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Concentration Level of Micronutrients in Soil, Vegetable, and Water Samples of the Farmland Area of Mera Kachori, Peshawar, Pakistan

Muhammad Ahmad[1], Fazal Wahid[1], Abdur Rahman[1], Sami Ullah[1], Rahman Saeed[1], Luqman Idrees Mahmood[2], Zulqarnain[3], Saif Ul Islam[3], Hussain Ahmad Kakar[3], and Muhammad Rahim[4]*

[1]Department of Chemistry, Government College Peshawar, Khyber Pakhtunkhwa, Pakistan

[2]College of Pharmacy, Kirkuk University, Kirkuk, Iraq

[3]Department of Botany, Government College Peshawar, Khyber Pakhtunkhwa, Pakistan

[4]School of Chemical Sciences, Universiti Sains Malaysia, 11800 Pulau Penang, Malaysia

Correspondence
Muhammad Rahim
kpk566@gmail.com

Abstract

Micronutrients such as zinc (Zn), iron (Fe), manganese (Mn), copper (Cu) and molybdenum (Mo) were analyzed in the soil, vegetables and water samples collected from Mera Kachori, Peshawar. The concentrations were examined using anatomic absorption spectrophotometer (Perkin Elmer 700). The findings showed a significant variation in the levels of micronutrients among various vegetables compared to permissible levels. Iron levels ranged from 9.663 mg/kg (Solanum melongena) to 32.704 mg/kg (Luffa acutangula), which were lower than the recommended level (50-250mg/kg), indicating possible deficiencies and physiological effects of iron, particularly interveinal chlorosis. The levels of zinc (1.333-2.849 mg/kg) and copper (0.174-0.267mg/kg) were also lower than the recommended levels, creating concern in terms of their effect on plant metabolism and growth. Manganese concentrations (7.514-8.597 mg/kg) were below the allowable levels but was not a sign of severe deficiency. On the other hand, molybdenum was surprisingly high, ranging from 204.200 mg/kg to 240.900 mg/kg, which is higher in comparison with the acceptable levels that may lead to toxicity. Soil and irrigation water analyses revealed that the micronutrients were mostly within the acceptable limits, with the exception of copper that was below the recommended soil limits. These results highlight the importance of specific micronutrient management activities to maximize the plant nutrition, growth and productivity.

KEYWORDS:

Micronutrients; heavy metals; soil; vegetable

1.0 INTRODUCTION

Micronutrients such as iron, zinc, manganese, boron, chlorine, copper, and molybdenum are essential for plant growth and metabolic functions. Despite their low need, they are important to plant health and play a role in plant metabolism [1-3]. These metals accumulate in plants in the following order: Mn, Fe, Zn, B, Cu, Mo. The sequence could be shifted, depending on the kind of plant and the external conditions [4]. Ni and Co, at low concentrations, are believed to be required for plant growth, according to convincing evidence [5]. Cobalt is essential for nitrogen fixation by bacteria in specific plants and serves as a vital component of vitamin B12 in animal nutrition [6, 7]. Manganese, iron, zinc, boron, copper, and molybdenum are classified as essential micronutrients for plants due to their physicochemical properties, although they are required in trace amounts

[4].

Soil scientists characterize soils as a three-phase system comprising solids, liquids, and gases [8]. The solid phase consists of both inorganic and organic materials, as well as living organisms. Soils exhibit a significant degree of chemical and physical diversity, not only in their composition but also in the dynamic transformations they undergo because of biological, gravitational, and environmental factors. Consequently, Micronutrients exhibit a wide range of chemical and physical forms, and these forms are likely to alter as the system experiences disruption. The aim of examining the types of micronutrients in soils is to identify how they are distributed between the solid and liquid phases, and to connect these forms to their bioavailability [2,9].

The composition of soils and rocks indicates that Zn, Mn, Cu and Mo are trace elements.However, Fe is a macro element [10]. It is evident that soil chemistry is of great importance because soil is a major source of macro and micro-nutrients [11]. The concentration of elements within the soil is in constant flux, influenced by various factors such moisture content, level of pH, temperature, theapplication of fertilizers and oxidation-reduction conditions. As soil moisture decreases, the concentration of ions in solutions increases, leading to potential adsorption or precipitation [2]. In the soil, the metallic micronutrients are complexed with both inorganic and organic ligands rather than being in a free ionic state. Hence, the abundance of chemical species has more significance than the total content in soil solution [12].Common components of prosthetic groups that are involved in redox processes by transferring electrons are micronutrients like Mn and Fe, and to a lesser extent, Mo and Cu. Enzymes and substrates often work together, and micronutrients can change this molecular arrangement to improve enzyme reactions [13,14].

Soil zinc content is affected by various factors, such as parent rock, weathering, organic matter, texture, pH and amounts of organic matter. On average, 50 mg/kg of zinc is present in normal soils, although the concentration can range from 10 to 300 mg/kg. The concentration of zinc in basic rock is greater than that in acid rock. Typically, heavier soils have a higher total zinc level, while lighter soils have a lower total zinc content [15]. The concentration of Zn on clay surface, hydrous oxide and organic matter are greater than in soil [16]. The emission of Zn arising from anthropogenic activities is twenty times higher than the natural sources [17]. Zinc deficiency represents a critical micronutrient issue in numerous crops [18]. Zinc deficiency was initially documented by Nene in Indian paddy fields. Zinc deficiency has been classified as Akagare type II in India, Hadda in Japan, Taya-Taya in the Philippines, and Apulapaya in Pakistan. It was later realized that zinc deficiency is a plant nutritional concern in rice-growing countries like Japan, the United States, Braziland the Philippines.In the case of acute zinc deficiency, symptoms included reduced stem elongation in tomatoes. Emerging Zn shortage symptoms in tomatoes were alleviated by Zn resupply, and protein and starch synthesis were reduced but sugar content remained same. Zinc deficiency can lead to several visible symptoms in plants, including root apex necrosis, interveinal or irregular chlorosis, and reddish-brown or bronze discoloration. Additionally, it may trigger responses resembling auxin deficiency, such as shortened internodes, epinasty (downward leaf curvature), inward curling of leaves and reduced leaf size. These signs collectively indicate insufficient zinc levels in the plant [19]. The toxicity of zinc is a consequence of the contamination of sediments by mining and smelting activities. In low-pH soils, anthropogenic inputs of zinc enrich the irrigation of agricultural soils with effluent water in urban soils [20]. Symptoms of toxicity typically appear in leaves at a concentration around 300 mg/kgof body weight, while certain cultivars exhibit symptoms at concentrations as low as 100 mg/kg [6]. Additionally, toxic thresholds can be quite variable, even within the same species. Reduced yields and stunted growth are among the symptoms of zinc toxicity. Significant variations exist among plants regarding their susceptibility to zinc toxicity. Typically, gramineous species are less susceptible to Zn toxicity than most dicots in acidic soils; however, this is not the case in alkaline soils. Plants such as

spinach and beet are susceptible to Zn toxicity due to the high Zn absorption capacity of leafy vegetable dicots. Sensitivity to Zn toxicity within the species may be influenced by genetic variation [19].

Iron ranks as the fourth most widely found element on Earth. It exists as hydroxides, ferric oxides and silicates, which are not readily accessible to plants. The concentration of Fe in soil varies by type and depth, ranging from 0.2% to 55%, with the maximum levels observed at depths of 2-15 cm [21-23]. The amount of Fe^{3+} in soil is primarily regulated by pH levels [24]. At pH 6.0 and below the availability of iron is optimal, the availability decreases at pH 7.0 and above, it declines significantly due to the precipitation of iron compounds, resulting in reduced availability for plant growth in many circumstances [25]. Approximately one-third of Earth's soil is estimated to be deficient in iron [26]. Factors affecting the availability and solubility of iron for plants are soil aeration, pH, soil redox potential, organic matter content and microbial populations, etc [27]. Iron is an essential micronutrient for plants due to its crucial role in many plant processes, including the production of nucleotides (building blocks of DNA and RNA), energy generation through mitochondrial respiration, and photosynthesis. It also supports nitrogen assimilation, regulates hormone activity, and facilitates the transport of nutrients within the plant [28]. Iron functions as a prosthetic group for various enzymes that regulate protein stability and activate numerous metabolic pathways. It supports many biochemical reactions in plants, making it one of the most essential elements for their survival [29]. More than 90% of iron in plants is used for chlorophyll synthesis, and it is also essential for maintaining the structure and function of chloroplast [30]. Iron-deficient soil is the primary cause of interveinal chlorosis (IVC) in immature rice leaves. The primary symptoms of iron deficiency in plants include interveinal chlorosis, resulting from thedecreased quantity of chlorophyll, and the symptoms of yellowing in the youngest leaves while the veins retain a green hue, ultimately leading to a substantial decline in yield and quality [31]. In severe acute conditions, cellular division takes place, causing leaves to turn white and leading to stunted growth [32]. As already discussed, iron is a crucial nutrient for plants. On the other hand, the high level of iron is quite toxic. The Fenton reaction is facilitated, resulting in the production of hydroxyl radicals that can damage macromolecules in plants. Plants need to manage stress caused by both insufficient and excessive levels of iron. Iron toxicity occurrence is affected by plant species and growth-related factors [33]. High levels of iron may decrease the concentrations of additional important nutrients, including manganese, phosphorus, potassium, calcium and magnesium in plants [34].

Manganese appears to be a component of primary and secondary minerals, while it can also be found in solutions, attached to the surfaces of minerals and organic substances, or assimilated by living things. Divalent manganese is the most common and important state of manganese, that is absorbed by clay minerals and organic materials, and the essential nutrient for plants to uptake [35-37]. In soil, manganese reactions are very complex. The organic matter, moisture content, pH and oxygen availability in soil all affect the quantity of available manganese in the soil [38]. Manganese is necessary for several plant biochemical processes. The Mn average concentration in cell is about 100 µM. Mn was first scientifically detected in the ash of many vegetable species in plant leaf tissue more than 200 years ago [39]. In the years that followed, it was noted that Mn was necessary for the growth and development of plants. For the first time, Prison and his colleagues showed that Mn is likely involved in photosynthesis and that plants cannot release oxygen if their growing media does not include Mn [40]. Spector and Winget extracted a protein complex which is catalytically active from spanich that contain manganese, demonstrating that manganese is a crucial metal cofactor in the water splitting complex, a crucial component of photosystem II (PSII) in photosynthesis, of higher plants [41]. Unlike other essential micronutrients such as copper, zinc, iron and molybdenum, which are enzyme substrates, manganese acts as an enzyme activator and also co-factor. Manganese affects processes including respiration, lignin biosynthesis, amino acid synthesis,

and hormone levels in plants by helping to activate enzyme-catalyzed reactions like phosphorylation, reduction, decarboxylation, and hydrolysis [42]. Common symptoms of manganese deficiency include interveinal chlorosis, early senescence of older leaves, and the emergence of dark brown patches on the foliage [43]. The symptoms due to manganese deficiency are the appearance of small yellow spots on the base of younger leaves in dicot plants, while in monocot plants, the base of the leaves has grey-green dots. A decrease in photosynthetic efficiency is the primary indicator of deficiency, resulting in an overall reduction in dry matter productivity and yield. Due to low metabolic activity in manganese uptake during the cold and wet seasons, the manganese deficiency will be more severe [37]. The symptoms appear because of Mn toxicity vary greatly from one plant species to another. Although different plant species exhibit Mn toxicity in different ways, brown patches on older leaves surrounded by a chlorotic zone are typical signs of Mn toxicity [44]. Accumulation of oxidized manganese leads to the brown necrotic spots on leaves [45]. According to reports, precipitated Mn compounds are present in the spots. [46]. However, Mn-induced symptoms of other mineral nutrient deficiencies, suchas those of Ca, Mg, and Fe, are frequently predominant [47]. Plant roots turn brown in severe manganese toxicity situations, usually after the shoots have suffered significant damage. However, it was discovered that browning of the roots occurred first, followed by browning of the lower leaves, when the Mn content was high. Browning of the roots indicates that oxidized Mn is present. As the level of toxicity rises, it gets darker in the vicinity of the root tips and spreads upward, concentrating on the older roots [48]. Water and nutrients cannot be absorbed by such roots [49].

Copper is an essential transition metal that participates in various plant physiological processes due to its redox properties. In biological systems, it commonly occurs in two oxidation states: Cu^{1+} and Cu^{2+}. Copper serves as a structural component in regulatory proteins and is involved in transport of electrons during photosynthesis, energy production in mitochondrial respiration, protection against responses to oxidative stress, cell wall metabolism and endocrine signaling [6]. Copper (Cu) is essential at the cellular level for signaling transcription and protein trafficking machinery, as well as for oxidative phosphorylation and iron mobilization. Therefore, plants need copper as a vital element for their normal development and growth. In the absence of this ion, plants have distinct symptoms of deficiency, that usually affect the reproductive organs and young leaves. The essentiality of Cu is attributed to its redox characteristics, which also directly lead to its intrinsic toxicity. The generation of toxic hydroxyl radicals, which can cause damage to DNA, lipids, proteins, and other biomolecules, may be facilitated by electrochemical redox cycling between Cu^{+2} and Cu^{+1}[50]. Copper content in living tissues must be kept at low levels due to its considerable toxicity resulting from its strong redox characteristics. In plant tissue, the average copper content is 10 $\mu g.g^{-1}$ as measured by dry weight [51]. In nutritional medium, the critical concentration of free copper varies 10^{-14} to 10^{-16} M. Plants generally experience an inconsistent availability of copper in the soil, suchasthe concentration of copper in soil solutions ranges from 10^{-6} to 10^{-9} M. However, plants can still need the metal to be reduced and solubilized. To date, no particular transporters responsible for the absorption of Cu from the environment have been identified. However, evidence indicates that Cu is being reduced. Plants with copper deficiency show changes in gene expression and the activation of morphological modifications, including changes in leaf and root structural features. Symptoms of copper deficiency typically initiate at the tips of the youngest leaves and progress towards the leaf edges. In addition, the leaves might show deformation or twisting, along with signs of chlorosis or necrosis [6]. Copper deficiency reduces electron transport in photosystem I (PSI) by decreasing the synthesis of plastocyanin, which is the primary site impacted by copper deficiency in photosynthesis [52]. Cu-deficient chloroplasts were also shown to have decreased photosystem II (PSII) activity. Droppa concluded that significant Cu deficiencies alter the environment of the PSII acceptor side, resulting in modifications in the thylakoid membranes [53]. Toxic concentrations of

copper naturally occur in certain soils, while others may exhibit higher copper levels due to anthropogenic heavy metal emissions. Copper concentrations beyond optimal levels have been shown to impede growth and disrupt essential biological functions, including respiration and photosynthesis [6,54]. High Cu concentrations typically cause plants to develop with chlorotic symptoms and decreased biomass. Under these growth conditions, leaves exhibit reduced levels of chlorophyll and changed thylakoid membrane composition and chloroplast structure [52,55,56]. Specifically, the formation of intra-thylakoidal inclusions, an increase in the quantity and size of plastoglobuli, and a breakdown of grana stacking and stroma lamellae were observed. It was suggested that Cu alters the protein composition and pigment of the photosynthetic membrane by interfering with the synthesis of the photosynthetic machinery [55,57].

Molybdenum is not found in nature in its pure metallic state. Instead, it is found in combination with other elements. The molybdate anion (MoO_4^{2-}), in dilute solution represents the main form of molybdenum, including soil and natural water. Molybdenum readily undergoes polymerization, forming various complex structures, including polymolybdates, in solutions with moderate to high concentrations of molybdenum. In terms of pollution, coal combustion, sewage sludge from municipalities, and mining and industrial processes are the primary human-caused sources of molybdenum. Apart from regions that mine molybdenum, the daily absorption of molybdenum from water and air is negligible in comparison to dietary intake [58]. The average molybdenum concentration in soil ranges from 1 to 2 mg/kg, though this amount varies significantly based on the geological minerals present [85]. Molybdenum-deficient soils exhibit concentrations of 0.2 mg/kg, whereas molybdenum-excessive soils are characterized by levels of 0.7 mg/kg [58]. The absorption of molybdenum by plants is affected by various soil factors, such as mineral content (including manganese, phosphorus, and sulphur), pH, the presence of sesquioxides, organic matter, and moisture levels [59].Molybdenum serves as the enzyme's catalytic center and demonstrates chemical flexibility, which benefits biological systems due to its redox activity in physiological conditions. Enzymes use molybdenum's adaptable redox chemistry to catalyze a variety of redox reactions. Several ligands control this redox chemistry at the Mo atom and in the enzyme environment [60]. Plants exclusively utilize the molybdate anion present in soils. Mo-containing enzymes are vital for life, significantly influencing the metabolism of each organism and the redox biogeochemical cycles of nitrogen, sulfur, and carbon on Earth [61]. Over 50 enzymes that contain molybdenum are recognized as being dependent on molybdenum. In the field of plants, five specific molybdenum-dependent enzymes have been identified [62,63]. In plants, a lack of Mo frequently results in a lack of N because NR is the main enzyme involved in the nitrate absorption pathway. Complex biosynthetic machinery converts molybdate into metal cofactors once it enters the cell. Further, these metal cofactors are integrated into several enzymes [64]. Deficiencies in molybdenum are linked to low levels of nitrogen, particularly when nitrate is the primary type of nitrogen that plants can use to grow. Lack of molybdenum causes a plant to grow and develop slowly, have pale leaves, have trouble producing blooms, and eventually wither. The most noticeable and typical symptoms in dicotyledons are abnormalities in the development of the leaf blade (whiptail) and a marked reduction in size. These are the outcomes of local tissue necrosis and inadequate vascular bundle differentiation during the early stages of leaf formation [65]. The loss of nitrate reductase activity in most plant species is associated with increased tissue concentrations of nitrate, leading to reductions in plant yields and growth [66]. That is why the activity of leaf nitrate reduction enzyme was decreased in spinach plants growing in Mo deficit, and the plants' ultimate yields were lower than those of the control group, which got a sufficient supply of Mo.Mo deficiency in wheat similarly caused diminished Nitrate Reductase enzyme activities, regardless of how the dark and light cycles regulate NR [67,68]. Mo exhibits minimal toxicity to plants under optimal agricultural conditions. The impact of soil characteristics and the presence of molybdenum as an

anionic species greatly influence its toxicity and bioavailability to plants. Plants assimilate molybdenum primarily as molybdate anions (MoO_4^{2-} and $HMoO^{4-}$), which are the dominant species in soil solution [69]. Protonation occurs at low pH levels, where $HMoO^{4-}$ (monoprotonated monomer) and H_2MoO_4 (diprotonated monomer) might play similar roles. In aqueous solutions with pH values ranging from 2 to 7 and molybdate concentrations between 0.03 mM and 0.1 M, an equilibrium was observed among three isopolymolybdates (the protonated heptamer, heptamer, and octamer) and three monomer species. Although, MoO_4^{2-} is the primary available form in soils with a pH higher than 4.0 [70]. Specific soil characteristics, including texture, Al hydroxides/oxides and amorphous iron (Fe) significantly influence the absorption of Mo by plants and affect the toxicity and bioavailability of divalent metal cations such as Ni, Co and Cu [71]. In contrast to cationic metals, the available amount of molybdenum to higher plant species often increases with rising soil pH [72]. The maximum quantity of Mo (1 mM) tested in Pisum sativum L. plants resulted in a reduction of shoot and root production by 35% and 50%, respectively. This reduction is associated with soil solution conditions and soil characteristics, while the accumulation of Mo in plants is also affected by the type of plant. Brassica species are recognized for their effective accumulation of molybdenum [73].

2.0 MATERIALS AND METHODS

2.1 Study Area

The study was carried out in Mera Kachori, a rural region with intense agricultural practices, situated in Peshawar, Khyber Pakhtunkhwa, Pakistan at coordinates 33°58'20.3"N, 71°40'56.6"E. Due to the good soil and favorable climatic conditions, farmers in the area cultivate a diverse range of vegetables and fruits.The temperature of Peshawar is highest in June (41 °C) and lowest in January (3.8 °C). The average annual rainfall has been recorded as 349.5 mm. October has the least amount of rainfall, while most of the precipitation is recorded in March.

2.2 Materials and Instruments

For the analysis, analytical grade chemicals (Merck Darmstadt, Germany) with a high purity of 99.9% were employed. Heavy metal standard solutions were preparedbydiluting certifiedstandard solutions (FlukaKamica Busch Switzerland) of the corresponding metal at a concentration of 1000 ppm. Atomic Absorption Spectrophotometer (Perkin Elmer AAS-700) was used to examine the samples for heavy metals.

2.3 Sampling

2.3.1 Soil Sampling

Soil samples were collected from 0-3-6 inch depth from three points. The samples were collected from rural area of Peshawar (Mera Kachori). Quantitative determination of micronutrients was carried out using Perkin Elmer atomic absorption spectrophotometer AAS-700.

2.3.2 Vegetable Sampling

Plant specimens of bitter gourd (Momordica charantia), Ridge gourd (Luffa acutangula), bottle gourd (Lagenaria siceraria), brinjal (Solanum melongena), and Lady finger (Abelmoschus esculentus), together with their corresponding soil samples, were gathered from agricultural land in the Mera Kachori Peshawar zone of Khyber Pakhtunkhwa, Pakistan in the summer of 2020.

The edible parts of the vegetables were rinsed with tap water and subsequently with distilled water in order to eliminate the dust residues. Using a clean knife, the samples were sliced and then vacuum-dried in an oven at 80 °C until they reached a consistent weight. The dry samples were then crushed using a pestle and mortar and stored in sterile plastic bags. The soil samples were dehydrated in an oven at 80 °C until they reached a consistent weight, then crushed and homogenized by passing them through a sieve.

2.3.3 Water Sampling

Samples of water were taken from the field channel next to the study area.High-density polyethylene (HDPE) bottles that had already been washed with detergent, deionized water and 10%

HNO_3, were used to take the samples from 10 to 15 cm below the water's surface to avoid surface debris.

2.4 Analysis

2.4.1 Digestion of Soil Samples

5g of soil samples were added into Teflon beaker and subjected to digestion using a mixture of 10mL HF and 10 mL $HClO_4$. Samples were then heated on hot plate for 15 minutes. After digestion, 20 mL of distilled water was added to the samples, which were then cooled, and the mixture was filtered. Samples were stored in plastic bottles and labelled after the filtrate was diluted up to 50 mL. The samples were then taken to the atomic absorption spectrophotometer for micronutrients analysis.

2.4.2 Digestion of Vegetable Samples

The dried vegetable sample weighing 4g was transferred into a beaker and then combined with 20mL of per chlorate acid,10mL of nitric acid and 10mL of sulphuric acid respectively, using a dropping pipette. The mixture was thereafter subjected to digestion on a hotplate oven until a clear solution was obtained. After cooling, the resultant mixture was filtered via filter paper. The filtrate was then diluted with distilled water to a final volume of 50mL. Filtered samples were stored in plastic bottles and labeled for micronutrients analysis through atomic absorption spectrophotometer.

2.4.3 Preparation of Water Samples

Digestion was performed on 100 mL of water samples in Teflon beakers using a mixture of 5 mL of HNO_3 and 2 mL of HCl (aqua regia). The samples were then digested in a microwave digestion machine at 180°C for 15 minutes. After digestion, the samples were cooled, and the mixture was subjected to filtration. The filtrate was diluted to 50 mL with deionized water, stored in acid-washed plastic bottles, and appropriately labeled. The samples were then taken to the atomic absorption spectrophotometer for micronutrient analysis.

3.0 RESULTS AND DISCUSSION

Different samples of soil, vegetable and irrigation water were collected from Mera Kachori area of Peshawar, Khyber Pakhtunkhwa, Pakistan. The summaries data of all samples have been shown in Fig. 1 and Table 1.

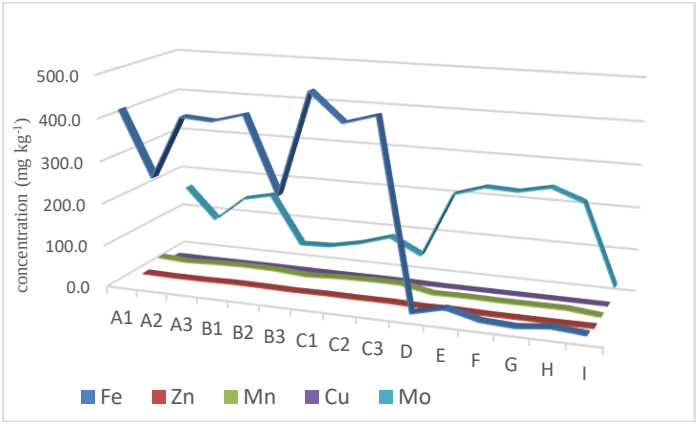

Fig. 1: Average concentration of Fe, Zn, Mn, Cu and Mo in soil, vegetables and water samples

3.1 Iron

The iron concentration measured in selected vegetables ranged between 9.663 mg/kg and 32.704 mg/kg, with the highest concentration detected in *Luffa acutangular* (32.704 mg/kg) and the lowest in *Solanum melongena* (9.663 mg/kg), as shown in Fig. 2. These values fall significantly below the recommended iron levels for vegetables, which range from 50 mg/kg to 250 mg/kg, predominantly in Fe^{2+} and Fe^{3+} forms [4]. This significant decrease may cause deficiency symptoms, particularly interveinal chlorosis in young leaves due to impaired chlorophyll synthesis [36]. It is interesting to note that despite adequate iron availability in the soil ranging from 249.900 to 489.804 mg/kg, which is within the permissible limits of 200 to 500,000 mg/kg, the uptake by vegetables remains poor [4]. Some of the likely reasons for this difference are high soil pH, low bioavailability of iron forms (Fe^{2+} or Fe^{3+}), soil texture, excess phosphate or competing ions limiting iron absorption. Additionally, the irrigation water contains 12.628 mg/kg of iron, which may contribute slightly to iron availability. However, its impact on vegetable iron uptake appears minimal. Therefore, it is essential to address iron bioavailability and uptake mechanisms within these agricultural conditions to

effectively mitigate nutritional deficiencies in crops.

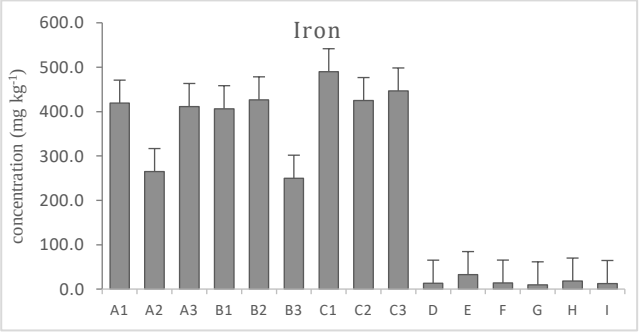

Fig. 2: Concentration of Fe in the tested samples

vegetables ranged from 1.333 mg/kg to 2.849 mg/kg, with the highest value recorded in *Luffa acutangular* (2.849 mg/kg) and the lowest in *Lagenaria siceraria* (1.333 mg/kg). These levels are considerably lower than the recommended range for vegetables, which is 20–100 mg/kg [4]. Zinc is an essential element of enzyme systems that affect many metabolic processes, such as the production of proteins, the generation of chlorophyll, the conversion of carbohydrates, and the control of sugar intake in plants. It also contributes to the formation of seeds and grains, plant height and the time of maturation. In citrus, tomatoes, and

Table-1: Average concentration of micronutrients in soil, vegetable and irrigation water samples collected from Mera Kachori, Peshawar

Sample ID	Sample Type	Fe	Zn	Mn	Cu	Mo
Soil Samples						
A1	0-inch depth (1 m from road)	418.999	4.098	21.291	1.504	161
A2	3-inch depth (1 m from road)	264.894	2.849	17.493	1.096	84.61
A3	6-inch depth (1 m from road)	411.502	3.165	20.942	1.437	143.9
B1	0-inch depth (20 m from road)	406.504	4.648	22.558	1.621	159.9
B2	3-inch depth (20 m from road)	426.496	4.215	21.441	1.621	42.32
B3	6-inch depth (20 m from road)	249.9	2.965	15.844	1.22	45.3
C1	0-inch depth (40 m from road)	489.804	3.932	20.275	1.438	60.69
C2	3-inch depth (40 m from road)	424.83	3.249	22.191	1.745	83.86
C3	6-inch depth (40 m from road)	446.488	3.632	22.391	1.465	46.5
Mean ± SD (Soil)		392.935 ± 81.23	3.638 ± 0.64	20.403 ± 2.23	1.416 ± 0.20	92.675 ± 47.82
Permissible Limits (Soil)		200–500,000	1–900	7–10,000	2–250	20–200
Vegetable Samples						
D	*Momordica charantia*	13.395	1.649	7.597	0.23	204.2
E	*Luffa acutangula*	32.704	2.849	8.597	0.231	228.1
F	*Lagenaria siceraria*	13.528	1.333	7.514	0.267	224.7
G	*Solanum melongena*	9.663	1.349	7.697	0.232	240.9
H	*Abelmoschus esculentus*	18.143	1.416	8.013	0.174	213
Mean ± SD (Vegetables)		17.487 ± 8.45	1.719 ± 0.58	7.884 ± 0.44	0.227 ± 0.03	222.180 ± 14.02
Permissible Limits (Vegetables)		50–250	20–100	20–300	5–20	0.1–0.5
Irrigation Water Samples						
I	Irrigation water	12.628	2.032	0.583	0.012	19.76
Permissible Limits		<5 (FAO)	<2 (FAO)	<0.2 (FAO)	<0.2 (FAO)	<0.01 (WHO)

3.2 Zinc

The average concentration of Zn in different samples has been shown in Fig. 3. The zinc level in tested samples of other crops, it acts as an anti-freeze when present in sufficient quantities in the leaves. With the highest concentration in sample B1 (0-inch depth, 20 meters from

the road) and the lowest in sample A2 (3-inch depth, 1 meter from the road), soil zinc levels corresponding to these vegetables ranged from 2.849 mg/kg to 4.648 mg/kg. These soil zinc levels fall within the permissible range of 1–900 mg/kg [4]. The zinc level in irrigation water also measured 2.032 mg/kg.

3.3 Copper

The copper concentration in the tested samplesof vegetables ranged from 0.174 mg/kg to 0.267 mg/kg, as shown in Fig. 4. The highest copper content was recorded in *Lagenaria siceraria* (0.267 mg/kg), whereas *Abelmoschus esculentus* showed the lowest concentration (0.174 mg/kg). These detected concentrations are much lower than the recommended copper levels for vegetables, which usually range between 5 - 20 mg/kg [4]. Consequently, such low copper levels might lead to deficiency symptoms. Plants experiencing copper deficiency usually demonstrate alterations in gene expression and morphological adaptations, particularly affecting root and leaf structures. Typical symptoms first appear at the young leaf tips and subsequently extend to the leaf margins, often resulting in twisted or distorted leaves exhibiting chlorosis or necrosis [61]. Moreover, copper deficiency has been linked to reduced electron transport in photosystem I (PSI), mainly because of diminished plastocyanin synthesis, a critical site impacted by copper limitation during photosynthesis [64]. Reduced activity of photosystem II (PSII) has also been identified in copper-deficient chloroplasts, with structural changes noted on the PSII acceptor side and alterations within thylakoid membranes, as reported by Droppa [53]. Similarly, copper concentrations in soil samples from the same site ranged from 1.096-1.745 mg/kg. Sample C2, which was taken 40 meters from the road and at a depth of 3 inches, had the highest concentration (1.745 mg/kg), while sample A2, which was also taken at a depth of 3 inches but closer to the road (1 meter), had the lowest level (1.096 mg/kg). Since these measured soil copper concentrations are below the permissible limits, which are normally between 2-250 mg/kg [4], they may suggest insufficient copper availability in the soil. The low copper concentration (0.012 mg/kg) in irrigation water further emphasizes the possibility of copper shortage in the evaluated agricultural ecosystem. Therefore, to lower the negative impacts of copper shortage on production and growth, proactive measures like changing irrigation methods or adding copper fertilizers to the soil should be considered.

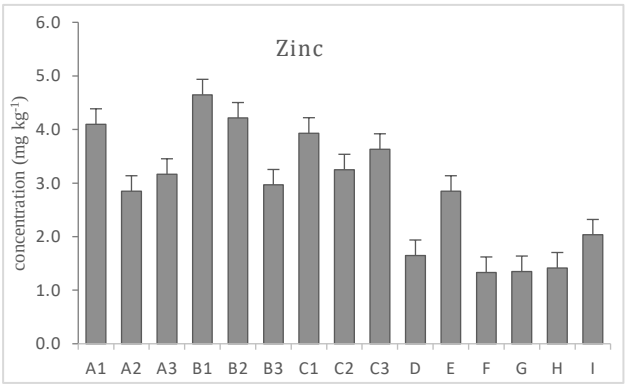

Fig. 3: Concentration of Zn in the tested samples

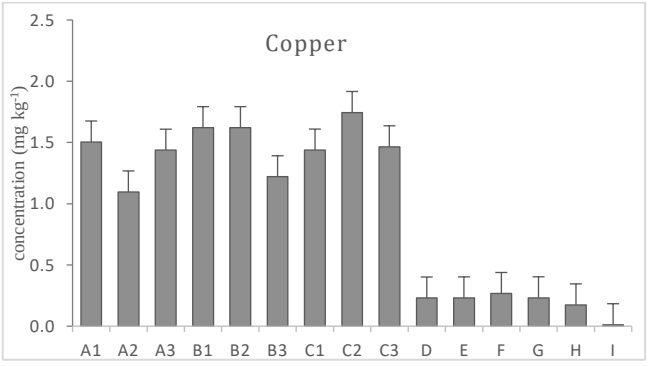

Fig. 4: Concentration of Cu in the tested samples

3.4 Manganese

Manganese concentration was investigated in vegetable samples ranged from 7.514 mg/kg - 8.597 mg/kg with highest level in the *Luffa acutangular* (8.597 mg/kg) while the lowest concentration in *Lagenaria siceraria* (7.514 mg/kg), as summarized in Fig. 5. The permissible level of manganese in vegetables is 20-300 mg/kg [4]. The result shows that the concentration of manganese is below the permissible level. Dark brown dots occur on the leaves, interveinal chlorosis, and early senescence of the older leaves are common symptoms of Mn deficiency [75]. Reduction in the efficiency of photosynthesis is the major symptom of deficiency that leads to a general decline in dry matter productivity and yield. Because of the lower metabolic activity in manganese uptake during the cold and wet seasons, the manganese deficiency will be more severe [76]. The level of manganese in soil of corresponding vegetables ranged from 15.844 mg/kg to 22.558 mg/kg. The highest concentration found in the soil sample B1 (0-inch depth and 20 meters away from road) is 22.558 mg/kg while the lowest concentration in the B3 (6-inch depth and 20 meters away from road) is 15.844 mg/kg. These valueslie within the permissible manganese range of 7-10,000 mg/kg, suggesting sufficient manganese availability in the

soil[4].However, the difference between sufficient soil manganese and deficient plant manganese indicates that other factors like soil pH or moisture conditions, may be influencing manganese uptake by the plants. Furthermore, manganese concentration measured in irrigation water was relatively low at 0.583 mg/kg, suggesting minimal contribution from irrigation water to manganese nutrition in these vegetables.

3.5 Molybdenum

The result indicates that the concentration of Molybdenum in the selected vegetables ranged from 204.200 mg/kg to 240.900 mg/kg with the highest concentration observed in *Solanum melongena* (240.900 mg/kg) while the lowest concentration in the *Momordica charantia* (204.200 mg/kg), as depicted in Fig. 6. These levels exceed the permissible level of 0.1-0.5 mg/kg [4], suggesting toxicity risks. Chronic exposure to elevated molybdenum levels can disrupt important trace element balance, notably copper metabolism, resulting in symptoms such as pain in the joints, headache, and gout-like symptoms in humans [77]. The level of molybdenum in corresponding soil samplesranged from 42.320 mg/kg to 161.0 mg/kg. The highest concentration of molybdenum in soil sample A1 (0-inch depth and 1 meter away from the road) is 161.0 mg/kg while the lowest for the sample B2 (3-inch depth and 20 meters away from road) is 42.320 mg/kg [4].Despite moderate soil concentrations, the disproportionately high amounts in plant tissue suggest that molybdenum bioavailability and absorption efficiency may be increased. Alkaline soil pH, organic matter content, and interactions with other nutrients all have a possibility to increase molybdenum mobility in the soil-plant system [78]. The irrigation water used in the study area also showed a molybdenum concentration of 19.76 mg/kg, which is rather high. Continuous irrigation with Mo-rich water can cause slow accumulation in plant tissues over time, which probably explains the high concentration of molybdenum in vegetables. Water management techniques should thus be closely watched to reduce the possibility of trace element pollution.

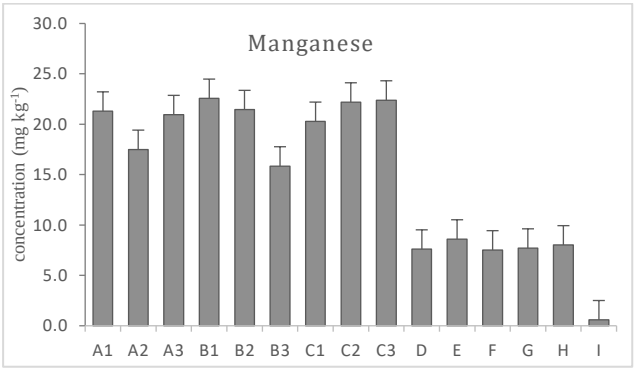

Fig. 5: Concentration of Mn in the tested samples

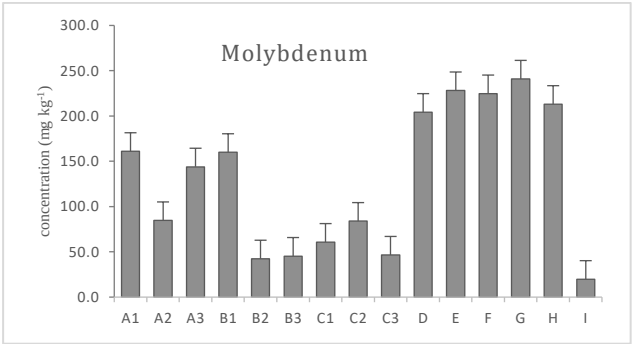

Fig. 6: Concentration of Mo in the tested samples

4.0 CONCLUSION

This study evaluated the concentrations of essential micronutrients like Iron (Fe), zinc (Zn), manganese (Mn), copper (Cu), and molybdenum (Mo)in vegetables, soil and irrigation water sourced from Mera Kachori, Peshawar. Atomic absorption spectrophotometry (AAS) demonstrated notable differences between the concentrations of these micronutrients in soils and their respective absorption in vegetable samples. Although soil concentrations typically remain within acceptable limits, the concentrations of Fe, Zn, Mn, and Cu in vegetables were significantly below the recommended levels, suggesting limited bioavailability or uptake inefficiencies potentially affected by soil characteristics (e.g., pH, organic matter) and environmental factors. Molybdenum concentrations in vegetables significantly surpassed safe limits, presenting potential toxicological risks to consumers, likely attributable to high levels in irrigation water and conducive soil chemistry that facilitates Mo accumulation. The results highlight the necessity for a comprehensive nutrient management strategy customized to local soil and water properties. It is

recommended to implement measures such as soil pH adjustment and precise monitoring of irrigation water quality to improve micronutrient absorption in cases of deficiency and to reduce accumulation in conditions of toxic levels. Although industrial impact in the research region seems negligible, the data indicates that natural soil variability and agricultural methods are essential in micronutrient dynamics. Consequently, consistent surveillance of heavy metals and micronutrients in agricultural ecosystems is imperative, not only to guarantee crop vitality and yield but also to safeguard public health via safe food consumption.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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