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Evaluating Exposure Risk of Consuming Cadmium Contaminated Spinach and Waterleaf Vegetables Grown by Roadside in Selected Areas of Kano State

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ABSTRACT

This study investigates the contamination of waterleaf and spinach, both known as Cadmium (Cd) accumulators, cultivated in open fields along roadsides exposed to vehicular emissions in five locations $B_1, B_2, B_3, B_4,$ and B_5. Microwave Plasma-Atomic Emission Spectroscopy (MP-AES) was utilized to quantify Cd levels, revealing concentrations ranging from 0.37 to 0.94 mg/kg in spinach and 0.22 to 1.08 mg/kg in waterleaf. The research identifies Cd concentrations exceeding the FAO and WHO permissible limit of 0.2 mg/kg for leafy vegetables, rendering the consumption of spinach and waterleaf from these locations unsafe due to elevated Cd levels resulting from vehicular pollution. An exception was noted in waterleaf from B_1, where Cd was not detected, attributed to a transfer factor. Ecological index evaluations produced contamination factor and Pollution Load Index (PLI) values of 1 and 0.01, indicating moderate contamination (1 < CF < 3) and the presence of pollution (PLI > 1). Average Daily Dose (ADD) calculations exceeded the Reference Dose limit for Cd (RfD of Cd = 0.001 mg/kg). The Estimated Daily Intake (EDI) results ranged from 0.01800 to 0.02200 mg/kg for Cd, while the Hazard Quotient (HQ) assessment based on unity classification for the analyzed vegetables showed Cd concentrations from 0.63700 to 0.01603 mg/kg. In conclusion, the computed values suggest the presence of heavy metals in the study areas, indicating an elevated risk of adverse health effects from exposure to these contaminants. The study underscores the urgent need for environmental management strategies to mitigate Cd contamination in leafy vegetables grown along roadsides.

Keywords:
Atomic Emission Spectroscopy (MPAES),
Cadmium (Cd),
Microwave Plasma,
Roadside,
Spinach,
Vehicular emissions,
Waterleaf.

INTRODUCTION

Vegetables constitute a crucial component of daily diets in many households, providing essential vitamins and minerals for human health. They also function as neutralizing agents for acidic substances formed during digestion (Thomson & Kelly, 1990). The typical daily vegetable consumption per individual in Kano Municipal and the surrounding metropolis is approximately 255 grams (Nafiu Abdu, 2010). Of these vegetables, around 20% are sourced from roadside cultivation (Abakpa *et al*., 2013). However, as human activities, especially those reliant on modern technologies, have escalated, pollution and contamination of the human food chain have become inevitable.

Vegetables can accumulate heavy metals by absorbing them from contaminated soils and through deposits on their surfaces from polluted environments (Sobukola *et al*., 2010). Plants growing in heavy metal-contaminated environments can accumulate high levels of trace elements, posing significant health risks to consumers. Regular monitoring of heavy metals in effluents, sewage, vegetables, and other food items is crucial to prevent excessive accumulation of these metals in the food chain (Arora, *et al.*,2008).

There has been considerable uptake of heavy metals by plants in air-polluted areas to some extent (Wong, 1996; Sukreeyaponse *et al*., 2002; Yusuf *et al*., 2003), leading to the accumulation of trace elements that are known to pose serious health risks to consumers (Let *et al*., 2003). Certain vegetables, have been recognized for their ability to adsorb heavy metal ions from aqueous solutions (Ikhuoria & Omonmheale, 2022; Okoye *et al*., 2010).

Water leaf (*Talinum triangulare*), and Spinach (*Spinacia oleracea*), are popular choices among the local population due to their nutritional value and availability. However, their cultivation alongside busy roads raises concerns about the potential accumulation of heavy metals from vehicle emissions and other sources.

The presence of heavy metals in the soil can be absorbed by the plant roots, leading to their accumulation in the edible parts of the vegetables. Consuming these contaminated vegetables can have serious health implications, including organ damage, neurological disorders, and even cancer.

Previous research indicates the potential contamination of these vegetables with toxic and persistent heavy metals. However, there is a lack of comprehensive literature specifically addressing the risk associated with consuming roadside-grown vegetables within Kano metropolis. To assess elements contamination in vegetables, some indexes of pollution were calculated by using the appropriate formulas.

Contamination Factor (CF)

The contamination factor is the ratio of the concentration of each heavy metal in roadside samples and the concentration of the respective heavy metals in background. The degree of contamination is defined as the sum of all contamination factors (Hakanson, 2008). The computing equation for contamination factor (CF) is as follows:

$$\boldsymbol{CF} = \frac{\boldsymbol{C_n}}{\boldsymbol{B_n}} \qquad (1)$$

where C_n is the concentration of the heavy metals found in roadside samples and B_n is the background value of heavy metals = Reference value for each element (in mg/kg). The classification of CF is described as CF < 1 ='low contamination'; 1 < CF < 3 = 'moderate contamination'; 3 < CF < 6 = 'considerable contamination'; and CF > 6 = 'very high contamination

Pollution Load Index (PLI)

The pollution load index (PLI) is obtained from the contamination factors (CF). This CF is the quotient obtained by dividing the concentration of each metal. The PLI of the place are calculated by obtaining the n-root from the n-CFs that were obtained for all the metals. Generally, the pollution load index (PLI) was developed by Tomlinson *et al*. (2012) which is shown as follows:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 - - - - - \times CF_n} \qquad (2)$$

where CF is the contamination factor for individual elements and n is the number of metals studied. PLI < 1 denotes 'no pollution'; PLI = 1 indicates that only baseline levels of pollutants are present; and PLI > 1 indicates deterioration of site quality (Tomlinson, 2012).

Estimated Daily Intake (EDI)

EDI is a measure used in toxicology and environmental science to estimate the amount of a particular substance or chemical that an individual or population is likely to be exposed to on a daily basis through various exposure pathways such as food consumption, inhalation, or skin contact (Uddin, Hasan & Dhar, 2019). The formula to calculate EDI can vary depending on the specific substance and the exposure route, but in a general sense, it is often calculated as:;

$$\boldsymbol{EDI} = \frac{\boldsymbol{C \times IR}}{\boldsymbol{BW}} \qquad (3)$$

Where EDI represents the Estimated Daily Intake. C is the concentration of the substance in the food or drink (usually expressed in milligrams or micrograms per kilogram). IR is the average daily intake rate of the food or drink (usually expressed in kilograms per day). BW is the body weight of the person or population being assessed (usually expressed in kilograms). (Ali & Hau, 2001; Saha & Rahman, 2012)

Target Hazard Quotient (THQ)

THQ is the rate of potential exposure to heavy metals intake and it is calculated by the following formula (Uddin *et al*., 2019),

$$\text{THQ} = \frac{\text{EDI}}{RfD} \qquad (4)$$

where THQ is the Target Hazard Quotient. EDI is the Estimated Daily Intake of a contaminant (in milligrams per kilogram of body weight per day). RfD is the Reference Dose, which represents the acceptable daily intake of a contaminant (in milligrams per kilogram of body weight per day) set by regulatory agencies or health organizations. If the THQ is greater than 1, it suggests that there may be a potential health risk associated with the exposure to the contaminant (USEPA, 2020).

Average Daily Dose (ADD)

To estimate the potential human health risk levels of selected heavy metals in vegetable samples, the average daily dose (ADD), in mg/kg/day, through the ingestion pathway (oral route) was calculated for both children and adults using the relation (Shafiuddin *et al*., 2021).

$$ADD = \frac{\text{Cm} \times IR \times Ef \times Ed}{Bw \times AT} \qquad (5)$$

where ADD is the Average Daily Dose in mg/kg/day, Cm is the Average heavy metal concentration in (mg/kg), IR is the Ingestion rate, Ef is Exposure frequency equal to 365 days/year, and ED is the duration of exposure, which is 60 and 6 years for adults and children respectively. AT is the average exposure time for life expectancy. AT for adults is 21,900 days while for children it is 2190 days (USEPA, 2020). BW represents body weight, which was considered to be 70 and 15 kg for adults and children respectively.

Hazard Quotient (HQ)

In order to evaluate the non-carcinogenic risk posed by the metals, hazard quotient (HQ) was calculated using the equation;

$$HQ = \frac{ADD}{RfD} \quad (6)$$

where RfD indicates the reference dose of individual metal (mg/kg/day) and ADD is the average daily dose of individual metal in mg/kg/day. The RfD gives an approximation of daily dose or exposure that is not likely to cause any risk or harm of deleterious (non-cancer) effects during a lifetime (Bhutiani *et al*; 2016) This means that exposures below the RfD are unlikely to produce an adverse health effect, above this value, an exposed individual may be at risk of any deleterious effect.

Hazard Index (HI)

HI is the sum of Hazard quotients of all metals. It is calculated by the following formula in equation (Uddin *et al*., 2019).

$$H1 = \Sigma HQ = HQ\ (Cd) \quad (7)$$

MATERIALS AND METHOD

Materials

i. Nitric acid (HNO_3) is a vital mineral acid. It is a colorless, corrosive liquid with a pungent odor (Whillock, et al., 2010). Nitric acid is commonly used in various industrial and laboratory applications due to its highly reactive nature (Whillock, et al., 2010). In the context of heavy metal experiments, nitric acid is frequently used to digest or dissolve solid samples containing heavy metals, such as lead or mercury, in order to convert them into soluble forms suitable for analytical techniques
ii. Hydrogen peroxide H_2O_2): This is a chemical compound consisting of two hydrogen atoms and two oxygen atoms, arranged as a water molecule with an additional oxygen atom. It is a powerful oxidizing agent and is commonly used in various chemical experiments and industrial applications. In the context of heavy metal experiments, hydrogen peroxide can be used to assess the presence of heavy metals in a solution. When added to a sample containing heavy metals, hydrogen peroxide can initiate chemical reactions that result in the oxidation of these metals, allowing for their detection or removal.
iii. Perchloric acid: ($HClO_4$): This is a strong mineral acid known for its high corrosivity and oxidizing properties. In the context of heavy metal experiments, perchloric acid is often used to digest or dissolve solid samples containing heavy metals for subsequent analysis. This acid facilitates the breakdown of the sample into a soluble form, making it suitable for analytical techniques.
iv. Deionised water (DI): This is water that has had its ions, such as salts and minerals, removed through a process called deionization. This treatment results in highly pure water with a very low concentration of ions, making it electrically conductive. In the context of a heavy metal experiment, deionized water is crucial as it serves as a pristine solvent that minimizes interference from extraneous ions, ensuring accurate and controlled conditions for the analysis of heavy metal concentrations in a sample.

Methods

The leaves were sampled from the locations according to the general procedure outlined by Ametepey, el al., 2018, and subsequently prepared for analysis according to protocols prescribed by Gupta, et al., 2022.

Study Area

The area of interest to the study is Kano State. It is located in the northern region of the country with geographical coordinates of 11^{o}55'30"N and 12^{o}4'30"N and 8^{o}24'0"E 8^{o}37'30"E.

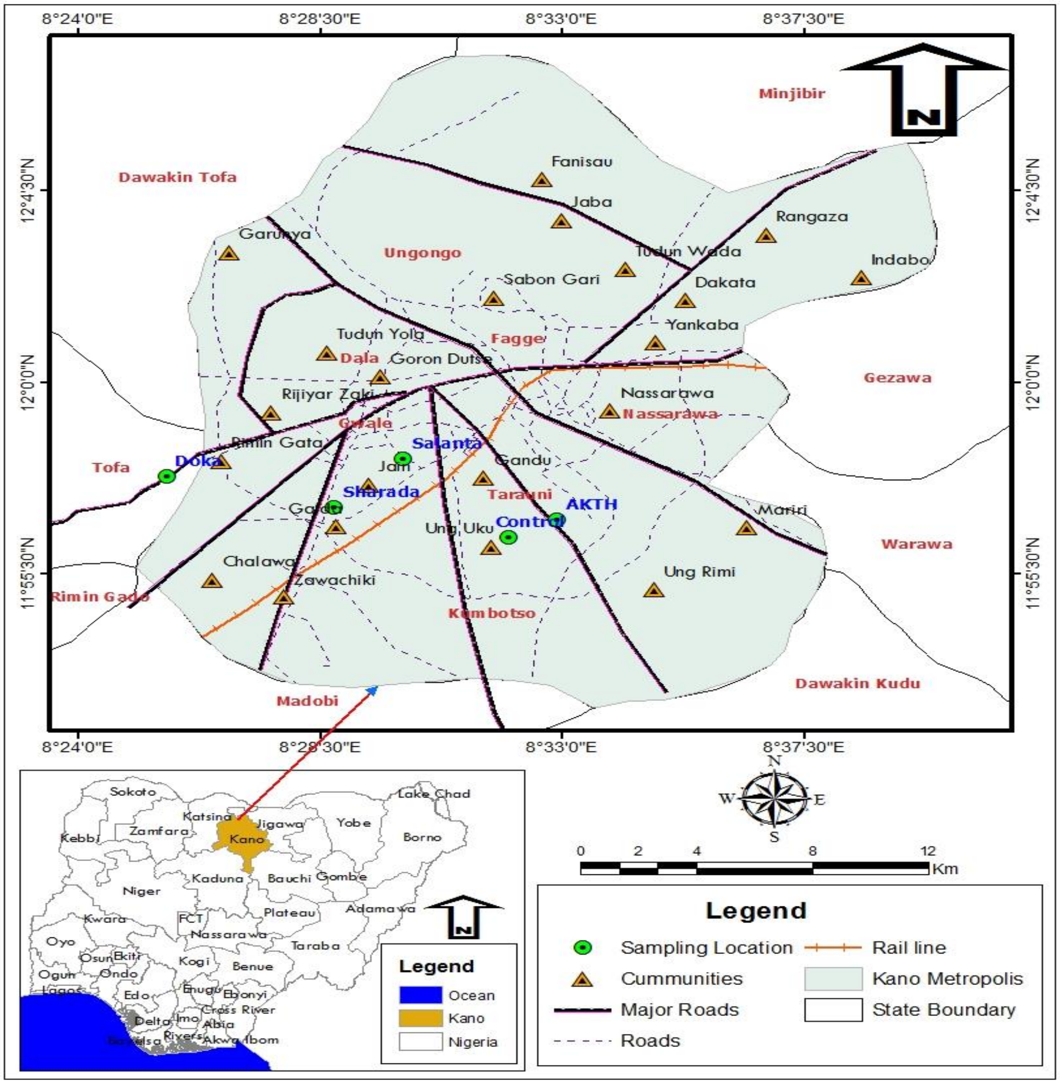


Figure 1. Map of Kano showing sampling Locations, Roads and the surrounding Communities

Sampling Locations

A total of five (05) sampling location identified. Four of them located within Kano metropolis and one location at the outskirts of Kano at a distance of 20km on Gwarzo Road in a town called Doka (Figure 1).

Experimental Procedure

All Cd content measurements in the samples were conducted using Agilent's model 4210 Microwave Plasma-Atomic Emission Spectroscopy (MP-AES). The sample introduction system included PVC peristaltic pump tubing (white/white and blue/blue), a single-pass cyclonic spray chamber, and the oneNeb nebulizer. Utilizing the Agilent MP Expert software, the background signal was automatically subtracted from the analytical signal. A background spectrum from a blank solution was recorded and subtracted from both standard and sample solutions during analysis. The software was employed to optimize nebulization pressure and viewing position for each selected wavelength to enhance sensitivity. Thanks to this optimization, and with all determinations carried out sequentially, each analyte was assessed under optimal conditions. Parameters were quickly and easily optimized using a standard reference solution.

RESULTS AND DISCUSSION

The results of the concentration of Cd, in vegetables samples grown by roadside collected from the five (5) different sampling sites: B_1, B_2, B_3, B_4 *and* B_5 are presented in Table 1. The results obtained were compared with WHO recommended limits of the selected heavy metals detected.

Table 1: Heavy Metals Content in Investigated Vegetable Samples

S/No	Sample	Location	Cd (mg/Kg)
1	Spinach	B_1	0.65
		B_2	ND
		B_3	0.94
		B_4	0.57
		B_5	0.37
2	Waterleaf	B_1	ND
		B_2	ND
		B_3	0.50
		B_4	1.08
		B_5	0.22

The Level of Cadmium in the Vegetable Samples

The concentration of Cd in the spinach vegetables samples ranged between 0.37-0.94 mg/kg as shown in Table 1, in all Spinach sample (with the exception of control sample) the Cd concentrations in the samples were more than the maximum permissible limit of 0.2 mg/kg for leafy vegetables (Figure 1) according to FAO and WHO. This study was found to be consistent with the reported results of 0.72 mg/kg roadside soils in Lancaster (Harrison *et al*, 2005), 0.47 mg/kg of Cd was reported on a highway roadside soil in London (Culbard *et al*, 1988). This suggests that roadside grown spinach vegetables in Kano metropolis are not safe for consumption.

In the case of Waterleaf, no Cd was detected in samples from B_1 could be attributed to transfer factor, which is the factor expressing the bioavailability of a metal at a particular position on a species of plant (Kachenko *et al.*, 2006; Tsafe *et al.*, 2012) because plant samples have significant differences in the transfer factors of metals relative to the availability of same metals in the soil. While sample from B_4 presented a slight excess above the WHO permissible limit (0.02 mg/kg). Sample from B_3 *and* B_5 exceeded the WHO maximum permissible limit with the highest Cd values of 0.50 mg/kg and 1.08 mg/kg respectively, found in Waterleaf. The highest Cd value was found in the samples from heavy traffic areas. This is further affirmed by the non-detection of any Cd presence in all of the control samples.

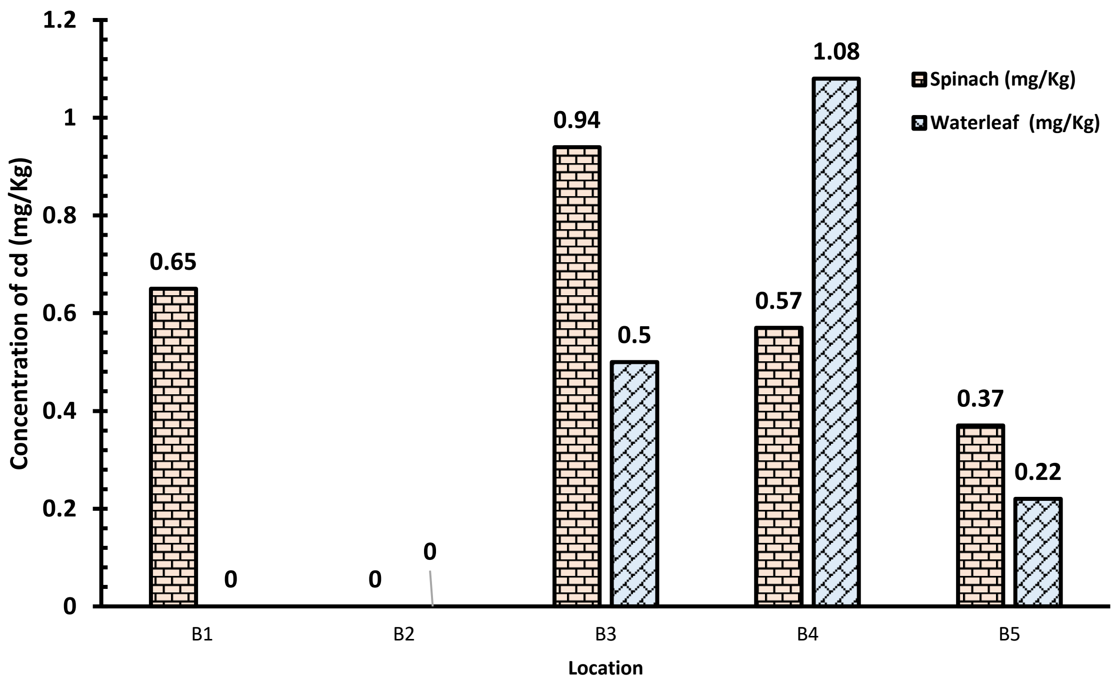


Figure 1: Concentration level of Cd in all vegetable samples

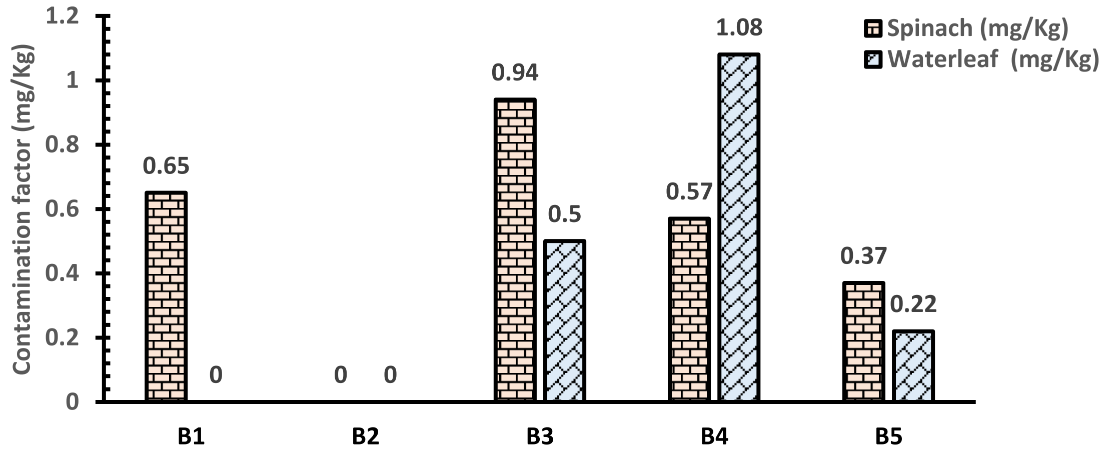


Figure 2: Contamination factor (CF) of Cd in roadside samples

The pollution load index (*PLI*) for the heavy metals was computed to be $PLI = 2.1$, if $PLI > 1$ denotes 'pollution presence' based on result, the presence of heavy metal in the different study area will cause pollution.
The computed EDI results are presented in Figure 3 and shows a generally low contamination status which is below the permissible limit approved by WHO with observed values of 0.00157- 0.01567 mg/kg for Cd.
Computed Average daily dose (ADD) is presented in Figure 4. results of Cd show values exceeding the Reference Dose limit for Cadmium (RfD of Cd = 0.001 mg/kg) with the exception of Waterleaf from B_1 sample location. The results obtained from Table 5 of Target Hazard Quotient shows high concentration on Cd ($HQ > 1$).
A high concentration for Hazard Quotient assessment is deduced from the result (Figure 6). On the basis of unity classification for the analyzed vegetables, the concentration of Cd ranged from 1.56785 - 18.06648 mg/kg, ($HQ > 1$) for both adult and children.

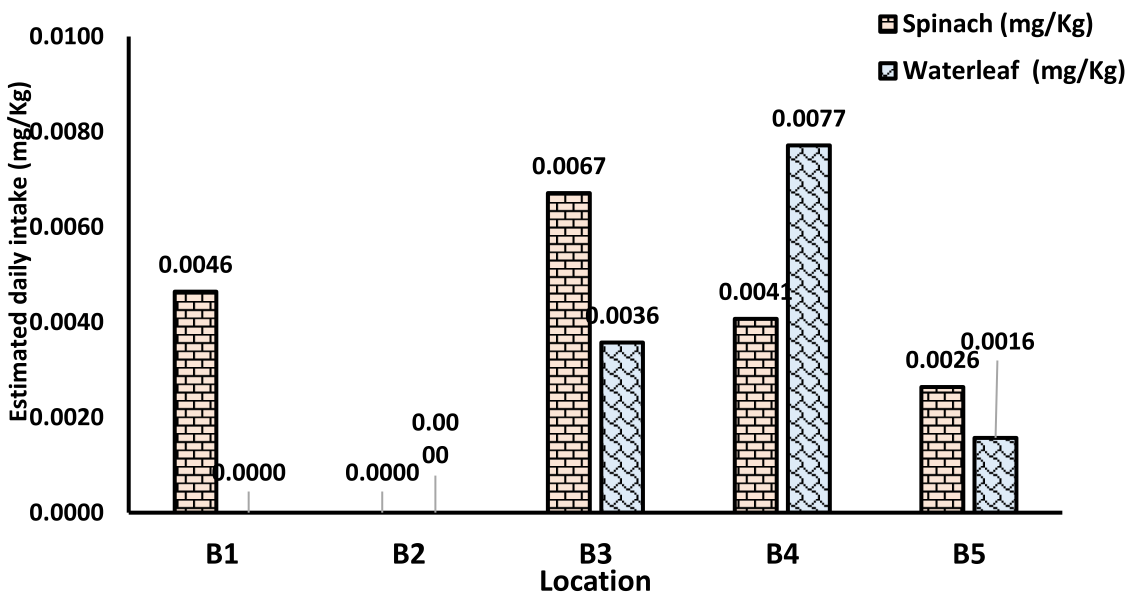
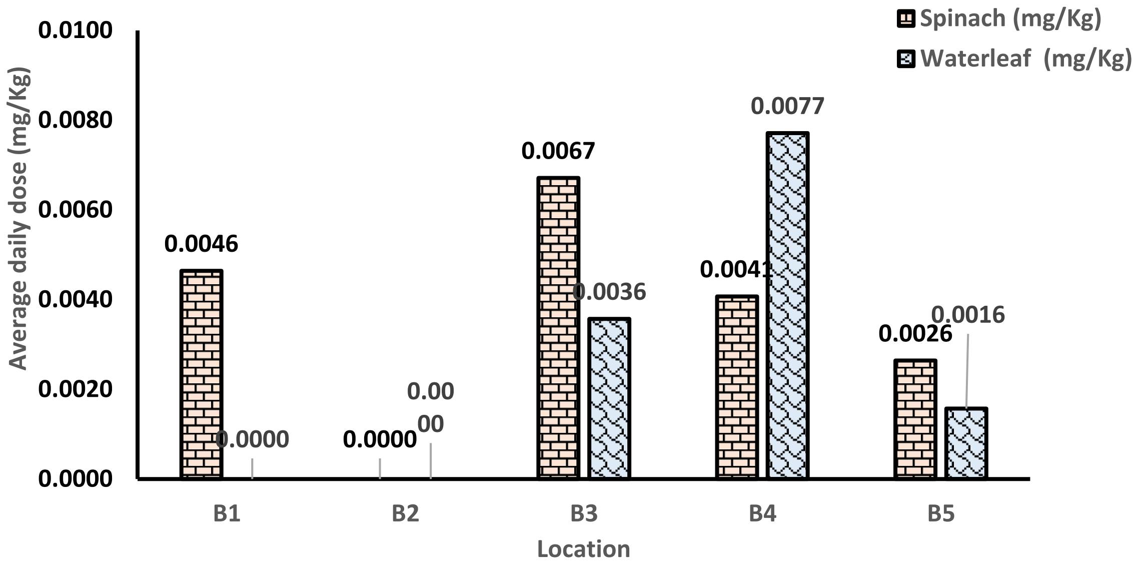
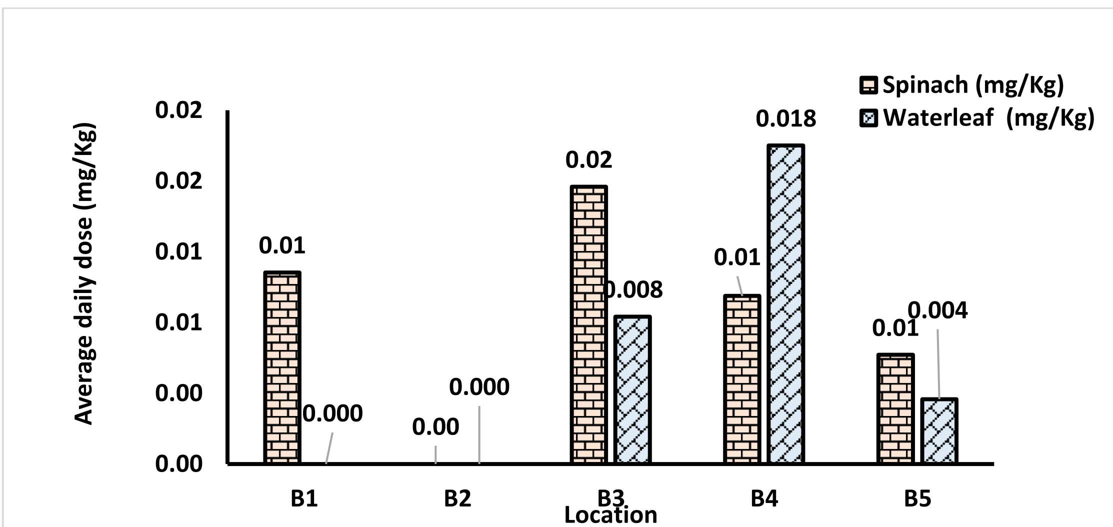


Figure 3: Estimated Daily Intake (EDI)

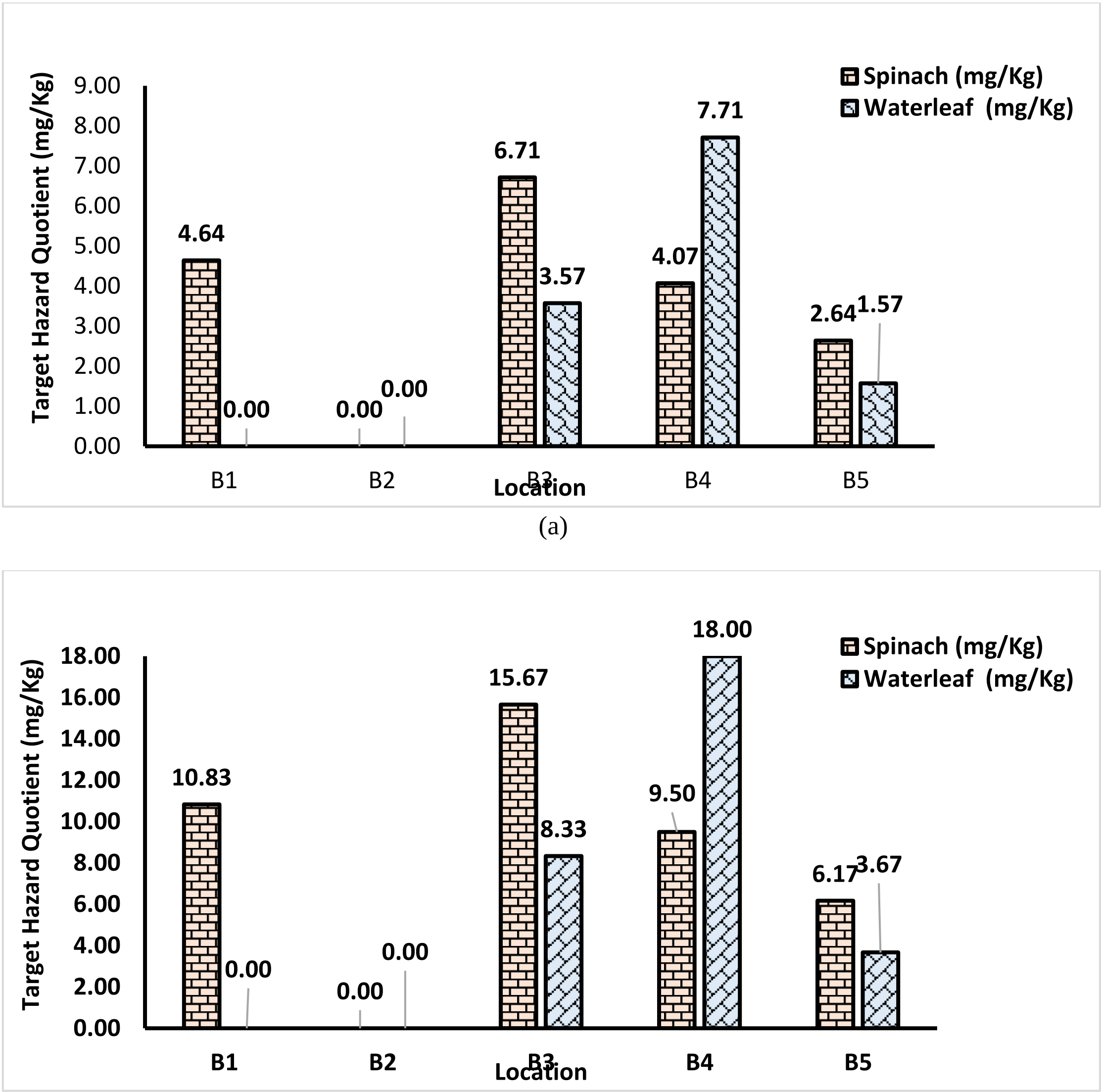


(a)



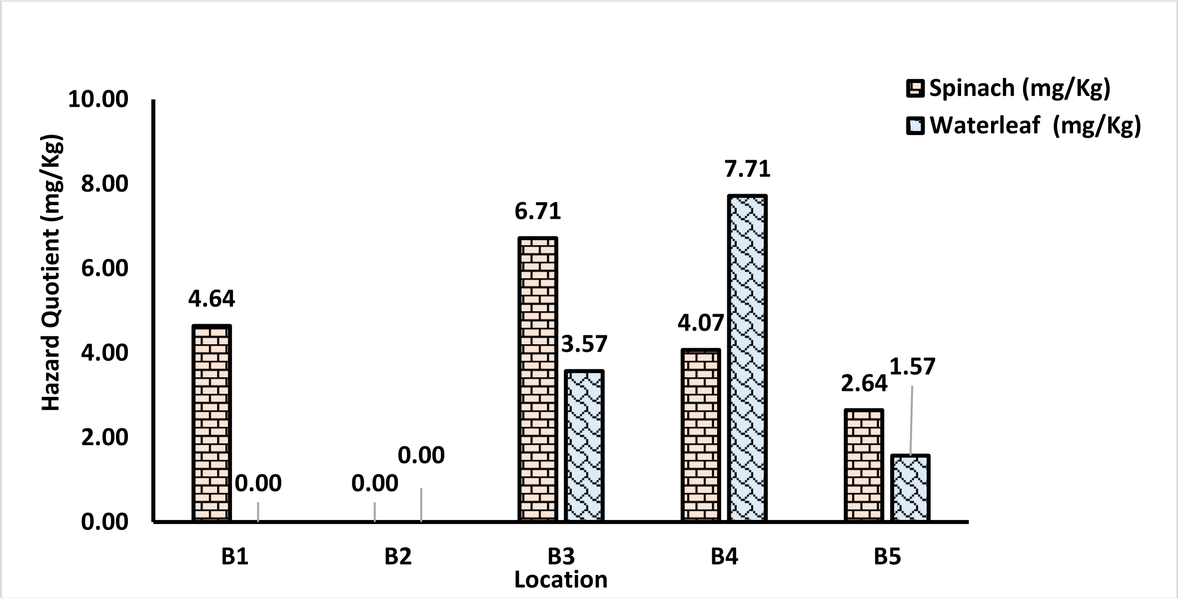
(b)

Figure 4: Average daily dose (ADD) (a and b)

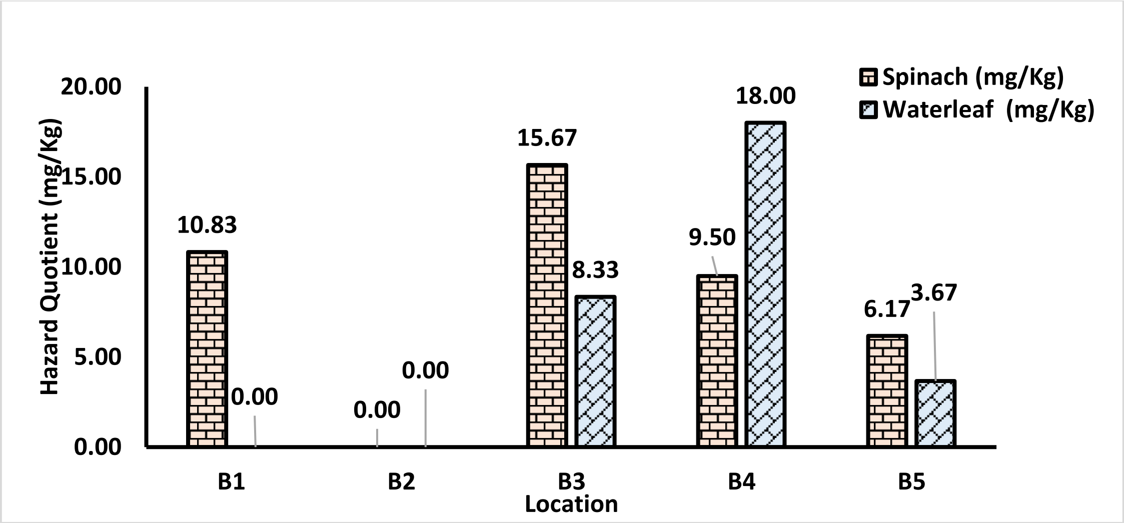


(b)

Figure 1: Target Hazard Quotient (THQ) (a and b)



(a)



(b)

Figure 2: Hazard Quotient (HQ)(a and b)

Hazard Index (HI)

Hazard quotients (HI) of all metals. It is calculated by the following formula in equation (Uddin *et al*., 2019).

H1 = ΣHQ=HQ (Cd)

$H1_{Adult}$= ΣHQ = 27.29482mg/kg

$H1_{Children}$= 72.19304 mg/kg

The average hazard index (HI) was determined to be above 1, indicating that, when considering exposure routes, children exhibited higher values than adults. This difference is likely attributable to incidental exposure in children compared to adults. Similar findings were documented in studies by Wu et al. (2009), Mitra et al. (2018), Shafiuddin Ahmed et al. (2021), and Kaur et al. (2019). Given that Cadmium poses the highest health risk, individuals exposed to it may be more susceptible to adverse effects, including an increased risk of kidney failure, renal diseases, and esophageal cancer, as indicated by Song et al. (2015).

CONCLUSION

Assessment of contamination for Waterleaf and Spinach cultivated in open-fields along the road side was undertaken. The vegetables are contaminated by vehicular emissions from the automobiles which led to Cd absorption by the leafy vegetable. The leaves from five locations B_1, B_2, B_3, B_4 and B_5 were investigated for Cd using Microwave Plasma - Atomic Emission Spectroscopy (MP-AES). The Cd level ranged between

0.37-0.94 mg/kg (spinach) and 0.22-1.08 mg/kg for (Waterleaf) which exceeded the permissible limit of 0.2 mg/kg for leafy vegetables according to FAO and WHO. Ecological index evaluation revealed moderate contamination for contamination factor ($1<CF<3$) and pollution presence identified through Pollution Load Index (PLI) of less than unity. The calculated Average Daily Dose (ADD) exceed the Reference Dose limit for Cd (RfD of Cd = 0.001 mg/kg). The EDI and Hazard Quotient (HQ) assessment gave values of 0.01800 - 0.02200 mg/kg and 0.63700 - 0.01603 mg/kg, respectively. In conclusion, the research finding established that consumption of spinach and waterleaf from the locations is not safe arising from elevated concentrations of Cd that exceeded the WHO/FAO permissible threshold values. The only exception is waterleaf sample from B_1 where the Cd was not detected due to transfer factor. Ecological index evaluation indicates that the presence of heavy metal in the different study areas is suggestive of an elevated risk of adverse health effects from exposure to this contaminant.

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