

Investigation of plant contamination to Ni, Pb, Zn, Cd and its relationship with spectral reflections

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Abstract

This study aims to investigate the toxicity of the plant to heavy elements (HMs). For this purpose, the estimated daily intake (EDI) parameters of potentially toxic elements (PTE) per kilogram of body weight, target hazard quotient (THQ) for non-carcinogenic disorders, total hazard index (HI), and bioconcentration factor (BCF) are determined in the plant at different stages of growth. In this study, the reaction of the plant to different electromagnetic waves at different stages of growth (DSG) is also investigated and the relationship between the THQ values and electromagnetic waves is prepared. The results show that Pb has the highest EDI value (5.97), Pb (74.67) and Cd (9.75) have the highest THQ values, and Cd has the highest BCF value (30.44). Also, the results show that HI values are higher than the threshold in the growth (69.98), flowering (71.38), and fruiting (68.06) stages. Results of BCF indicate Pb, and Cd has absorption rate in Capsicum towards. Contaminated capsicum plants submitted to electromagnetic waves showed a significant relationship between Pb and the b490, and b560 spectra, Cd and Ni the b450 spectrum, and Zn the b460 spectrum. This finding highlights the salience of employing electromagnetic waves in assessing contamination in plants. Put differently, THQ can be estimated using electromagnetic waves without any need for laboratory studies.

Keywords: heavy metals, plant contamination, *Capsicum annuum L.*, Electromagnetic wave.

Introduction

Soil contamination by potentially toxic elements (PTEs) is a global concern as they can cause serious health problems to humans and ecosystems (Liu et al. 2019; Nawar et al. 2019; Zhou et al. 2019). Among them, eight PTEs, including lead (Pb), chromium (Cr), arsenic (As), zinc (Zn),

cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni) are considered as the most common elements found in soils (Massadeh et al. 2009; Fan et al. 2020). Cd, Zn, and Ni are also among the most mobile elements in the soil that can be easily absorbed by plants and find a trajectory to aerial organs and accumulate at large quantities (Yang et al. 2010). Studies focusing on assessment of contamination by heavy metals (HMs) through consumption of agricultural products grown in the vicinity of the Dabushan Mine, Southern China, sought to determine the concentrations of Zn, Pb, and Cd in soil and agricultural products, to assess the potential hazards of HMs for human health. The results were suggestive of high rates of Cd, Pb, and Zn contamination in grown plants, reaching beyond the maximum threshold in China (Ping et al. 2009).

The over-abundant accumulation of PTE in agricultural soils not only causes secondary environmental pollution but also increases the risk of plant bioaccumulation and thereby significantly affects the quality and safety of food supply and nutrition (Muchuweti et al. 2006; Liang et al. 2018).

Absorption of PTE from soil transgressing the maximum allowed concentration cause also significant reduction and at times cessation in the growth rate of the corresponding plant due to changes in chlorophyll amount, and subsequent changes in the structure of the leaves and fruits (Sridhar et al. 2007; Yang et al. 2009). These changes also affect directly or indirectly the spectral characteristics of the leaves (Slonecker 2011) and reduce the absorption of red and blue waves for the production of chlorophyll in plants and lead to disruption at different stages of plant growth (Kabata-Pendias and Pendias 2011).

Spectral analysis of vegetation indices in conjunction with HMs from 1970-1980 was conducted by Collins et al. (1984) and Milton et al. (1989), all of which succeeded in identifying a relationship between contaminated vegetables and electromagnetic waves.

On the other hand, to accurately predict plant, soil contamination by electromagnetic waves, it is necessary to understand correctly the relationship between spectral activities (amount of electromagnetic reflectance) and the amount of heavy elements in the plant and soil (Philippe et al. 2008; Minasny and McBratney 2009).

Therefore, it is important to present the relationship between the measured values (heavy elements in plant and soil) in the laboratory and the amount of reflection and use of results in future studies without performing laboratory studies. Studies showed that with increasing distance from contaminated sources, the rate of contamination of the plant decreases, and with increasing HMs concentrations in soil decrease the amount of nutrients absorbed by the plant (Lu et al. 2019; Song et al. 2019). Therefore, it is important to investigate the contamination rate in plants near to contaminated sources (Li et al. 2019). Because these Cd, Zn, Pb, and Ni elements lead to dangerous diseases when they enter the human body, they were selected in the study and their potential toxic effects on plant and soil surrounding a petrochemical factory in Marvdasht County, Fars Province, southern Iran was investigated. The toxic effects were determined based on the use of different indices including the estimated daily intake (EDI) index, the target hazard quotient (THQ) for non-carcinogenic disorders, and the bio-concentration factor (BCF).

This study provided the required base for this research to employ electromagnetic waves for assessing plants contaminated by HMs. Around 40,000 hectares of agricultural land in Marvdasht County (north of Fars province, Iran) are located around the Kor River. On the other hand, there are several factories around the river, including petrochemicals whose effluent on the water quality of the Kor River, and the other hand, any agricultural product by this water is contaminated (Sheykhi and Moore 2012). Therefore, investigating the contamination of agricultural products in these areas is important. Due to the many activities of factories around the Kor River in recent

years, the Kor River has become more polluted than before leading to polluted agricultural lands. Therefore, rapid and non-destructive studies are important for determining and predicting the physicochemical and biological characteristics of the plant and soil. Traditional methods to determine plant, soil, and water characterizations require a considerable amount of time and expense so that the users generally do not tend to use the results of the laboratory. Spectroscopic studies can be used as a suitable alternative method for estimating plant, soil, and water properties (Lênio Soares et al. 2008).

Considering the properties of capsicum (*Capsicum annuum L.*) (reduce cancer, help the nervous system, slow down the aging process, help the respiratory health and help maintain proper blood flow) and its high consumption in Iran in recent years and cultivation of this plant in infected areas and using chemical fertilizers, the target material of the investigation is plant *Capsicum*. Recently, in Iran, this plant is cultivated in the contaminated area by elements Ni, Zn, Cd, and Pb. So the rate of absorption of different HMs in samples of the capsicum (*Capsicum annuum L.*) is determined. The study also investigated the sensitivity and bioaccumulation of the plant to different HMs using electromagnetic waves. Among other proceedings include attempts at identifying a relationship between reactions of contaminated plants to electromagnetic waves during different stages of growth (DSG) (to study the process of absorption of these elements until fruit stage), to determine appropriate relations for estimating THQ through the sole application of electromagnetic waves. So, in the study, the relationship between the measured values (heavy elements in plant and soil) in the laboratory and the amount of reflection of the electromagnetic waves were determined. So that farmers can determine the amount of contamination in plants and soil using electromagnetic waves. Therefore, the contaminated areas can be used as the results of the study to determine the amount of contamination in the plant or soil.

Materials and method

Study area

The case study is a small part of agricultural land located in the west of the Kor Watershed in Marvdasht County, Iran, between 29°18'N - 30°48' N and 51°42'E - 53°24' E (Fig. S1).

The average annual rainfall is 300 mm in the southeastern parts, but reaches over 800 mm in mountainous areas, with a mean value of 400 mm/year (Fars Regional Water Company, Meteorological Station, 2010 to 2017). The average annual air temperature of the region is 16 °C, with average annual evaporation of 2,252 mm. The primary soils in the region include aridisol, antisol, and inceptisol soil types. About 55% and 30% of the region is covered by rangelands and agricultural lands.

Current sources of contamination of the Kor River water that is used to irrigation of agricultural lands include urban wastewater and effluents from the Petrochemical factory that is located in western sectors of the study region.

Heavy metals analysis in soil and plant systems

Forty soil samples (10 soil samples with three repetitions for each HM and 10 soil samples for control samples) were initially pounded and passed through 2mm filters to a powder. Before planting, the content of the toxic elements (Cd, Ni, Zn, and Pb) was measured in the soil samples, using AAS (Atomic Absorption Spectrophotometry-PERKIN ELMER 8000).

Given that the water used to irrigate these agricultural lands by farmers is highly contaminated with heavy elements that lead to soil contamination, this water was used to irrigate the soils. It is worth mentioning that the amount of Cd, Ni, Pb, and Zn elements in the water of Kor River are 14, 6, 8, and 220 mg /l, respectively (Mokarram et al. 2020).

To prevent plant stress due to lack of moisture and nutrients, sufficient fertilizer and water were added to the samples at the right time. The plant samples (50 samples) were irrigated every 3 to 4 days. Leaves were then extracted from each vase at the DSG of the plant. The extracted leaves were dried at 72°C for 48 h. After drying out, the leaves samples were pounded to a powder. The samples are transferred to 100 ml containers and mixed with 15 ml of 70% pure nitric acid, 65% pure perchloride, and 70% pure sulfuric acid. After the extractions, the samples were transferred to an 80 ° oven. Finally, 50 ml of distilled water was added to the samples. The content of the elements (Cd, Pb, Ni, and Zn) from the extract was measured using AASPE PG 990. It is worth noting that the reflectance from each plant leaf was measured at three stages of growth in a spectral range from 0.4 to 1.1 micrometers. The final data were then analyzed using a statistical program (SPSS V.22).

Methodology of health risk assessment

At first, the amount of pollutant absorbed (Cd, Pb, Ni, and Zn) by the nutrient per kilogram of the body per day (EDI), calculated accordance with Eq. (3) (USEPA 2000):

$$EDI = (CF * IR * FI * EF * ED) / (BW * AT) \quad (3)$$

where EDI is the estimated daily intake ($\mu\text{g kg}^{-1}\text{day}^{-1}$), CF: concentration of contaminants in food ($\mu\text{g kg}^{-1}$) (HMs values in the plant), IR: intake per day (g day^{-1}) (325 g day^{-1}) (Miranzadeh Mahabadi et al. 2020) that share of *Capsicum annuum L.* in the total vegetables consumed on day 3.25 g day^{-1} was considered, FI: the amount of contaminants by bodies (a coefficient between 0.25-0.4, which in the case of this study was set at 0.4 to account for the worst scenario), EF: estimated frequency of consumption per year (days year^{-1}) ($365 \text{ days year}^{-1}$), ED: exposure duration (70

years for adults), BW: body weight (kg) (70 kg on average per adult), and AT (average time): the product of ED and the number of days per year.

THQ was calculated from the ratio between the amount of HM to the maximum allowable concentration according to Eq. (4) (USEPA 2011).

$$THQ = EDI / RfD \quad (4)$$

where THQ is the target hazard quotient for non-carcinogenic disorders, RfD: the reference dose ($\text{mg kg}^{-1} \text{ day}^{-1}$) for Cd, Ni, Pb, and Zn are 0.2, 66.7, 0.3, and 60 $\text{mg/kg mg kg}^{-1} \text{ day}^{-1}$, respectively (USEPA 1989, 2000 and 2011). The THQ value of higher than 1, demonstrates a high risk of non-carcinogenic hazards (USEPA 1989).

Total HI was obtained as the sum of individual THQs for different metals. An HI value close to 1 indicates a high risk of non-carcinogenic hazards, which can be obtained as shown in Eq. (5) (Street et al. 1977):

$$HI = \sum_{n=1}^i THQ_n \quad (5)$$

BCF, indicating the ratio of HMs within the plant organs (leaves and fruits) to the concentration of contaminants in soil was obtained using Eq. (6) (Arnot and Gobas 2006):

$$BCF = \frac{C_{Plant\ tissue}}{C_{Soil}} \quad (6)$$

$C_{plant\ tissue}$ represents the measured concentration of contaminants in the plant tissue and C_{soil} shows the concentration of HMs in soil. A BCF value close to 1 indicates higher accumulation of contaminant mass and therefore greater contamination per mass unit.

The method of the spectrometer measurements of reflectance intensity

Leaves of the Capsicum were placed under fiber optics working at a reflectance range of visible and near-infrared using the spectrometer (MICS-D10, Germany) to assess the reaction of the plant against electromagnetic waves. Twelve consecutive scans were taken from each sample (50 samplings) to improve accuracy and reduce the noise. The average of values was obtained and presented. It should be mentioned that the main source of illumination is the halogen-W lamp was used as the main source of illumination.

Each sample was then placed horizontally within wooden containers to register the spectral reflectance of the Capsicum. The wooden container was further placed in a small room to prevent any disturbances from other light sources (Fig. S1). To access the level of the metal bioaccumulation the following spectral ratios (Eqs. (7) - (12)) were used (Broge et al. 2002).

$$NDVI = (NIR-R)/(NIR+R) \quad (7)$$

$$SAVI = [(NIR-R)/(NIR+R+0.5)]*1.5 \quad (8)$$

$$RVI = NIR/R \quad (9)$$

$$NRVI = (RVI-1)/(RVI+1) \quad (10)$$

$$IPVI = NIR/(NIR+R) \quad (11)$$

$$PD = (R-B)/(R+B) \quad (12)$$

where NDVI: Normalized Difference Vegetation Index, SAVI: Soil-Adjusted Vegetation Index, RVI: Ratio Vegetation Index, NRVI: Normalized Ratio Vegetation Index, IPVI: Infrared percentage Vegetation Index, PD: Potential Different, NIR: Near-infrared (805 nm), B: blue (450 nm), G: green (548 nm) R: red. (655 nm).

It is used to investigate results of the applied electromagnetic waves and biophysical characteristics. The same method is used in different studies (Hansen et al. 2003; Ferwerda et al. 2005; Næsset et al. 2005).

Accordingly, the present study proceeded to employ multivariable regression as a means for obtaining the most optimal wavelengths for assessing HM contamination in plants using electromagnetic waves in conjunction with the THQ index in SPSS V.22 environment.

In the end, utilizing a regression model, the relationship between THQ and electromagnetic waves for each HM was determined. The purpose of the regression model is to predict THQ values using electromagnetic waves and use these results in future studies to avoid laboratory studies.

Results and Discussion

The concentration of heavy metals in soil

Descriptive statistics of chemical elements such as Ni, Pb, Zn, and Cd of the soil samples have been listed in Table 1 for different samples. As evident, the studies samples are of a loam form with an average electroconductivity of 0.04 ds/m and a pH level of 7.65, thus rendering the samples as non-saline with appropriate acidity for the growth of vegetables. The average concentrations of Cd, Ni, Pb, and Zn were obtained as 0.08, 14.50 19.50, and 210 mg/kg. It is worth that the toxicity threshold value for Cd, Ni, Pb, and Zn in the soil is 1, 50, 60, and 200 mg/kg respectively that according to Table 1, Zn is higher than the threshold value in the soil. As a result of pollution in the Kor River and the use of contaminated water for irrigation of agricultural lands, soil is also polluted (Mokarram et al. 2020). Therefore, industrial wastes in the Kor River are the source of pollution in water and soil in the study area.

The concentration of heavy metals in plant

The toxicity range for Cd has a threshold of 0.2 mg/kg (Joint 2010), that the concentration of Cd in the leaves and fruits of the target species exceeds the maximum allowed concentrations in all growth stages. The toxicity range for Ni has a maximum allowed concentration of 66. 7mg/kg. The concentration of Ni in the capsicum plant had not breached the maximum threshold in any of the growth stages. The maximum allowed concentration of Zn was reported at 60 mg/kg (Joint 2010), which as evident from Fig. 1, had reached beyond the threshold in the growth, flowering, and fruiting stages. The maximum allowed concentration for Pb was reported as 0.3mg/kg. Fig. 1 showed that the concentration of Pb in the target samples had breached the maximum threshold in all states except the first stage of growth, corresponding to a high bioconcentration factor.

The present study also indicated the amount of contamination by Zn, Cd, and Pb at DSG was high. Studies conducted in Chung King, China also indicated large concentrations of Pb and Cd in vegetables sold in stores, reaching rates higher than the maximum allowed concentrations reported by WHO/FAO. An assessment of contamination by HMs in vegetables in the southern sectors of Nigeria also showed transgression of the maximum allowed concentrations for Cd, Pb, and Ni, which is also consistent with the result of this study (Orisakwe et al. 2012)

The findings of this study are indicative of the high sensitivity of the target plant against HMs, warning of severe health hazards should the species be planted in regions with long-term contamination.

Resulted of EDI

Fig. 2 illustrates the rate of absorption of contaminants through consumption per kg of body weight per day. As can be observed, the third and fruiting stage is consonant with the highest rate of absorption. It is also evident that the absorption Pb was highest. This indicates that regions with

high degrees of Pb pollution are not suitable for the plantation of the target species. Alternatively stated, Pb tends to be easily absorbed by plants at a rate reaching concentrations 100 times higher than the maximum allowed concentrations (USEPA 2011).

Results of THQ and HI

According to Fig. 3(a), the THQ values of higher than 1 for each element, demonstrates a high risk of non-carcinogenic hazards. As can be seen, plants reaching the second, third, and fruiting stages are potentially hazardous in terms of non-carcinogenic disorders (THQ>1). Fig. 3(a) further elucidates a higher risk of subsuming to disorders resulting plants contamination by Pb, Cd, and Zn, which is consistent with findings proposed by Orisakwe (2012). This study showed that the estimated amounts of contaminants in vegetables found in the southern regions of Nigeria contaminated by Cd, Pb, Zn, mercury, and Ni were higher than the maximum allowed concentrations. It should be noted that plants contaminated by Ni were rendered as non-hazardous for non-carcinogenic disorders, i.e. the target plant can grow in regions contaminated by Ni without absorbing the contaminant. Results from THQ analysis indicated high risks of illnesses resulting from the use of such products among consumers. Exceeding the maximum allowed concentrations for HMs, particularly Cd, causes severe damages to the kidneys, lungs, and bones (Al Jassir et al. 2005).

Total HI for the present study, obtained as the sum of individual THQs, has been shown in Fig. 3 (b). As evident, the plant samples show high values of HI during the growth, flowering, and fruiting stages, indicative of the improper quality of the study region for planting said species.

Bioconcentration factor (BCF)

Bioconcentration factor (BCF), as the most salient parameter for assessing contamination in plants, represents a plant's capacity for absorbing chemical elements from the environment in which they are grown and can be obtained using Eq. (6). In this study, the mean of HMs in different vegetative stages in plant and soil for 50 sample points was measured and the ratios were calculated. Fig. 4 shows the results from BCF analysis at DSG. According to this figure, BCF was higher for plants contaminated by Cd at both flowering and fruiting stages, suggesting a higher accumulation of contaminant mass during these stages. Thus, the absorption rate of the target plant for Cd was significantly higher compared to other HMs, even at rather insignificant doses (Llobet 2003).

Mahmood and Malik (2014) reported in their assessment of the risks of HM contamination in vegetables containing Cd of the severe hazards accompanied by consumption of plants contaminated by this HM. Cd generally enters agricultural products through contaminated soil and irrigation by sewage sludge, atmospheric pollution, and the application of organic fertilizers, and must thus be constantly monitored to prevent its introduction to agricultural products through chemical fertilizers, most of which contain Cd.

Response of Leaf of Capsicum to Electromagnetic Waves

According to Figure 5, the change in the appearance of the plant is different according to the amount of absorption at DSG, which has led to a change in the amount of reflection of electromagnetic waves. So that in stage 3, when the amount of element absorption is higher, the amount of reflections is very different than the control plant with no contamination. According to Figure 5, the trend of changes in the control plant is the same for 4 elements, which indicates the health of the plant at DSG.

The results, however, prove the efficiency of electromagnetic waves in assessing different potential hazards and contamination as well as tensions introduced in plants (Dobrowski et al.

2005; Eitel et al. 2006; Seelig et al. 2008; Cozzolino, 2014). HMs can significantly affect the presence of chlorophyll in the leaves and the structure of leaves (Kabata-Pendias and Pendias 2011).

Plants contaminated by Cd show the highest reflectance in the 400-500 and 500-600 nm range at the second stage of growth, indicative of the weak production of chlorophyll. The present study also attempted at scrutinizing the reaction of the contaminated samples of the target plant at DSG against electromagnetic waves, the results of which are shown in Fig. 5 for a spectral range of 400-1050 nm for the plant leaves.

Similar conditions hold for both mentioned spectral ranges at the third and first stages of growth of plants contaminated by Cd, compared to control samples. A decrease in reflectance levels is also evident from Fig. 5 for spectral ranges of 800 nm and above, pointing to the lack of the plants yield. Trends for other HMs follow the same pattern, as maintained by Fig. 5, i.e. higher reflectance in the chlorophyll production sectors (400-500nm and 600-700nm).

Reflectance is minimized in control samples in the blue (near-purple) (400-500nm) and red (600-700nm) ranges, which include waves that are absorbed at high rates by the chlorophyll and are quite effective in vegetation and formation of plant organs (Fig. 5).

The reflection of waves in the range of 700-750 nm in the control sample is less that the plant needs these waves to germinate, accelerate fruiting, etc. Also, in the range of 850-940 and 500-600 nm, more reflection indicates that the plant is healthier and greener, which in the control sample is more in this range.

Spectral ratios were then employed to obtain a relationship between HMs values in contaminated plants and the reflection rate of electromagnetic waves. Table 2 lists the values for NDVI, SAVI, PD312, NRVI, RVI, and IPVI—among the most common vegetation indices—at

three levels of growth for both contaminated and control samples. The highest value was observed in the PVI index, wherein a higher value indicated lower contamination. The lowest value for all HMs was observed in the PD312 index, for which a lower value suggests higher toxicity of HMs. Overall, all indices, except for PD312, showed higher values in the case of lower contamination of the target plant. One of the most frequently used indices for estimating vegetation and yield of plants is the NDVI index, which was also investigated in this study as a means for assessing contamination by HMs at different stages. Based on the findings, only the control samples appear to have a good yield, whereas, yield in contaminated plants seems to diminish significantly. Increases in NDVI are accompanied by a decrease in reflectance in the red spectral range—required for chlorophyll production—, such that values closer to 1 indicate higher yield and healthier, uncontaminated plants. These results are in line with findings of other studies that show the reactivity of contaminated plants in both the infrared and near-infrared spectral ranges (Slonecker et al. 2009; Slonecker 2011).

Results of regression

Tables 3 and 4 show the results for plants contaminated by Pb. model 1 with the highest R^2 has been identified for estimating THQ values. Based on the results, the spectra b_{560} , b_{940} , and b_{460} are the most relevant spectra for estimating potential non-carcinogenic hazards of samples from the Capsicum contaminated by Pb.

Table 4 shows the two selected THQ regression models along with the most relevant spectrums, formulated in the following (Eqs. (13) and (14)):

$$THQ_{pb} = 57.886 - 43.967b_{560} \quad (13)$$

$$THQ_{pb} = 28.681 - 36.199b_{560} - 41.1678b_{490} \quad (14)$$

A total of two regression models with the highest R^2 value were also obtained for assessing THQ in the case of contamination by Ni (Table 3). The most relevant bands for assessing non-carcinogenic hazards in plants contaminated by Ni were b_{450} and b_{720} .

Table 4 shows the two selected THQ regression models formulated in Eq. (15):

$$THQ_{Ni} = 0.005 + 0.022b_{450} \quad (15)$$

According to Table 3, the b_{450} and b_{460} spectrum appear as the most relevant spectrum for assessing potential non-carcinogenic hazards in plants grown in soil contaminated by Cd and Zn respectively.

Table 4 shows the most appropriate THQ regression model for samples contaminated by Cd and Zn in Eq. (16) and (17) respectively:

$$THQ_{Cd} = -4.859 + 13.783b_{450} \quad (16)$$

$$THQ_{Zn} = -10.873 + 107.994b_{460}$$

(17)

Estimated THQ values were then compared with observed values for each element to assess the accuracy of the results. The most optimal model for estimation of THQ is shown in Fig. 6 for plants contaminated by Pb and can be formulated using Eq. (14). The best models for contamination by Cd, Ni, and Zn were obtained as Eqs. (15), (16), and (17), respectively. Fig. 6 elucidates the capability of the application of remote sensing approaches to accurately estimate THQ using electromagnetic waves.

Finally measured THQ and predicted THQ by electromagnetic waves for each metal were statistically significant using t-Test at $p < 0.05$ (Table 6). The results of statistical tests (t-Test) showed that all of the p-values were < 0.05 . Therefore, there is no significant difference between measured THQ and predicted THQ and should utilize the results of electromagnetic waves to

predict THQ value. The results of this study indicated a significant relationship between increases in HM concentrations in soil and the Capsicum. Ping et al. (2011), reported a positive and significant relationship between metals found in agricultural products and contaminated soil.

Conclusion

Cd concentrations in leaf and fruit exceeded the maximum allowed concentration (0.2 mg/kg) in all stages except for the first stage of growth, indicating the higher absorption of the plant for Cd. Ni concentration remained below the maximum allowed concentrations (66.7 mg/kg) for all growth stages. Zn concentrations transgressed the maximum allowed concentration (60 mg/kg) in the growth, flowering, and fruiting stages, while Pb content in the leaves had exceeded the maximum threshold (0.3 mg/kg) in all stages, excluding the first stage of growth, suggestive of the high bioconcentration factor of the target plant. The results of EDI evident that the absorption Pb was highest. While the results of THQ showed that the higher risk of subsuming to disorders resulting from plants contaminated by Pb, Cd, and Zn and plants contaminated by Ni was also rendered as non-hazardous for non-carcinogenic disorders, i.e. the target plant could grow in regions contaminated by Ni without absorbing the contaminant. The results of HI showed that the high values of HI during the growth, flowering, and fruiting stages, indicative of the improper quality of the study region for planting said species. Overall, metals such as Pb, Zn, and Cd were abundant in the target plant, rendering it highly hazardous to human health, even at small percentages. In addition to assessing concentrations of HMs during DSG, the present study also proceeded to analyze the reaction of contaminated plants to electromagnetic waves at various growth phases. As maintained by the findings, increases in HM contents in plants cause a decrease in the amount of reflectance in the 400-500 and 600-700nm range, which is essential to the

production of chlorophyll. Reflectance in the 500-600nm range which generally corresponds to the highest reflectance decreased for contaminated samples. This points to the feasibility of employing remote sensing approaches as an alternative to laboratory researches for the assessment of contamination and potential risks of non-carcinogenic hazards in plants. It can be the prospective, initial phase of an investigation of the level of contamination of edible plants by toxic elements.

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Consent to Publish Not applicable

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409 **References**

- 410 Al Jassir MS, Shaker A, Khaliq MA, (2005) Deposition of Heavy Metals on Green Leafy Vegetables
411 Sold on Roadsides of Riyadh City, Saudi Arabia, *Environ. Con Tox* 75: 1020–1027.
- 412 Arnot JA, Gobas FA (2006) A review of bioconcentration factor (BCF), and bioaccumulation factor
413 (BAF), assessments for organic chemicals in aquatic organisms. *Environ Rev* 14(4): 257-297.
- 414 Broge NH, Mortensen, JV (2002) Deriving green crop area index and canopy chlorophyll density
415 of winter wheat from spectral reflectance data. *Remote Sens Environ* 81(1): 45-57.
- 416 Collins W, Chang SH, Kuo JT (1984) Detection of hidden mineral deposits by airborne spectral
417 analysis of forest canopies.[Spirit Lake, Washington; Catheart Mountain, Maine; Blacktail
418 Mountain, Montana; and Cotter Basin, Montana]. 61.
- 419 Cozzolino D (2014) Use of infrared spectroscopy for in-field measurement and phenotyping of plant
420 properties: instrumentation, data analysis, and examples. *Appl Spectrosc Rev* 49(7) : 564-584.
- 421 Dobrowski SZ, Pushnik JC, Zarco-Tejada PJ, Ustin SL (2005) Simple reflectance indices track heat
422 and water stress-induced changes in steady-state chlorophyll fluorescence at the canopy scale.
423 *Remote Sens Environ* 97(3) : 403-414.
- 424 Eitel JU, Gessler PE, Smith AM, Robberecht R (2006) Suitability of existing and novel spectral
425 indices to remotely detect water stress in *Populus* spp. *Forest Ecol Manag* 229(1-3): 170-182.
- 426 Fan J, Cai C, Reid B.J, Coulon F, Zhang Y, Hou Y (2020) Remediation of cadmium and lead
427 polluted soil using thiol-modified biochar. *Journal of Hazardous Materials*. 388: 1222037

428 FAO, (2010) Codex Alimentarius Commission: Procedural Manual. 19th ed. Rome: Food and
 429 Agriculture Organization of the United Nations.

430 Ferwerda JG, Skidmore AK, Mutanga O (2005) Nitrogen detection with hyperspectral normalized
 431 ratio indices across multiple plant species. *Int J Remote Sens* 26(18) : 4083-4095.

432 Hansen PM, Schjoerring JK (2003) Reflectance measurement of canopy biomass and nitrogen status
 433 in wheat crops using normalized difference vegetation indices and partial least squares regression.
 434 *Remote Sens Environ* 86(4): 542-553.

435 Joint FAO (2010) Fats and fatty acids in human nutrition. Report of an expert consultation, 10-14
 436 November 2008, Geneva

437 Kabata-Pendias A, Pendias H (2011) Trace Elements in Soils and Plants; CRC Press: Boca Raton,
 438 FL, USA 951–974.

439 Lênio Soares G, Antônio Roberto F, Eduardo Guimarães C, (2008) Relationships between the
 440 mineralogical and chemical composition of tropical soils and topography from hyperspectral
 441 remote sensing data. *ISPRS J Photogramm Remote Sens* 63:259 – 271.

442 Li L, Zhang Y, Ippolito JA, Xing W, Qiu K, Yang H, (2019) Lead smelting effects heavy metal
 443 concentrations in soils, wheat, and potentially humans. *Environ Pollut* 113641.

444 Liang C, Xiao H, Hu Z, Zhang X, Hu J (2018) Uptake, transportation, and accumulation of C60
 445 fullerene and heavy metal ions (Cd, Cu, and Pb) in rice plants grown in an agricultural soil.
 446 *Environ Pollut* 235: 330-338.

447 Liu YM, Liu DY, Zhang W, Chen XX, Zhao QY, Chen XP, Zou CQ (2019) Health risk
 448 assessment of heavy metals (Zn, Cu, Cd, Pb, As and Cr) in wheat grain receiving repeated Zn
 449 fertilizers. *Environ Pollut* 113581.

450 Llobet JM, Falco G, Casas C, Teixido A, Domingo JL, (2003) Concentrations of arsenic, Cd,
 451 mercury, and lead in common foods and estimated daily intake by children, adolescents, adults,
 452 and seniors of Catalonia, Spain. *J Agr Food Chem* 51(3): 838-842.

453 Lu J, Lu H, Li J, Liu J, Feng S, Guan Y (2019) Multi-criteria decision analysis of optimal planting
 454 for enhancing phytoremediation of trace heavy metals in mining sites under interval residual
 455 contaminant concentrations. *Environ Pollut* 255:113255.

456 Mahmood A, Malik RN (2014) Human health risk assessment of heavy metals via consumption of
 457 contaminated vegetables collected from different irrigation sources in Lahore, Pakistan. *Arab J*
 458 *Chem* 7(1): 91-99.

459 Massadeh AM, Jaradat QM, Momani KA, Saleem MA, (2009) Distribution of heavy metals in some
 460 tree leaves along the main road in an agricultural area. *Commun. Soil Sci Plan* 40(7-8): 1254-1267.

461 Milton NM, Ager CM, Eiswerth BA, Power MS (1989) Arsenic-and selenium-induced changes in
 462 spectral reflectance and morphology of soybean plants. *Remote Sens Environ* 30(3): 263-269.

463 Minasny T, McBratney B, (2009) Regional transferability of mid-infrared diffuse reflectance
 464 spectroscopic prediction for soil chemical properties. *Geoderma* 153: 155-162.

465 Muchuweti M, Birkett JW, Chinyanga E, Zvauya R, Scrimshaw MD, Lester JN (2006) Heavy metal
 466 content of vegetables irrigated with mixtures of wastewater and sewage sludge in Zimbabwe:
 467 implications for human health. *Agriculture, Ecosyst Environ* 112(1) : 41-48.

468 Næsset E, Bollandsås OM, Gobakken T (2005) Comparing regression methods in estimation of
 469 biophysical properties of forest stands from two different inventories using laser scanner data.
 470 Remote Sens Environ 94(4): 541-553.

471 Nawar S, Cipullo S, Douglas RK, Coulon F, Mouazen AM (2019) The applicability of spectroscopy
 472 methods for estimating potentially toxic elements in soils: state-of-the-art and future trends.
 473 Applied Spectroscopy Reviews. Doi: 10.1080/05704928.2019.1608110

474 Orisakwe OE, Nduka JK, Amadi CN, Dike D, Obialor OO (2012) Evaluation of potential dietary
 475 toxicity of heavy metals of vegetables. J Environ Anal Toxicol 2(136): 2161-0525.

476 Philippe L, Baret F, Feret JB, Maderia Netto J, Robbez-Masson JM (2008) Estimation of soil clay
 477 calcium carbonate using laboratory, field, airborne hyperspectral measurements. Remote Sens
 478 Environ 112: 825-835.

479 Ping LIU, Zhao HJ, Wang LL, Liu ZH, Wei JL, Wang YQ, Zhang YF (2011) Analysis of heavy
 480 metal sources for vegetable soils from Shandong Province, China. Agr Sci China 10(1): 109-119.

481 Ping Z, Murray BM, Hanping X, Ningyu L, Zhian L (2009) Health risk from heavy metals via
 482 consumption of food crops in the vicinity of Dabaoshan mine, South China. Sci Total Environ 407:
 483 1551-1561.

484 Seelig HD, Hoehn A, Stodieck LS, Klaus DM, Adams Iii WW, Emery WJ (2008) Relations of
 485 remote sensing leaf water indices to leaf water thickness in cowpea, bean, and sugarbeet plants.
 486 Remote Sens Environ 112(2): 445-455.

487 Sheykhi V, Moore F (2012) Geochemical characterization of Kor River water quality, fars province,
 488 Southwest Iran. Water Quality, Exposure and Health 4(1): 25-38.

489 Slonecker ET (2011) Analysis of the effects of heavy metals on vegetation hyperspectral reflectance
 490 properties. *Hyper Remote Sens Veg* 561-578.

491 Slonecker T, Haack B, Price S (2009) Spectroscopic analysis of arsenic uptake in *Pteris* ferns.
 492 *Remote Sens* 1(4): 644-675.

493 Song C, Ye F, Zhang H, Hong J, Hua C, Wang B, Chen Y, Ji R, Zhao L (2019) Metal (loid) oxides
 494 and metal sulfides nanomaterials reduced heavy metals uptake in soil cultivated cucumber plants.
 495 *Environ Pollut* 255 : 113354.

496 Sridhar BM, Han FX, Diehl SV, Monts DL, Su Y (2007) Spectral reflectance and leaf internal
 497 structure changes of barley plants due to phytoextraction of Zn and Cd. *Int. J. Remote Sens* 28(5):
 498 1041-1054.

499 Street JJ, Lindsay WL, Sabey BR (1977) Solubility and Plant Uptake of Cd in Soils Amended with
 500 Cd and Sewage Sludge. *J Environ Qual* 6(1): 72-77.

501 USEPA (US Environmental Protection Agency) (2011) Risk- based concentration table
 502 environmental protection agency. Philadelphia PA/Washington DC.

503 USEPA (1989) Risk assessment guidance for superfund. Human Health Evaluation Manual, Part A.
 504 EPA/540/1- 89/002. Office of Health and Environmental Assessment, Washington, DC, USA.

505 USEPA (US Environmental Protection Agency) (2000) Risk-Based Concentration Table. Office of
 506 Health and Environmental Assessment, Washington, DC, USA

507 Yang J, Guo H, Ma Y, Wang L, Wei D, Hua L (2010) Genotypic variations in the accumulation of
 508 Cd exhibited by different vegetables. *J Environ Sci* 22(8) : 1246-1252.

509 Yang Y, Zhang FS, Li HF, Jiang RF (2009) Accumulation of Cd in the edible parts of six vegetable
510 species grown in Cd-contaminated soils. *J Environ Manage* 90(2): 1117-1122

511 Zhou L, Liu G, Shen M, Hu R, Sun M, Liu Y (2019) Characteristics and health risk assessment of
512 heavy metals in indoor dust from different functional areas in Hefei, China. *Environ. Pollut* 251 :
513 839-849

514 Yu R, He L, Cai R, Li B, Li Z, Yang K (2017) Heavy metal pollution and health risk in
515 China. *J Public Health* 1(1): 47-55

516 Miranzadeh Mahabadi H, Ramroudi M, Asgharipour MR, Rahmani HR, Afyuni M (2020)
517 Assessment of heavy metals contamination and the risk of target hazard quotient in some
518 vegetables in Isfahan. *Pollution* 6(1): 69-78

519 Prichard E, Barwick V (2007) *Quality Assurance in Analytical Chemistry*. John Wiley and
520 Sons: New York, ISBN 978-0131291928, 86–88

521 Mokarram M, Saber A, Sheykhi V (2020) Effects of heavy metal contamination on river water
522 quality due to release of industrial effluents. *J. Clean. Prod.* 277, 123380
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Figures caption

Fig. 1 HM concentrations in Capsicum during DSG.

Fig. 2 Rate of absorption of contaminants by the Capsicum at DSG.

Fig. 3 (a): Potential risk of non-carcinogenic hazards, (b): HI values at DSG of the Capsicum.

Fig. 4 Absorption rate of HMs in the leaves and fruits of the Capsicum.

Fig. 5 Reaction of the leaves of the Capsicum at DSG to various HM contamination treatments.

Fig. 6 Estimated and observed THQ values for plants contaminated by HMs.

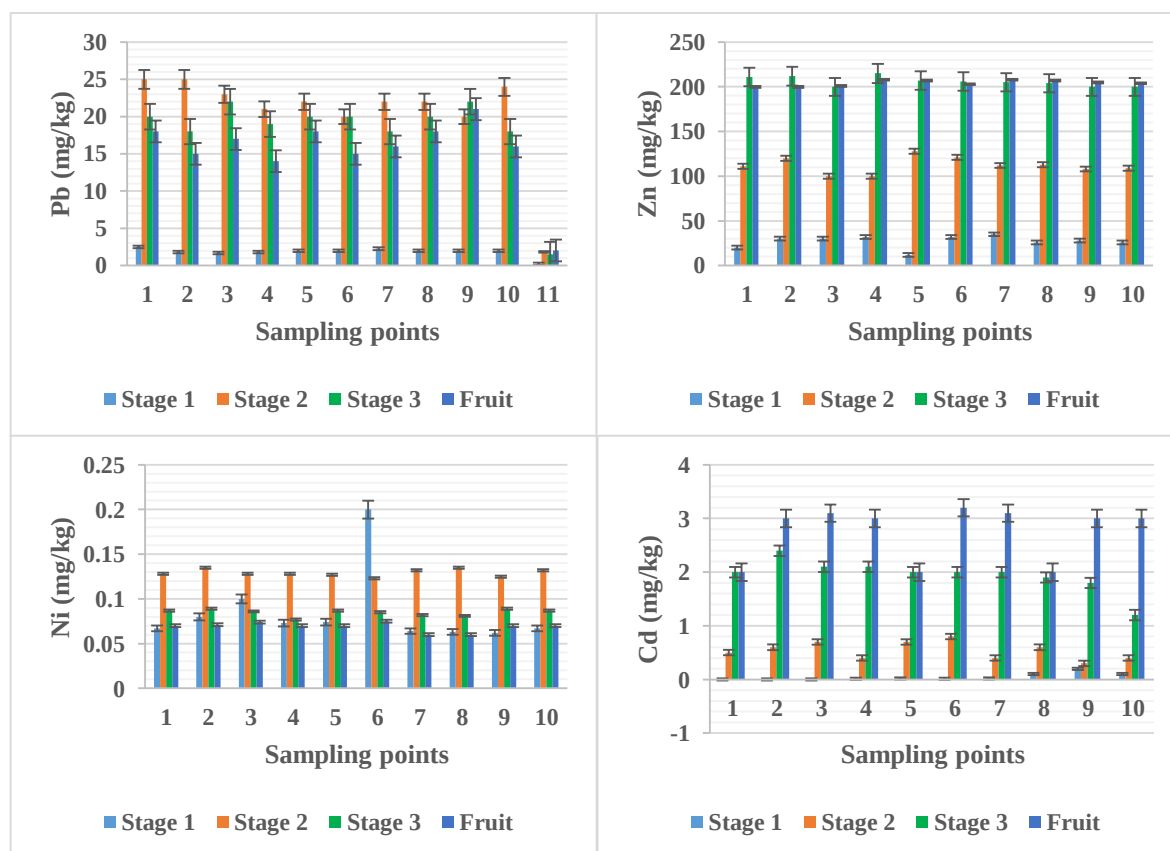


Fig. 1 Heavy metal concentrations in Capsicum during different stages of growth.
(a): Pb, (b): Ni, (c): Zn, (d): Cd.

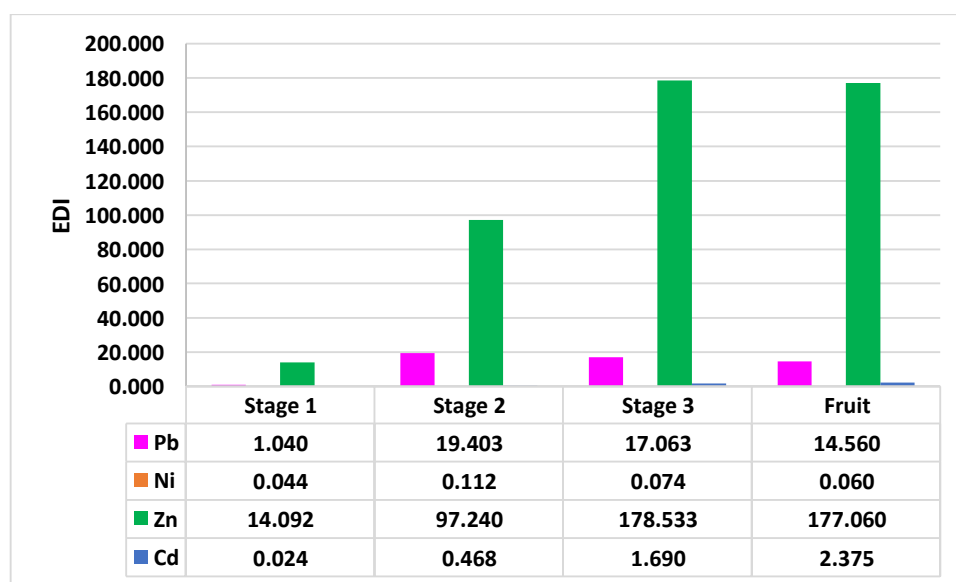


Fig. 2 Rate of absorption of contaminants by the Capsicum at different stages of growth.

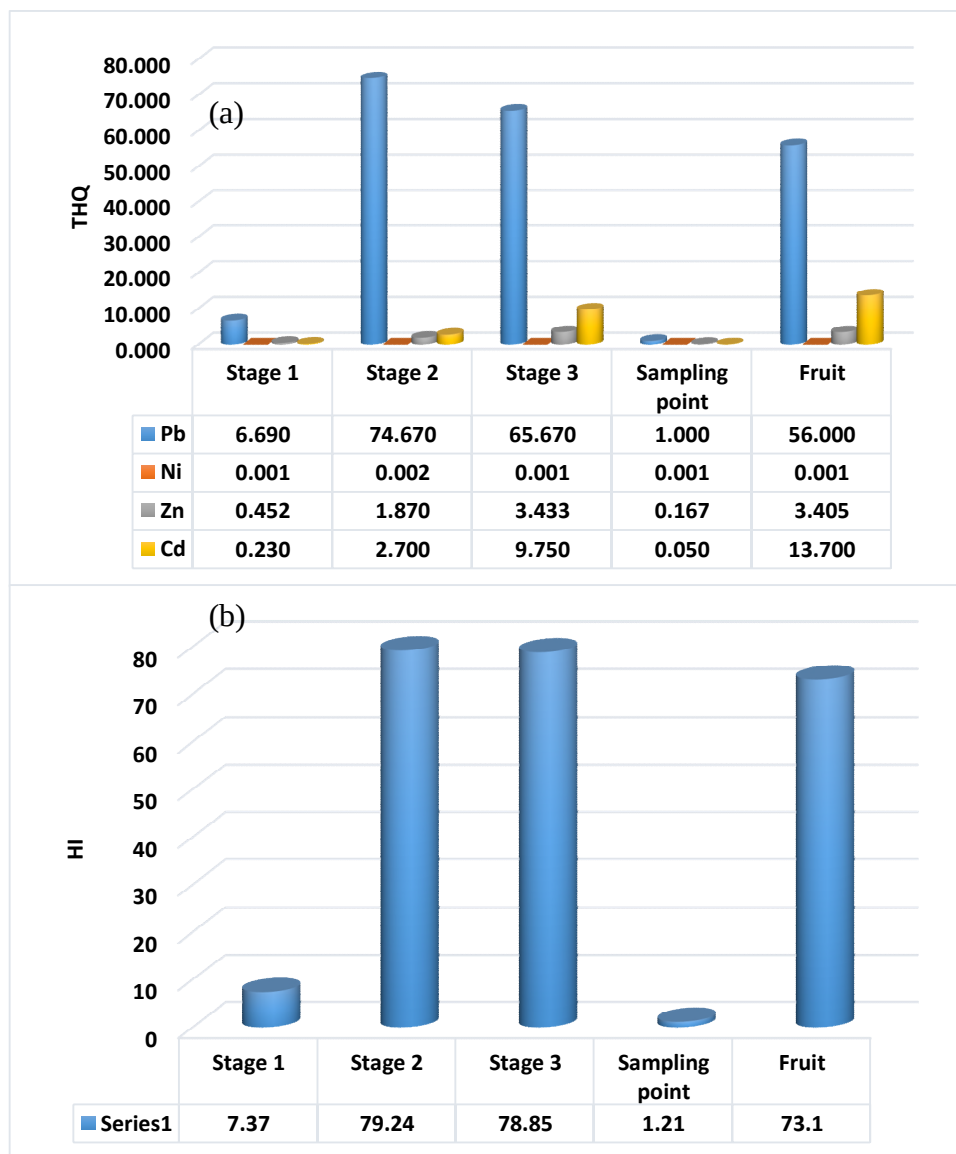


Fig. 3 (a): Potential risk of non-carcinogenic hazards, (b): HI values at different stages of growth of the Capsicum.

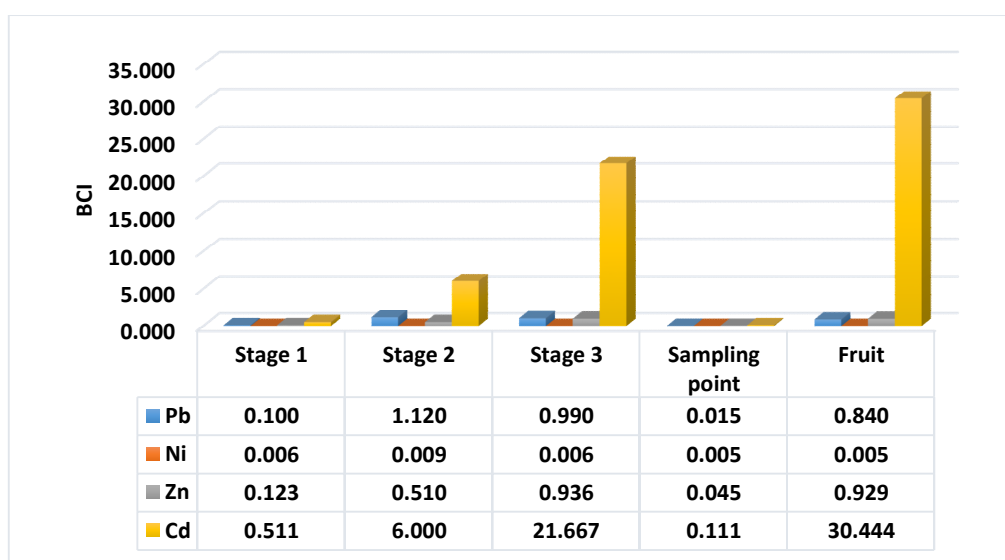


Fig. 4 Absorption rate of heavy metals in the leaves and fruits of the Capsicum.

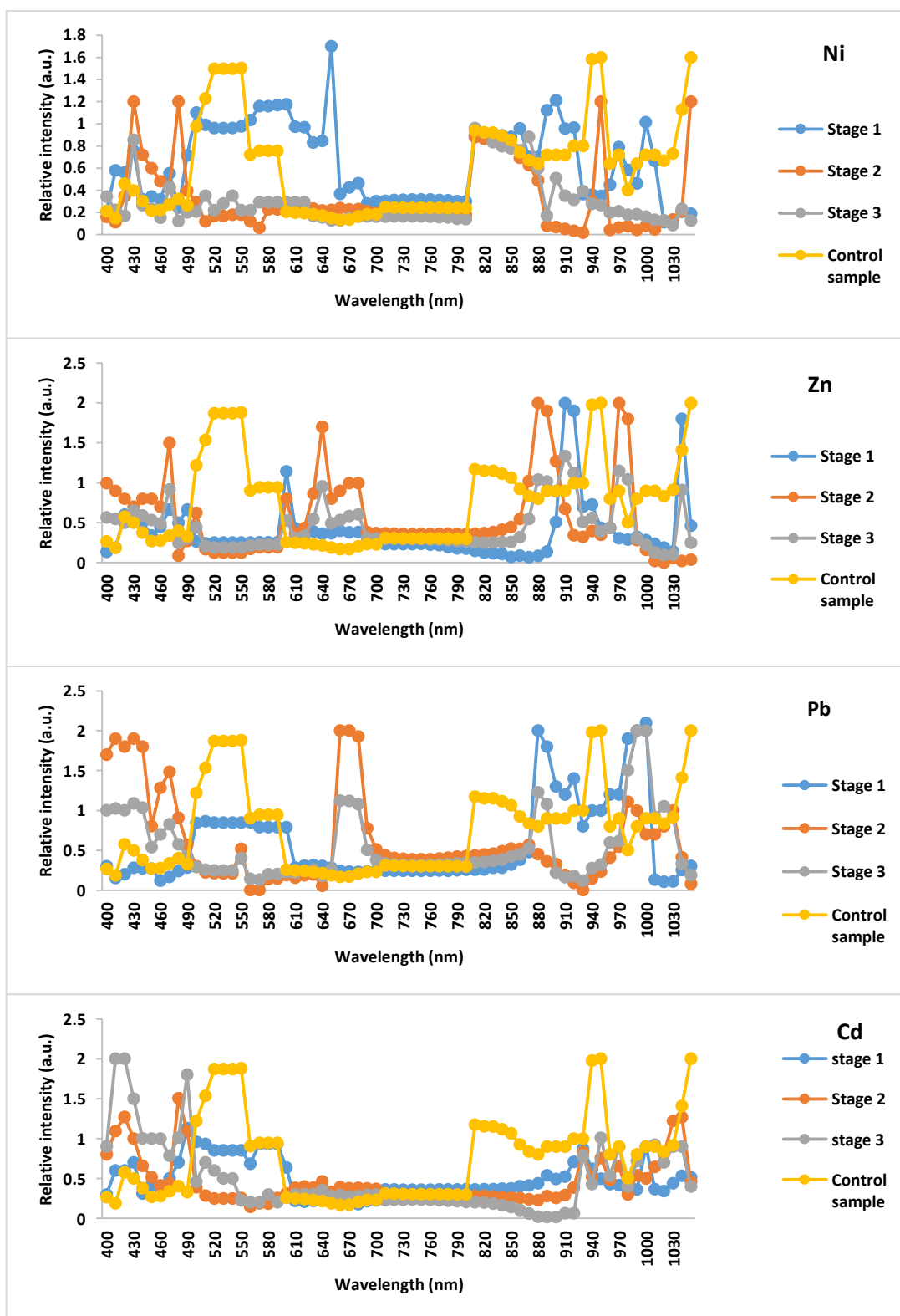


Fig. 5 Reaction of the leaves of the Capsicum at different stages of growth to various heavy metal contamination treatments.^a Relative Intensity

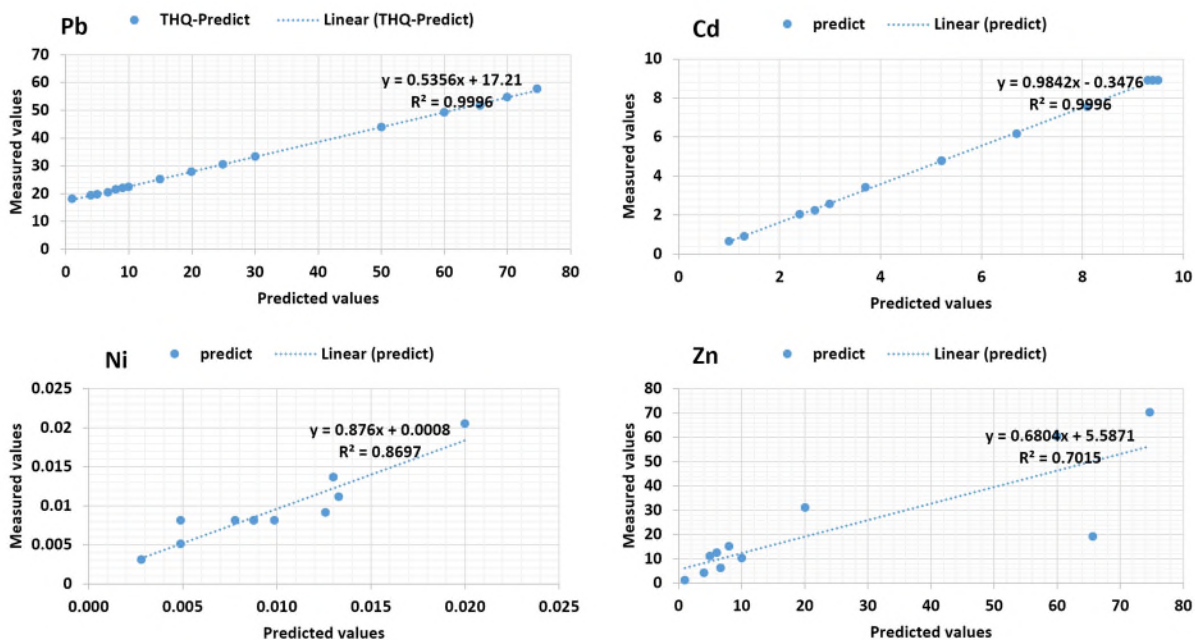


Fig. 6 Estimated and observed THQ values for plants contaminated by heavy metals.

Table 1 Statistics on the physical and chemical characteristics of soil samples

Parameter	Unit	Minimum value	Maximum value	Average $\pm$ STDEV
pH	-	7.1	8.2	7.3 $\pm$ 0.77
EC ¹	ds/m	0.01	0.07	0.03 $\pm$ 0.04
Cd	mg/kg	0.05	0.12	0.1 $\pm$ 0.04
Pb	mg/kg	14	25	22 $\pm$ 7.77
Ni	mg/kg	9	20	15 $\pm$ 7.77
Zn	mg/kg	180	240	221 $\pm$ 41.40

¹ Electrical Conductivity

Table 2 Results of vegetation indices for different treatments at different stages of growth

Cd					Pb			
Vegetation index	Stage 1	Stage 2	Stage 3	Control sample	Stage 1	Stage 2	Stage 3	Control sample
NDVI	0.38	0.10	0.15	0.61	0.51	-0.26	0.08	0.61
SAVI	0.33	0.09	0.14	0.65	0.52	-0.28	0.08	0.65
PD312	-0.53	-0.31	-0.55	-0.33	-0.09	-0.05	-0.02	-0.33
PVI	2.23	1.22	1.36	4.15	3.04	0.59	1.17	4.15
DVI	0.26	0.08	0.11	0.75	0.55	-0.33	0.09	0.75
IPVI	0.69	0.55	0.58	0.81	0.75	0.37	0.54	0.81
Ni					Zn			
Vegetation index	Stage 1	Stage 2	Stage 3	Control sample	Stage 1	Stage 2	Stage 3	Control sample
NDVI	-0.20	-0.08	0.03	0.61	0.07	-0.13	0.02	0.61
SAVI	-0.21	-0.07	0.02	0.65	0.06	-0.15	0.02	0.65
PD312	0.14	-0.42	-0.11	-0.33	-0.11	0.08	0.01	-0.33
PVI	0.67	0.86	1.06	4.15	1.15	0.76	1.04	4.15
DVI	-0.23	-0.05	0.02	0.75	0.06	-0.18	0.02	0.75
IPVI	0.40	0.46	0.52	0.81	0.53	0.43	0.51	0.81

Table 3 THQ estimation model for assessment of heavy metal contamination in the target plant

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate	Change Statistics				
					R Square Change	F Change	df1	df2	Sig. F Change
Pb									
1	.807 ^a	.651	.626	16.16338	.651	26.137	1	14	.000
2	.973 ^b	.947	.939	6.51295	.296	73.226	1	13	.000
Cd									
1	.897 ^c	.804	.788	1.4793	.804	49.263	1	12	.000
Ni									
1	.820 ^d	.673	.637	.002937	.673	18.512	1	9	.002
Zn									
1	.773 ^e	.598	.554	18.87561	.598	13.399	1	9	.005

a. Predictors: (Constant), b₅₆₀, b. Predictors: (Constant), b₅₆₀, b₄₉₀, c. Predictors: (Constant), b₄₅₀, d. Predictors: (Constant), b₄₅₀, e. Predictors: (Constant), b₄₆₀

Table 4 Significance levels of parameters for the THQ regression model using Pearson's Coefficient in plants contaminated by heavy metal

Model		Unstandardized Coefficients		Standardized Coefficients	Sig.
		B	Std. Error	Beta	
Pb					
1	(Constant)	57.886	7.046	-	0.00
	b560	-43.967	8.600	-.807	0.00
2	(Constant)	28.681	4.439	-	0.00
	b560	-36.199	3.582	-.664	0.00
	b490	41.167	4.811	.563	0.00
Cd					
1	(Constant)	-4.859	1.527	-	0.05
	b450	13.783	1.964	.897	0.02
Ni					
1	(Constant)	.005	.001	-	0.008
	b450	.022	.005	.820	0.034
Zn					
1	(Constant)	-10.873	11.034	-	0.5
	b460	107.994	29.502	.773	0.1

Table 5. Heavy metal contamination different studies (mg/kg)

Region	Pb	Ni	Zn	Cd	Reference
Iran	16.8	0.053	27	2.74	This research
Yangtze River Delta, China	1.5	7.8	56	1.10	Hu et al., 2017
Mojo River, Oromia Regional State	7.56	4.13	23.53	1.56	Gebeyehu and Bayissa, 2020
Temeke district, Tanzania	2.92	-	11.11	-	Kacholi and Sahu, 2018
China	2.84	0.74	0.58	0.68	Yu et al., 2017

1 **Table 6.** Comparative between THQ measured and predicted by electromagnetic waves

THQ	One-sample t-Test					
	t	df	p-value	Mean Difference	95% Confidence Interval of the Difference	
					Lower	Upper
THQ _{Pb} (measured)	7.693	19	.001	43.42650	31.6114	55.2416
THQ _{Pb} (predicted)	7.693	19	.001	43.86077	31.9276	55.7940
THQ _{Ni} (measured)	18.889	19	.002	.00134	.0012	.0015
THQ _{Ni} (predicted)	18.879	19	.002	.00148	.0013	.0016
THQ _{Zn} (measured)	5.248	19	.000	1.92683	1.1583	2.6954
THQ _{Zn} (predicted)	5.235	19	.000	2.11927	1.2720	2.9665
THQ _{Cd} (measured)	4.304	19	.001	5.39900	2.7736	8.0244
THQ _{Cd} (predicted)	4.431	19	.001	6.15284	3.2463	9.0594

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Investigation of plant contamination to Ni, Pb, Zn and Cd and its relationship with spectral reflections

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