were applied at the post-emergent while the control was left untreated and sixteen treatments were conducted. The Knapsack pressure spray (TWK, Howick, SA) with a four nozzles bar was used with a constant pressure of 200 KPa providing, a 1 m/s application velocity with the nozzles positioned at a 70 cm height from the soil. In each plot, six rows were prepared with 100 cm spacing in between and the seeds were sown at a depth of 2.54 cm in October 2021. The maize was allowed to grow for 5 months to allow full maturity. The plant inter distance was 24 cm and the irrigation was done weekly. Hoeing and weeding were conducted after three weeks in the early stages of seeding establishment.

Sampling and sample storage

Soil and plant samples were collected from the experimental field. Soil samples were sampled on the upper surface of the soil (0 – 0.15 m surface layer) using an auger. The plant samples were collected every 4 weeks after plantation until the harvesting stage. Samples were stored in polyethylene bags and transported to the laboratory. Upon arrival, soil samples were air-dried at room temperature for 36 hours, then pulverized and passed through a 2.0 mm sieve. The maize plant samples were washed with tap water to remove soil particles and finally rinsed with deionized water. The water was then wiped out with a paper towel, then left overnight to dry on the pre-cleaned bench top while ensuring no contact between the sample and bench top surface. The plants were then subdivided into different plant segments (roots, stalk, tassel, leaves, and maize corn). Thereafter, all plant samples were freeze-dried on Lyophilizer (Antech scientific, South Africa), followed by microwave digestion.

Microwave extraction procedure

A 1 g sample was weighed into the extraction vessel followed by the addition of 12 mL of the hexane-acetone mixture (1:2, v/v). The vessels were closed and the hand agitated for 1 minute. Extraction was conducted using a microwave set eat 400 W (100% output) irradiation power and the temperature program used was ramped from 0 to 160°C for 2 minutes, holding at 160°C for 8 minutes. After extraction, the vessels were allowed to cool for 15 minutes at room temperature before opening. The supernatant was filtered through a Buchner funnel packed with a GF/C grade glass microfiber filter obtained from Whatman (Maidstone, UK) for the removal of suspended solid particulates. The samples were concentrated to dryness under a gentle stream of nitrogen overheating water at 40°C. The residues were re-dissolved in 100 µL dichloromethane, and 1 µL of the extracted sample was injected into the GC-FID for analysis without a need for further cleanup procedure (Merdassa *et al.* 2013).

Gas chromatography – flame ionization detector conditions

The chromatographic studies were assessed using a Bruker scion Model 436 GC from Gibbs Technologies (Durban, South Africa) along with a flame ionization detector (FID). Herbicide separation was performed on a Gibbs Technologies VF-5ms capillary column (length 30 m, 0.25 mm i.d, 0.25 m film thickness). The injector and detector temperatures were both set at 250ºC. The temperature program was as follows: a starting temperature of 60ºC was maintained for 1 minute, ramped at a rate of 30ºC/min to 150ºC/min and held for 4 minutes, then ramped at a rate of 15ºC to 250ºC and held for 5 minutes. The carrier gas used was nitrogen, and the injection mode was split with a purge duration of 0.10 min and a split of 1:50. The sample injection volume was 1µL and the FID was supplied with 30 mL/min hydrogen and 300 mL/min synthetic air.

Pesticide toxicity index (cumulative risk)

Cumulative risk assessment is an imperative way to study hazards related to various residues. The toxicity quotient (TQ) is used to evaluate the toxicity level of the individual pesticide and is calculated from the ratio between each pesticide residue concentration and the corresponding maximum residue levels (MRLs). The pesticide toxicity index (PTI) which is a screening method for determining the degree of toxicity exposure to complex pesticide mixtures, is then calculated as the total of the TQ for each pesticide compound, as shown in equation 1.

$$TQ = \frac{C}{MRL} while\ PTI = \Sigma\ TQ \quad (1)$$

Where: C represents the measured individual

pesticide residue concentrations (µg/L), and MRL represents the individual pesticide maximum residue limits (µg/L). PTI tolerable target of less than 1.00, stances no detriment to the consumer (Ramadan *et al*. 2020; Shalaby *et al.* 2021).

Health risk assessment

The health risk index (HI) is used to characterize the health risk (HR) assessment of consumers posed by the intake of pesticide-contaminated vegetables. As shown in equation 2, the HI is calculated by dividing the estimated daily intake (EDI) by the corresponding values of the WHO/FAO-established acceptable daily intake (ADI), (Khan *et al*. 2020). If the HI is less than 100%, it means that there is no risk to human health (Akoto *et al*. 2016).

$$EDI = \frac{A\ X\ B}{C} \quad \text{and} \quad HI = \frac{EDI}{ADI}\ X\ 100 \qquad (2)$$

Where: A is the concentration of the pesticide residue detected in the crop (µg/L). B represents the average daily vegetable consumption. C represents the average body weight for South Africans (70.8 kg for adults and 20.8 kg for children) (Walpole *et al*. 2012).

Statistical analysis

The residue data were analysed using the Statistical Package for Social Science (SPSS version 25.0 SPSS Inc, Chicago, IL, USA). For all repeat measurements, the mean values and standard deviations of all samples were computed and the Kruskal Wallis nonparametric test was used to detect the significant differences in the residue concentration of samples. The Mann-Whitney U test was used to determine the specific differences when the significant difference was identified at a 95% confidence limit.

RESULTS AND DISCUSSION

Herbicides uptake assessment

On each sampling day, the maize plants were sampled with their corresponding soils in each treatment plot. The soil, root, stalk, and leaves samples were analysed in the first three months until maize and tassel started shooting in the fourth and fifth months of the planting season. The varying concentrations were observed in each plot. In this study the soil texture showed high clay content of 56.41%. In all treatments, the pesticides showed the ability to be taken up by roots thereby translocated into different parts of the maize crop because of the direct contact between soil and roots. The absorption of *glyphosate* by soil was observed to be higher than the other herbicides in all treatments (0.25, 0.50, and 0.75 g/L) with concentrations ranging between 0.23 – 0.53 µg/L, 0.55 – 0.78 µg/L and 0.73 – 0.99 µg/L, respectively. There were significant differences observed in *glyphosate* mean concentrations in all treatments as 0.25 g/L showed ($p < 0.021$), while 0.50 g/L showed $p < 0.002$ then 0.75 g/L showed $p < 0.035$. This could be due to the *glyphosate* ability to bind to minerals and soil organic matter in the soil through carboxyl, amine, and phosphate functional groups thereby generating bidentate and tridentate complexes with soil structures (Duke *et al*. 2012). Also, it was observed that *2.4-D* absorption by the soil was the least in all treatments (0.25, 0.50, and 0.75 g/L) yielding 0.05 – 0.25 µg/L, 0.30 – 0.56 µg/L and 0.51 – 0.72 µg/L, respectively (Table 1, 2 and 3). This could be due to its intermediate solubility resulting in its lower absorption ability by clay through the carboxylic group, with sorption being negatively connected to the amounts of hydrogen ions (H^+) present on clay soil (pH 5.95), (Paszko *et al*. 2016). The 2.4-D showed significant differences at 0.25 g/L treatment, soil showed $p < 0.002$, stalk $p < 0.012$, leaves $p < 0.043$, corn $p < 0.039$, and tassel $p < 0.045$. The most important physicochemical properties of the herbicides such as low solubility and log K_{ow}, affect the rate of absorption in the soil thus, affecting their translocation to different maize segments. In the studied herbicide, *glyphosate* has a lower solubility (mg/L) and lower log K_{ow} (17 and –3.40) followed by *mesotrione* (22 and 0.90), *atrazine* (34 and 2.61) then *2.4-D* (64 and 5.78), (Farajzadeh *et al*. 2019). The lower solubility and log K_{ow} of *glyphosate* and *mesotrione* favoured their rapid absorption in soil and crops as compared to atrazine and *2.4-D*. As a result, their absorption in soil showed ascending order of *glyphosate>mesotrione>atrazine>2.4-D* in all treatments.

Pandey *et al*. (2020) reported significant leaching of 21.99 µg/L and surface runoff of 42.25 µg/L loss-

es of *chlorantraniliprole* insecticide due to high rain which occurred after 4 hours of pesticide-application. In the 2021/2022 planting season, the province of KwaZulu-Natal (current study area) experienced a high volume of rain which might have resulted to surface run-off and leaching of herbicides leading to their loss to non-target areas due to water stagnation and high-intensity rains that happened immediately after pesticide application. Thus, lesser herbicides were available in the soil for uptake and translocation, which could be the reason for lower concentrations found in different parts of the plants. The wet growing season influenced mesic (moist) conditions which resulted in a thinner and more polar cuticle as compared to crops produced under xeric (dry) conditions (Comas *et al*. 2013). The cuticle is the part of a leaf that consists of plates and protuberances of wax entrenched in different layers of cutin- a mixture of polymers of dicarboxylic and hydroxycarboxylic acid ester. This explains the high absorption of all four herbicide traces in the leafy segment of the maize plant based on the "like dissolve like" phenomenon as compared to other studied segments. The exterior region of the cuticle allows non-polar

Table 1

Concentrations (µg/L dry weight) of residues from 0.25 g/L treatment plot

Days	Herbicide	Concentration					
		Soil	Roots	Stalk	Leaves	Corn	Tassel
30	*Atrazine*	0.27±0.29	0.20±0.42	0.10±0.45	0.25±0.35	–	–
60		0.31±0.42	0.19±0.89	0.22±0.76	0.28±0.75	–	–
90		0.25±0.68	0.31±0.23	0.25±0.90	0.36±0.21	–	–
120		0.42±0.04	0.32±0.11	0.45±2.12	0.61±0.01	0.34±0.81	0.12±0.97
140		0.39±0.08	0.36±2.41	0.40±1.56	0.42±0.98	0.28±0.11	0.26±1.21
p-value		0.009	0.046	0.001	0.032	0.022	0.035
30	*2.4-D*	0.10±0.86	0.09±3.42	0.11±0.74	0.15±2.14	–	–
60		0.05±1.34	0.11±1.42	0.19±0.21	0.36±1.12	–	–
90		0.15±0.95	0.15±0.88	0.29±0.89	0.31±0.56	–	–
120		0.20±0.10	0.19±0.56	0.32±1.45	0.42±0.97	0.24±4.21	0.09±0.25
140		0.26±0.29	0.22±0.05	0.42±0.32	0.45±0.81	0.29±2.12	0.16±0.12
p-value		0.002	0.003	0.012	0.043	0.039	0.045
30	*Glyphosate*	0.23±1.36	0.25 ±0.64	0.22±0.87	0.28±0.19	–	–
60		0.36±2.42	0.32 ±0.15	0.39±0.46	0.30±2.04	–	–
90		0.42±0.45	0.39 ±0.97	0.32±0.32	0.46±0.86	–	–
120		0.46±0.68	0.33 ±0.68	0.38±0.12	0.40±0.72	0.30±0.16	0.20±1.45
140		0.53±0.70	0.42 ±0.89	0.39±0.05	0.48±0.69	0.38±0.98	0.28±1.05
p-value		0.021	0.001	0.042	0.008	0.007	0.041
30	*Mesotrione*	0.28±0.89	0.28±2.89	0.26±3.45	0.32±2.56	–	–
60		0.25±4.12	0.42±2.00	0.35±0.15	0.31±1.48	–	–
90		0.36±0.15	0.44±0.74	0.49±0.01	0.53±0.23	–	–
120		0.30±0.36	0.49±0.91	0.43±0.34	0.49±0.05	0.34±0.24	0.11±2.45
140		0.48±1.78	0.59±0.82	0.60±0.31	0.65±0.75	0.42±1.45	0.25±1.11
p-value		0.032	0.002	0.04	0.039	0.051	0.03

herbicides to enter, whereas the inner portion allows polar herbicides to be absorbed (Matzenbacher *et al*. 2014). The corn and tassel detected lower residues when compared to other plant parts which could be due to the maize sending fewer residues in the most prominent part of the plant (Dlamini 2015)**.**

The detected concentration showed an increasing trend as the treatment concentration increased with time, which was observed in all treatments. The 0.25 g/L, 0.50 g/L and 0.75 g/L showed increasing *mesotrione* concentration after 120 and 140 days with 0.34 µg/L and 0.42 µg/L (Table 1), 0.42 µg/L and 0.51 µg/L (Table 2), and 0.74 µg/L and 1.71 µg/L (Table 3), respectively. However, atrazine showed 0.34 µg/L after 120 which decreased to 0.28 µg/L after 140 days. This could be due to the fact that *atrazine* has a shorter lifetime in acidic soil resulting in its degradation of clay structures as the growth time increases consequently affecting the translocation (Pérez *et al*. 2022).

Glyphosate and *mesotrione* both showed a high absorption rate in soil, roots, stalk, and leaves while

T a b l e 2

Concentrations (µg/L dry weight) of residues from 0.50 g/L treatment plot

Days	Herbicide	Concentration					
		Soil	Roots	Stalk	Leaves	Corn	Tassel
30	*Atrazine*	0.44±1.56	0.25±0.77	0.36±0.86	0.32±0.75	–	–
60		0.35±0.46	0.39±0.65	0.38±4.52	0.31±0.49	–	–
90		0.38±0.97	0.31±0.87	0.49±0.89	0.53±0.68	–	–
120		0.46±1.15	0.41±0.44	0.43±0.17	0.49±0.47	0.28±3.42	0.22±0.99
140		0.43±0.59	0.40±1.24	0.60±1.86	0.65±0.05	0.22±0.47	0.30±1.26
p-value		0.032	0.045	0.03	0.001	0.05	0.028
30	*2.4-D*	0.30±0.45	0.18±0.64	0.21±0.86	0.28±0.47	–	–
60		0.48±1.56	0.38±2.56	0.42±5.42	0.48±5.20	–	–
90		0.32±6.45	0.28±1.45	0.38±1.52	0.45±1.56	–	–
120		0.38±2.14	0.33±0.08	0.28±2.32	0.36±0.46	0.15±3.20	0.20±0.89
140		0.56±0.48	0.42±1.45	0.32±1.03	0.62±1.89	0.30±1.56	0.26±0.18
p-value		0.021	0.035	0.015	0.028	0.048	0.012
30	*Glyphosate*	0.55±2.45	0.35±0.56	0.41±0.86	0.48±0.03	–	–
60		0.65±1.45	0.52±5.12	0.39±2.35	0.49±0.25	–	–
90		0.68±0.56	0.49±2.36	0.42±2.10	0.56±0.45	–	–
120		0.76±0.68	0.63±1.20	0.58±0.25	0.65±0.02	0.42±0.35	0.33±0.56
140		0.78±0.95	0.62±1.45	0.59±1.56	0.68±1.02	0.31±2.15	0.29±0.11
p-value		0.002	0.009	0.035	0.038	0.049	0.031
30	*Mesotrione*	0.62±5.23	0.30±0.45	0.20±0.62	0.38±1.26	–	–
60		0.51±0.25	0.48±2.36	0.42±0.11	0.40±1.00	–	–
90		0.56±4.23	0.48±0.65	0.50±2.56	0.62±2.30	–	–
120		0.58±0.54	0.50±0.52	0.49±2.45	0.52±0.45	0.42±0.56	0.31±0.35
140		0.72±1.25	0.59±1.11	0.62±2.65	0.69±5.62	0.51±2.51	0.42±1.45
p-value		0.052	0.026	0.035	0.014	0.018	0.033

mesotrione was also highly absorbed in corn and tassels in all treatments. This is due to the fact that *mesotrione* adsorbs on the soil through the hydrogen of the aromatic ketone and the adsorption is mostly higher in acidic soils, where *mesotrione* primarily exists as a neutral molecule rather than anion (Pintar *et al*. 2020). The corn concentrations showed significant differences at 0.75 g/L treatment with *atrazine* showing $p<0.032$, *2.4-D* ($p<0.041$), *glyphosate* ($p<0.028$), and *mesotrione* $p<0.015$ in soil. The tassel concentrations showed significant differences at 0.75 g/L treatments with *atrazine* showing $p<0.016$, *2.4-D* ($p<0.052$), *glyphosate* ($p<0.044$) and *mesotrione* $p<0.025$ after 140 days (Table 3). Fauzi and Ngawit (2021), studied the effect of herbicide residues (*glyphosate, atrazine, alachlor, oxadiozon,* and *2,4-D amine*) on maize growth and yield. *Glyphosate* and *atrazine* were observed to be highly efficient against weed management in maize, while *alachlor, oxadiozon*, and *2,4-D amine* were efficient against broadleaf weeds. In this study, *glyphosate* and *atrazine* residues were 0.086 µg/L and 0.088 µg/L in soil.

T a b l e 3

Concentrations (µg/L dry weight) of residues from 0.75 g/L treatment plot

Days	Herbicide	Concentration					
		Soil	Roots	Stalk	Leaves	Corn	Tassel
30	*Atrazine*	0.55±0.52	0.45±5.32	0.41±0.65	0.48±0.45	–	–
60		0.65±4.52	0.62±2.15	0.59±0.75	0.49±0.65	–	–
90		0.68±0.65	0.49±1.52	0.42±1.25	0.56±0.68	–	–
120		0.76±1.45	0.63±0.25	0.58±2.65	0.65±0.52	0.52±0.65	0.43±2.35
140		0.70±2.56	0.62±0.62	0.50±0.95	0.68±3.25	0.50±1.56	0.39±0.52
p-value		0.042	0.032	0.042	0.012	0.032	0.016
30	*2.4-D*	0.62±0.65	0.30±0.65	0.20±2.65	0.38±0.35	–	–
60		0.51±2.56	0.48±2.65	0.42±1.30	0.40±5.23	–	–
90		0.56±1.36	0.48±0.35	0.50±2.65	0.62±2.30	–	–
120		0.58±1.01	0.50±1.52	0.49±0.82	0.52±1.65	0.42 ±2.45	0.31±3.45
140		0.72±0.56	0.59±0.62	0.62±1.55	0.69±0.25	0.62 ±1.25	0.57±4.12
p-value		0.025	0.036	0.024	0.006	0.041	0.052
30	*Glyphosate*	0.73±3.56	0.65±4.21	0.58±0.48	0.68±2.32	–	–
60		0.66±1.56	0.72±2.65	0.51±0.25	0.69±0.65	–	–
90		0.82±0.85	0.69±2.39	0.55±0.62	0.76±5.62	–	–
120		0.86±4.51	0.78±0.32	0.92±3.21	0.98±0.35	0.62±0.65	0.50±0.65
140		0.99±0.65	0.82±0.28	0.79±0.45	1.02±1.5	0.78±0.81	0.68±0.58
p-value		0.035	0.029	0.048	0.036	0.028	0.044
30	*Mesotrione*	0.68±2.45	0.78±2.56	0.66±4.56	0.69±2.32	–	–
60		0.75±6.52	0.62±3.65	0.55±3.56	0.71±0.18	–	–
90		0.78±0.32	0.64±5.21	0.79±2.65	0.83±0.98	–	–
120		0.80±6.24	0.71±0.24	0.73±0.65	0.89±2.65	0.74±0.35	0.51±0.65
140		0.88±2.35	0.81±1.25	0.89±5.26	0.75±1.45	0.82±2.36	0.71±1.45
p-value		0.03	0.042	0.036	0.025	0.015	0.025

Pesticide toxicity index (PTI) values (cumulative risk)

The pesticide toxicity index (PTI) was used to estimate toxicity for a combination of all herbicides investigated, whereas the toxicity quotient (TQ) was used to assess toxicity for the individual herbicide. All maize treatments showed a PTI value of >1 (Table 4), thereby suggesting the possibility of a health hazard to the consumer of this maize (Khan *et al*. 2020). The 0.75 µg/L treatment showed >50 PTI compared to other treatments, indicating that the application of a higher concentration of herbicides results in higher exposure. Chaikasem and Roi-et (2020) reported a high PTI value of 31.20 on maize corn collected from the River Basin area (India) that was irrigated with contaminated surface water. Shalaby *et al*. (2021), reported a PTI value of 128.44 in potatoes harvested from Dakahlia (Egypt). The increased health risk is correlated to the daily intake of the maize under investigation.

Health risk assessment

The potential health effect and the residue levels of exposure over time are considered in assessing health risk status. When the HI exceeds the ADI value of 222 g/person/day and hence exceeds 100% will expose the consumer to chronical harmful pesticide residue (Shephard *et al*. 2002). For all the treatments, the HI data for both children and adults were below 100% (Table 4) hence, the risk assessment findings for the tested maize crops revealed that there is no possible health risk linked to the intake of these crops by both adults and children. On the 0.75 µg/L treatment, it was observed that *glyphosate* and *mesotrione* showed higher HI in children compared to other treatments in 120 and 140 sampling days with 3.10, 3.90, and 3.70, 4.10, respectively. This is due to the lower average body weight for children compared to adults, thereby posing a higher risk to children than to adults. Hossain *et al*. (2015) reported HI for *carbaryl* in tomato (1.09), *chlorpyrifos,* and *carbofuran* in brinjal were 1.97 and 1.17, respectively. Shalaby *et al*. (2021) reported <100% HI in potatoes, pepper, cucumber, and eggplant crops obtained from Dakahlia's agricultural areas. Although ingestion of these maize crops is unlikely to produce immediate health problems, continuous exposure can lead to adverse health effects due to the toxicity and carcinogenicity of these herbicides to consumers (Gandhi *et al*. 2021).

CONCLUSIONS

This study concludes that all the assessed herbicides are taken up by the soil and translocated

Table 4

Toxicity quotient and health risk assessment detected in maize crops

Days	Herbicides	0.25 g/L treatment			0.50 g/L treatment			0.75 g/L treatment		
		TQ	HI [%] adult	HI [%] children	TQ	HI [%] adult	HI [%] children	TQ	HI [%] adult	HI [%] children
90	*Atrazine*	6.80	0.49	1.70	5.60	0.40	1.40	10.40	0.74	2.6
120	*Atrazine*	5.60	0.40	1.40	7.00	0.50	1.75	12.40	0.89	3.1
90	*2.4 D*	0.48	0.34	1.20	0.30	0.21	0.75	0.84	0.60	2.1
120	*2.4 D*	0.58	0.41	1.45	0.60	0.43	1.50	1.24	0.89	3.1
90	*Glyphosate*	0.15	0.43	1.50	0.21	0.60	2.10	0.31	0.89	3.1
120	*Glyphosate*	0.19	0.54	1.90	0.16	0.44	1.55	0.39	1.11	3.9
90	*Mesotrione*	5.67	0.49	1.70	7.00	0.60	2.10	12.33	1.06	3.7
120	*Mesotrione*	7.00	0.60	2.10	8.50	0.73	2.55	13.67	1.17	4.1
	PTI	26.47	–	–	29.37	–	–	51.58	–	–

Note: PTI – pesticides toxicity index; TQ – toxicity quotients; HI – health index.

to different maize segments, particularly the leafy segment. These findings suggested that both livestock and humans could be harmed by the daily intake of maize crops contaminated by these herbicide residues as they might build over time, potentially leading to harmful long-term consequences on individuals. The absorption showed ascending order of *glyphosate>mesotrione>atrazine>2.4-D* in all treatments. The PTI of all residues showed potential health risks to humans more than the individual risk index, however, the HI revealed that the maize corn is considered acceptable for consumption. Nevertheless, the results suggest a need for strict monitoring and regular scrutinizing of herbicide residues and their accumulation in all agricultural farms in South Africa. Moreover, a need for harmless herbicides like biopesticide should be investigated as pest control-safe replacements for these harmful herbicides. Furthermore, the results showed that maize can be used for the phytoremediation of the studied herbicides.

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