Assessment of Zinc and Nickel Profile of Vegetables Grown in Soil Irrigated with Sewage Water

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Abstract: The current investigation assessed the nickel and zinc contents of the soil, and the vegetables grown in wastewater irrigated areas. Atomic Absorption Spectrophotometer (AA-6300 Shimadzu Japan) assessed the metal profile of the samples. The mean concentrations of metals in soil samples varied from 0.085 to 1.611 mg/kg for Ni and 0.453 ~ 0.908 mg/kg for Zn. In vegetables, the maximum Ni concentration was observed in Capsicum baccatum consequent to wastewater irrigation, while its minimum concentrations were noticed in Capsicum frutescens after canal water irrigation. Sewage water irrigation resulted in the highest Zn contents in Solanum lycopersicum and the lowest Zn contents were noticed in Capsicum baccatum after canal water irrigation. The daily intake values of Ni and Zn were higher caused by sewage water irrigation as compared to the canal water irrigation in all tested vegetable samples. Health risk index (HRI) values for Ni and Zn accumulation in vegetables fell within the permissible limit in Pakistan and these were regarded as appropriate for human intake.

Keywords: Trace metal, sewage water, health risk, Pollution load index

1. Introduction

Metals have been categorized as essential and non-essential based on their metabolism in biological systems [1-5]. The higher quantities of essential heavy metals may be highly poisonous [6,7]. These elements have a great impact on many metabolic pathways of living organisms [8-13]. Living organisms may store heavy metals upon their entry in the body in various forms which can be categorized into three forms namely extracellular accumulation, cell surface binding and intracellular accumulation. The binding over cell surface could be by inactive or active microorganisms as it is independent of metabolism. The intracellular and extracellular accumulation of metals occurs in the living cells occurs by active transport. Even trace quantities of some heavy metals in organisms prove to be harmful since they interfere with the metabolic functions of the cells [14-18].

The ecosystem and environment are affected unfavourably by the soil degradation caused by heavy metal contaminants throughout the world [19-21]. Many health problems occur owing to the intense metal concentrations in soil which are absorbed by the growing plants resulting in food chain contamination [22-24]. Owing to industrial manufacturing, municipal solid wastes, industrial effluents, mining and smelting, pesticides, fertilizers and wastewater irrigation in agriculture, the soil is polluted with heavy metals and soil contamination has radically enhanced in recent past [25- 29]. The vegetative tissues of the crop plants get maximum heavy metals from the contaminated rhizosphere and pose high health risk to humans [30-33]. If the wastewater irrigation of crops continues for a longer duration, it will result in the food web contamination [34- 37].

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Wastewater from industrial and drug production activities have higher concentrations of heavy metals [38-40]. Metals accumulation in vegetables could be attributed to the excessive use of wastewater in agricultural activities [12,13,41]. Al-Jassir et al. [42] demonstrated the toxic limits of heavy metals in food items. Prolonged use of large quantities of these elements in the form of contaminated vegetables consumption can lead to many disorders in humans and other organisms and may prove lethal if exceeds the safe limits [43-49].

Keeping in view of the published literature, aim of the current investigation was to determine the Ni and Zn concentrations in soil samples watered with fresh (canal) and waste (sewage) water; to determine these metals accumulations in vegetables grown in these soils, and to evaluate the health risk caused by the consumption of contaminated vegetables by human.

2. Materials and methods

2.1. Study area

Current investigation was carried out in Sargodha City, Punjab, Pakistan (32.0740° N, 72.6861° E) (Figure 1). The areas watered with sewage wastewater and canal water in the Sargodha city. Most of the agricultural areas of the city are saline soils. The vicinity of the city is mostly irrigated with industrial wastewater. Two sites were selected for the current research work based upon the irrigation practice i.e. site 1, irrigated by canal water (CWI) and site 2, where irrigated by industrial sewage water (SWI).

![Figure 1: Location map of the study site](https://example.com/map)

2.2. Sample preparation

In present research, *Brassica rapa* L. (roots), *Capsicum frutescens* L. (fruit), *Capsicum baccatum* L. (fruit), *Capsicum annuum* L. (fruit), *Curcuma longa* L. (rhizome), *Raphanus sativus* L. (roots), *Solanum lycopersicum* L. (fruit) and *Zingiber officinale* Roscoe (roots) were chosen as vegetables samples. The vegetable samples were collected at maturity.
2.3. Wet digestion process
  Double acid digestion was accomplished before the analyses of samples for metals accumulation. Soil and plant samples were soaked in concentrated acid overnight, then digested with H₂O₂ using hot plate. The volume of digested samples were made upto 50 ml using distilled water. Diluted samples were filtered and stored for further analyses [50].

2.4. Nickel and Zinc analysis
  Atomic absorption spectrophotometer (AAS-6300 Shimadzu Japan) performed analysis of samples for Ni and Zn.

2.5. Statistical Analysis
  The statistical significance of variations among different samples was analysed using SPSS (Statistical Package for Social Sciences). One-way ANOVA (Analysis of Variance) determined the statistical significance of different concentrations.

2.6. Daily intake of metals (DIM)
  DIM is the amount calculated to the intake of trace metals orally. It is calculated as:[51].

  \[
  DIM = \frac{Concentrations \ of \ metal \times \ Daily \ consumption \ of \ vegetable \ (kg \ per \ person)}{Average \ body \ weight \ of \ a \ person}
  \]

2.7. Pollution load index (PLI)
  The concentration of metals in soil was evaluated by PLI. It was determined by the formula:

  \[
  PLI = \frac{metal \ concentrations \ in \ soils}{metal \ concentration \ taken \ as \ reference}
  \]

2.8. Health risk index
  Health risk index (HRI) was determined relative to DIM value and oral reference dose (RfD) according to following expression: [52].

  \[
  HRI = \frac{DIM}{Oral \ reference \ dose}
  \]

2.9. Bio concentration factor
  Metal concentration accumulated in the body of living being is called bioconcentration factor (BCF) [53]. It was computed using the given formula:

  \[
  HRI = \frac{Vegetable \ metals}{Soil \ metals}
  \]

3. Results and discussions
3.1. Nickel and Zinc contents of sampled soils
  The mean Ni concentration in soil differed from 0.805 to 1.611 mg/kg. Highest concentration of Ni in soil was detected during SWI and the lowest concentration was observed for CWI. The ANOVA results exhibited the variations to be non-significant (p > 0.05) in Ni concentration with respect to the irrigated sites (Table 1). The mean Zn concentration in soil varied from 0.453-0.908 mg/kg. The maximum Zn values were present in the soil irrigated with sewage water while the minimum values were observed by canal water irrigation. The ANOVA results depicted significant (p≤ 0.05) impact of irrigation source on Zn concentration (Table 1).
Table 1. Analysis of variance and mean values of nickel and zinc (mg/kg) in soil and vegetables treated with canal and sewage water

| Vegetables | Nickel | | Zinc |
|------------|--------|------------------|------------------|
|            | Mean ± S.E. | Mean Square | Mean ± S.E. | Mean Square |
|            | CWI | SWI | | CWI | SWI |
| Soil       | 0.805±0.175 | 1.611±0.350 | 4.249** | 0.453±0.061 | 0.908±0.123 | 11.039* |
| R. sativus  | 0.461±0.020 | 0.919±0.039 | 110.4*** | 4.000±0.570 | 7.999±1.139 | 9.853* |
| B. rapa     | 0.450±0.006 | 0.899±0.013 | 999.0*** | 4.324±0.933 | 8.645±1.867 | 4.284** |
| Z. officinale | 0.466±0.022 | 0.934±0.041 | 101.5*** | 1.905±1.142 | 4.763±2.308 | 1.232** |
| C. baccatum | 0.513±0.032 | 1.023±0.063 | 51.76*** | 7.479±0.521 | 14.954±1.043 | 1.232** |
| C. frutescens | 0.324±0.042 | 0.646±0.085 | 11.55* | 1.936±0.494 | 3.870±0.989 | 41.142** |
| C. annuum   | 0.444±0.023 | 0.886±0.046 | 73.00*** | 4.688±0.676 | 9.360±1.351 | 11.552* |
| S. lycopersicum | 0.394±0.023 | 0.786±0.046 | 57.43*** | 3.791±1.215 | 1.036±1.351 | 13.074* |
| C. longa    | 0.436±0.020 | 0.869±0.039 | * | 98.721** | 3.668±0.898 | 8.499±1.139 | 11.094* |

*, **, ***= significant at 0.05, 0.01 and 0.001 levels, ns = non-significant.

Soil acts as the pivotal part of agricultural system and the metals and mineral reserves in soil govern the amassing of heavy metal in producers. Levels of heavy metals in soil samples detected during the current study were lesser when compared to the safe allowed limit of Ni (50 mg/kg) and Zn (200 mg/kg) as advised by Rowell et al. [54]. This might be due to soil factors like pH, concentration of humus, oxidation and reduction potential and rate of addition of metals into the soil which in turn control the capacity of soil to hold them.

3.2. Nickel and Zinc concentrations in vegetable samples

In vegetable samples, the mean Ni contents (mg/kg) fluctuated from 0.461 to 0.919 (Raphanus sativus), 0.450 to 0.899 (Brassica rapa), 0.466 to 0.934 (Zingiber officinale), 0.513 to 0.023 (Capsicum baccatum), 0.324 to 0.646 (C. frutescens), 0.444 to 0.886 (Capsicum annuum), 0.394 to 0.786 (Solanum lycopersicum) and 0.436 to 0.869 (Curcuma longa) (Table 1, Figure 2). The highest Ni concentration was present in C. baccatum under SWI and the lowest Ni contents were noticed in C. frutescens under CWI. Analysis of variance (ANOVA) exhibited the significant effects (p≤ 0.05) of water quality on the Ni contents of various vegetables (R. sativus, C. annuum, S. lycopersicum, Z. officinale, C. frutescens, B. rapa, C. longa and C. baccatum) (Table 1, Figure 2).
The Ni concentrations in the investigated plant samples were lower than its safe limit of 2 mg/kg disclosed by Chiroma et al. [55]. Orisakwe et al., [56] observed the Ni concentration of 0.66 mg/kg in fluted pumpkin (T. occidentalis), which might be due to differences in geographical location or soil characteristics. The absorption of Ni depends upon its compound chemical form, the water-soluble forms (chloride, nitrate, sulphate) being more easily absorbed [57,58]. The extended exposure to heavy metals like Ni, Zn, Cu and As can lead to injurious health complexities in humans [59]. The Ni contents can be easily extracted from soil and the plants anchored in it [60-65].

In the assessed vegetable samples, the mean Zn concentrations (mg/kg) was observed between 4.0-7.999 (R. sativus), 4.324-8.645 (B. rapa), 1.905-4.763 (Z. officinale), 7.479-14.954 (C. baccatum), 1.936-3.870 (C. frutescens), 4.688-9.360 (C. annuum), 3.791-1.036 (S. lycopersicum) and 3.668-8.499 (C. longa) (Table 1, Figure 3). The maximum Zn values were present in S. lycopersicum irrigated by wastewater and the minimum Zn values were present in C. baccatum irrigated by canal water. ANOVA depicts significant effects of irrigation water (p≤ 0.05) on Zn concentration in C. frutescens, C. annuum, C. longa, R. sativus, and S. lycopersicum, whereas non-significant effect (p > 0.05) was depicted in B. rapa, C. baccatum and Z. officinale, (Table 1, Figure 3).
The Zn content of vegetables was lower than the safe limit of Zn (50 mg/kg) as suggested by Chiroma et al. [55]. The current research explored a relative enhancement of Zn content of different vegetables compared with the values proposed by Singh et al. and Itanna, who suggested that the Zn contents (3.56–4.592 mg/kg) were falling in the permissible international standard values [66,67]. Contrarily, current results were in close concordance with the results of Al Jassir et al., who found Zn values between 14.14 and 76.28 mg/kg in some vegetables.

Sobukola et al., have described Zn level of 0.011, 0.070 and 0.050 mg/kg in the aerial parts of different plants [68-71]. The quantities of Zinc in various vegetables observed were less than the permissible levels determined by the FAO/WHO in vegetables [71-73]. Continuous utilization of contaminated vegetables within safe limits may help to protect from the severe consequence of zinc deficiency in human consuming it as Zn deficiency results stunt production and delay in sexual maturity because of its position in organic processes of nucleic acid and formation of different proteins [74]. Zn is considered as less toxic and important metal for humans as it is essential for regulation of the immunity operations of the body. Low Zn intake affects more severely as compared to Zn toxicity.

Zn is used for supplementation and bio-fortification of staple crops. Zn proves to be pivotal for cellular activity and catalysis done by biological catalysts. In the arena of metals, Zn has the lowest noxious effect and critical component of diet as it boosts immunity, protein production and hastens the attenuation of injuries. The mean daily intake of Zn is 7.00 -16.3 mg Zn per day; but the suggested daily intake 15 mg Zn per day for males and 12 mg Zn per day for females. Conversely, its excessive intake may lead to problems such as nausea, kidney unrest and muscular pangs. Analysed Zn value in coriander was under the limit so it is considered as secure for dietary intake.

3.3. Bioconcentration factor

The values of BCF for Ni and Zn in samples were given in Table 2. The BCF values of Ni ranged from 0.573 to 0.570 (R. sativus), 0.559 to 0.558 (B. rapa), 0.579 to 0.580 (Z. officinale), 0.637 to 0.635 (C. baccatum), 0.402 to 0.401 (C. frutescens), 0.551 to 0.550 (C. annuum), 0.489 to 0.488 (S. lycopersicum) and 0.542 to 0.539 (C. longa). The highest value of BCF was noticed for C. baccatum and the lowest value of BCF was calculated for C. frutescens by SWI. Other way around, the BCF values of Zn differed from R. sativus (8.840-8.814), B. rapa (9.555-9.526), Z. officinale (4.210-5.248), C. baccatum (16.528-0-16.478), C. frutescens (4.279-4.264), C. annuum (10.359-10.314), S. lycopersicum (8.378-1.142) and C. longa (8.105-9.365). The highest BCF values were recorded for C. baccatum during CWI and the lowest concentration was present in C. frutescens caused by SWI.

| Vegetables   | Nickel | Zinc |
|--------------|--------|------|
|              | CWI    | SWI  | CWI    | SWI  |
| R. sativus   | 0.573  | 0.570| 8.840  | 8.814|
| B. rapa      | 0.559  | 0.558| 9.555  | 9.526|
| Z. officinale| 0.579  | 0.580| 4.210  | 5.248|
| C. baccatum  | 0.637  | 0.635| 16.528 | 16.478|
| C. frutescens| 0.402  | 0.401| 4.279  | 4.264|
| C. annuum    | 0.551  | 0.550| 10.359 | 10.314|
| S. lycopersicum| 0.489 | 0.488| 8.378  | 1.142|
| C. longa     | 0.542  | 0.539| 8.105  | 9.365|
The value of BCF less than 1 (BCF ≤ 1) presents plant only absorption of the metal by the plant body with zero build up. When the value of BCF exceeds 1, it depicts the gathering of metal in plant tissues. The values of BCF of Ni was lower than the values of previous studies [75,76]. Iqbal et al., recorded similar values of BCF for Ni (0.34-0.93) while comparing with current findings [77]. The value of BCF for Zn in current research was higher than the values recorded by Alghobar and suresha [78].

3.4. Daily intake of metal and health risk index

DIM values of Ni and Zn were given in Table 3. The DIM values recorded for Ni ranged from 0.003 to 0.005 (B. rapa), 0.003 to 0.005 (Z. officinale), 0.003 to 0.005 (R. sativus), 0.003 to 0.006 (C. baccatum), 0.002 to 0.004 (S. lycopersicum), 0.003 to 0.005 (C. annuum), 0.002 to 0.004 (C. frutescens) and 0.002 to 0.005 (C. longa). In collected sample vegetables, DIM values of Ni posed to be higher with SWI than those of CWI. The DIM values for Zn ranged from 0.023 to 0.046 (R. sativus), 0.025 to 0.049 (B. rapa), 0.011 to 0.027 (Z. officinale), 0.043 to 0.085 (C. baccatum), 0.011 to 0.022 (C. frutescens), 0.027 to 0.053 (C. annuum), 0.022 to 0.006 (S. lycopersicum) and 0.021 to 0.048 (C. longa). DIM values for Zn were higher during sewage water irrigation as compared to canal water irrigation in all assessed samples.

The DIM values for Ni and Zn found in the current investigation were below tolerable daily intake (TDI) of Ni (1.40 mg/kg/day) and Zn (60 mg/kg/day). The result showed that HRI of Ni and Zn were lower than 1 for all vegetables; thus, within the safe limits. In the vegetable samples, the HRI for Ni and Zn was greater when irrigated with sewage water and lesser with canal water (Table 3). During current research, HRI of Ni and Zn was found to be within the safe range and the vegetables were appraised harmless for humans. The current consequences were in concordance with those of Zhuang et al. [79].

Table 3. Daily intake of metals and health risk index of nickel and zinc contents via intake of different vegetables from canal and sewage wastewater irrigated sites

| Vegetables | Nickel | Zinc | Nickel | Zinc |
|------------|--------|------|--------|------|
|            | Daily intake of metal | Health risk index |
|            | CWI | SWI | CWI | SWI | CWI | SWI | CWI | SWI |
| R. sativus | 0.003 | 0.005 | 0.023 | 0.046 | 0.15 | 0.25 | 0.0767 | 0.1533 |
| B. rapa    | 0.003 | 0.005 | 0.025 | 0.049 | 0.15 | 0.25 | 0.0833 | 0.1633 |
| Z. officinale | 0.003 | 0.005 | 0.011 | 0.027 | 0.15 | 0.25 | 0.0367 | 0.0900 |
| C. baccatum | 0.003 | 0.006 | 0.043 | 0.085 | 0.15 | 0.30 | 0.1433 | 0.2833 |
| C. frutescens | 0.002 | 0.004 | 0.011 | 0.022 | 0.10 | 0.20 | 0.0367 | 0.0733 |
| C. annuum  | 0.003 | 0.005 | 0.027 | 0.053 | 0.15 | 0.25 | 0.0900 | 0.1767 |
| S. lycopersicum | 0.002 | 0.004 | 0.022 | 0.006 | 0.10 | 0.20 | 0.0733 | 0.0200 |
| C. longa   | 0.002 | 0.005 | 0.021 | 0.048 | 0.10 | 0.25 | 0.0700 | 0.1600 |

3.5. Pollution load index

PLI values for Ni and Zn for the investigated sites were presented in Table 4. The PLI values for Ni in soil samples were 0.0889 and 0.1778 for canal water treatment and sewage wastewater irrigation and for Zn, these values were 0.0101 and 0.0202. Soil metal contamination can be visualized by PLI, which comparatively assesses the quality of irrigation water. Zero PLI value depicted lowest risk level.
As the value increases to 1 and above, it shows the gradual collapse of the irrigated soil with such water [70, 81].

| Sites | Nickel | Zine |
|-------|--------|------|
|       | Reference value | PLI | Reference value | PLI |
| CWI   | 9.06<sup>a</sup> | 0.0889 | 44.19<sup>a</sup> | 0.0101 |
| SWI   | 9.06<sup>a</sup> | 0.1778 | 44.19<sup>a</sup> | 0.0202 |

Source*: [31]

4. Conclusions

Scarcity of fresh water resources forces the agriculturists to use the sewage wastewater to get the maximum output of crops. Wastewater contains huge amounts of micro and macronutrients required for the growth of plants. The results from present work demonstrated that the concentration of Ni and Zn in the samples were found within the allowable range (25 mg/kg and 20 mg/kg, respectively. The bioconcentration factor of Ni and Zn in all vegetable samples was lower than 1. The values of PLI for Ni and Zn in both sites were found within the safe limit. The values of HRI for Ni and Zn for both canal and sewage water irrigated sites were less than 1 indicating that the consumption of these vegetables was safe for human.

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