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Assessment of Soil, Water and Vegetable Crops for Zinc Deficiency in Gadap Basin for Agricultural Solution

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Abstract: Present study aimed to examine the impact of physico-chemical factors of agricultural soil on zinc availability for plant uptake in the Gadap Basin. Bio accessibility and availability were assessed for the vegetable and fruit plants. For this purpose, water (n = 6), soil (n=11), and plant (n=12) samples were collected from agricultural-fields. Data revealed that both water (Range: 7.14 to 8.34; mean: of 7.99) and soil (Range: 7.8 to 8.4) pH is alkaline. The soil Eh is oxic which span between +120 and+134 mV. Similarly, High soil salinity (Range: 163 to 322 mg/kg) is causing increasing soil pH, which is leading to less availability of zinc to plants. According to soil classification, soil of Gadap is found to be coarse grained where 85% of the soil retained between 60 and 100 meshes, while 5% stayed between 17 and 200 meshes, and other 10% comprises clay. The zinc concentration in soil ranged between 25–40 mg/kg, which is extremely low. On the other, hand zn concentration in plant samples is found to be 10.71mg/Kg-21.35mg/Kg. It is concluded that agricultural soil of Gadap town is deficient in Zn content which is affecting the crops nutrient index.

Key words: Physicochemical factors, availability, meshes, nutrient index..

Introduction

Background

Zinc deficiency is the most ubiquitous problem in world crops (Alloway, 2009). It is essential for both plants and animals because it's structural constituents are involved in many biochemical pathways. Living organisms require Zn as a trace element at minimal levels for regular metabolic activities (Sturikova et al., 2018). Zinc is an essential trace element that plays an important role both on a structural component of protein and as a co factor in 300 enzymes. World Health Organization (WHO) estimates that zinc deficiency affects 31 % with the prevalence rates ranging from 4 to 73 % in various regions of the world's population with a high number in a Industrial countries (Simone et al, 2016).

Zinc Deficiency in World and Pakistan

Zinc deficiency is a global health problem. Despite the proven benefits of adequate Zinc nutrition, approximately 2 billion people remain at the risk of Zinc deficiency (Khalid, 2014). Based on the Food and Agriculture Organization of the UniNationsons' (FAO) Food Balance Sheets, at least 17% of the world's population is at risk of inadequate zinc intake.

In South-East Asia, it was estimated as 43% whereas in Pakistan 50% of the children were stunted, 40% were weighted, and 9% were wasted (Bellamy, 2000).

Pakistan is a developing country and since this country's birth mal nutrition has been recognized a key factor that is significantly affecting infants, children and woman (Khalid, 2014). In Pakistan, zinc deficiency has been found in malnourished population and children suffering from persistent diarrhea. (Anwar et al, 2014).

The cases of clearly diagnosed, acute Zn deficiency in crops in the field have only been reported in the literature since 1973, and the first case of Zn deficient human was not recognized until the 1960s (Brown et. Al, 1993; Welch 1993). Over last 50 years, in many parts of the world, acute Zn deficiency was encountered for the first time when new, high yielding varieties of crops were grown. The new crops varieties also require high levels of nitrogen (N) phosphate (P) and potassium (K) fertilizers to normalize their yield potential and high levels of pH values generally exacerbate the Zn deficiency problems (Alloway, 2009).

Zinc Deficiency in Agriculture

Zinc (Zn) is an important micronutrient for plants since it is involved in many key cellular functions such as metabolic and physiological processes, enzyme activation, and ion homeostasis (Yang et al., 2020; Alsafran et al., 2022). Zinc deficiency occurs when plant growth is limited because the plant cannot take up sufficient quantities of this essential micronutrient from its growing medium. It is one of the most widespread micronutrient deficiencies in crops and pastures worldwide and causes large losses in crop production and crop quality (Alloway, 2009). Zinc fertilization plays a crucial part in obtaining sufficient yield to feed the growing population, and improve the diet of billions, since the zinc in the plants is absorbed by humans As a result, there's a growing demand for Zinc as micronutrient in agriculture (Alloway, 2008).

Deficiency of Zinc in Study Area

Karachi is densely populated city and there is a deficiency of zinc in every other individual which directly leads to source of zinc intake. The Gadap Basin has been an important source of agricultural commodities to the Karachi metropolis for centuries (Ahmad et al, 2019). It is mainly drain by Hub River followed by other small streams. However, in recent decades it has been observed that, the agricultural activities in this peri-urban area of Karachi has shown a declining trend. Increasing manifestation of dwarfism, early hair loss and whitening in teenagers are the symptoms of dietary zinc deficiency which is turn associated with soil zinc deficiency in agricultural belts of Karachi. Unfortunately, no work has been carried out so far to assess the level of zinc in soil and it's bioavailability in agricultural plants. Therefore, present study is aimed at assessment of agricultural soil, water and vegetables for the occurrence and bioavailability of zinc.

Figure 1 An aerial view of studied area of Gadap town, pointing all the accessible locations for sample collection.

Material and Methods

Study Area

Gadap town is a subdivision of Malir district which is located in the northwestern part of Karachi city (Figure 1). These areas are also forming the provincial border between Sindh and Balochistan while to the north and east are Jamshoro district and the Kirthar Mountains. The Gadap town has an 8 council with over 400 rural villages accommodating the population of about 289,564 (1998). The Gadap basin is influenced by ephemeral channels occuring in the outskirt of Karachi city and mainly influenced by the agriculture activities. Over the last decade, the Gadap is transformed into semi-urban area. It is a sub basin of the Malir basin, drained by the Lyari, Watanwari thaddo and Konkar rivers.

Geology of Study Area

Gadap basin is considered as a sub-basin of the Malir basin and it has its own watersheds. The basin comprises of three geomorphic unit namely; the hilly catchment, the Gadap plain and the lower basin (Ahsanullah, 1971).

Geologically, study area is a large ises of Manchar, Gaj and Nari formation in the north of Karachi division dome structure like a syncline basin surrounded by mountain ranges on three sides namely Manghopir (west) Khand anticline (north) and Pawalo anticline (east) compr

Drainage System of Study Area

Most of the area is covered with alluvial deposit of recent origin carried by sheets flood during rain from the catchment area of Watanwari, Thaddo and Konkar. These rain-fed streams (locally Nadi) are the main source of the underground water. The western part of basin is drained by the Lyari River. In the upper course Watanwari Nadi consists of Bombari and Kirmatiani which join near Gadap city (Ahmed, 2019).

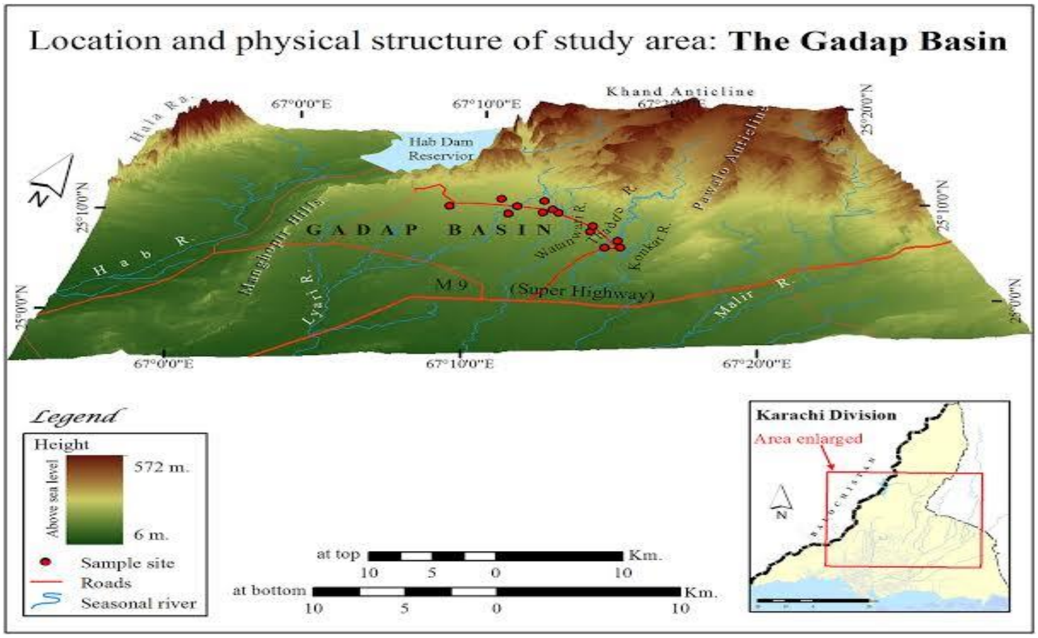

Figure 2: The Gadap basin 100-200m + MSL (main sea level) is located in the north of the Karachi (Ahmed, 2019).

Agricultural study of the area

Karachi division, the most urbanized area of country, has a very limited agricultural land and ground water resources. Peri urban agriculture is not just limited to provide fresh vegetables and fruits to the city dwellers but also involves raising livestock for the urban market to fulfil dairy needs and is reckoned to be a fast flourishing industry around urban centers. Gadap and other Peri urban areas are under various environmental threats. Beside urban sprawl, such as overgrazing, water scarcity and lowering of metal content in the agricultural soil.

Peri urban areas around large urban centers and megacities have always been very important (Pribadi et al, 2016).

Sample Collection

Water sampling from Study Area

Five groundwater (W) and one surface water (W) samples were collected for physicochemical analysis from agricultural lands through tube wells. Collection of electrically pumped water was carried out after 4-5 minutes in pumping out of standing water in the well to collect representative sample. Surface water sample was collected from the Thaddo dam.

Samples locations of all wells were plotted on the map by using global positioning system (GPS). Groundwater samples were carefully kept in two plastic bottles of one litre and 200ml capacity, for physicochemical analysis. These bottles were properly rinsed with distilled water and filled with the sample water during sample collection on respective locations. Physical parameters including taste, color, odor, temperature, pH and Eh/ORP which were determined immediately after collections, and further chemical parameters were analyzed in the laboratory.

Table 1: List of sample sites and their GPS coordinate.

S.no.	Sample Location	Latitude	Longitude
1	S1 L1	25°09’99.33”	67°24’70.18”
2	S2 L1	25°09’99.33”	67°24’70.18”
3	S3 L1	25°09’99.33”	67°24’70.18”
4	S4 L2	25°02’86.23”	67°24’33.14”
5	S5 L2	25°10’28.62”	67°24’33.14”
6	S1 L3	25°09’55.42”	67°24’51.15”
7	S2 L3	25°09’55.42”	67°24’51.15”
8	S3 L3	25°09’55.42”	67°24’51.15”
9	S1 L4	25°06’78.32”	67°26’58.16”
10	S2 L4	25°06’78.32”	67°26’58.16”
11	S3 L4	25°06’78.32”	67°26’58.16”

11 soil samples from 4 locations (Location 1 under cultivation field = 3, Location 2 Sem field = 2), Location 3 Choriyaan (Sem type) field = 3 and Location 4 lemon and papaya field =3) soil samples were collected.

Physiochemical Soil and water

The details of these analyses with further physicochemical characteristics of groundwater and soil includes classical as well as analytical methods that are given in (Table.2).

Table 2: Physicochemical parameters analyzed by using following spectroscopy and titration method.

S.no	Parameters	Equipment
1	pH	pH meter (Adwa AD111) for (G) and (S)
2	TDS/Electrical conductivity	EC/TDS meter (Adwa AD330) for (G) and (S)
3	Temperature.	EC/TDS/T°C meter (Adwa AD330) for (G) and (S)
4	Hardness	EDTA titration standard method for (G)
5	Sodium (Na+)	Photometer (JENWAY PFP7) for (G)
6	Potassium (K+)	Flame photometer (JENWAY PFP7) for (G)
7	Zinc (Zn2+)	AAS for (Zn2+)
8	Chloride (Cl-)	Argentometric Titration method for (G)
9	Bicarbonate (HCO3-)	Titration method for (G)
10	Sulfate (SO42-)	Gravimetric method for (G)
11	Magnesium.	Magnesium is calculated by use of formula

All tests were carried out in the laboratory of Department of Geology, in University of Karachi. The methods for analysis used before detection of cations and anions in groundwater samples were performed involving standardization of some reagents as well as some standard stock solutions. Sodium and potassium calibrated standards of analytical grade (Scharlau) were purchased.

Soil sampling for Study Area

The soil samples were collected from the 4 field sites. The first field was under cultivation for the crop of Daucus Carota (carrots) while other were in cropping phase of Hyacinth beans (Sem), Choriyaan, lemon and papaya vegetables and fruit. The samples were collected in 1 Kg air tight plastic bags in order to perform physiochemical analysis petrography to determine the mineral contents in collected samples. The physical properties of soil involve color, texture, and temperature. The pH, Eh,/ORP and TDS which determined immediately after collection. Further chemical parameters were analyzed in the laboratory.

Soil Sample Analysis

1) Soil physical parameters

To measure the pH, Eh/ORP, and TDS of soil the samples were first weighted to yield the desired amount for the measurements of physical parameters. 200g of soil was poured into a beaker and 150ml of distilled water was poured into it and mixed. After 24 hours, the pH, Eh and TDS were measured.

2) Soil zinc determination

The methods used to determine the zinc concentration involves air drying of soil sample under the sunlight for a week after sampling. Soil samples they were oven dried for one day under the temperature of 180°C. Physical methods of crushing and pulverizing the samples of soil samples were used to acquire fine powder form for digestion process. These samples were passed through 200 mesh sieve, then run through AAS for zinc.

3) Grain size Analysis

The soil samples were analyzed for their grain size distribution. 200g soil samples for the sieve analysis. Samples were passed through 4 different meshes (60, 90, 100, 170mm). Different size fractions of soil samples were kept in different air tight bags and then weighted.

4) Petrographic Analysis

The soil samples were also used for the petrographic analysis to determine optical microscope texture and mineral. 1g dried loose and friable sample of soil was put on a petri dish to examine under microscope.

5) Vegetables sampling for Zinc Determination

The plant samples were also collected from 4 locations. The first field was under cultivation but at second location plant sample of Hyacinth beans (Sem) crop was collected. The sample collection includes the fresh leaves and stems these plants samples were kept in a zip lock bag. 1 plant sample as collected from 3 locations. The third location got the fields of Bush Bean (Sem Phalli) and at fourth location there was the field of lemon and papaya that were collected for study.

The plants samples were dried for 1 week under sunlight and on being dried The methods used to determine the zinc concentration involves the physical methods of crushing and pulverizing the samples of vegetables to fine powder form. These samples then were passed through the 200 mesh. At least 1g of sieved sample is required for the assessment of zinc, which was run through AAS.

Results and Discussion

In present study, the collected samples of soil, water and vegetables plants were tested for the determination of zinc in agricultural soil of Gadap Town Basin.

Physical Parameters of Water

The water samples from the study area, (Groundwater =5, surface water =1) were examined for their physicochemical parameters including pH, Eh, TDS and temperature.

1) **pH**

The data reveal that water sample Groundwater = 5 pH ranges between 7.14-8.34 with a mean of 7.99 (alkaline) and the surface water = 1 pH is 7.99 in Table 3. The pH affects most biological processes in water such as solubilization and uptake of certain micronutrients into plants (Mafiana, 2016). However, alkaline soil of study area can reduce the availability of most of the nutrients. Area having water and soil pH above 6.5, which results in decreased extract ability and plant availability of soil Zn (Amodu, 2016).

Table 3. List of groundwater and surface water sample physical parameters, according to WHO standards of water.

Sno.	Locations	pH	Eh	Temperature	TDS
1.	Sarang Farmhouse (L1)	7.2	210	27.2	543
2.	Sarang Farm Tubewell (L1)	7.14	200	27.5	600
3.	Agriculture Tubewell (L2)	7.66	186	27.5	1010
4.	Thaddo Dam boring well (L3)	7.52	181	27.7	574
5.	Thaddo Dam Water (SW)	7.99	167	27	436
6.	Lemon/Papaya Field (L4)	8.34	158	27.1	735
	WHO Limits	8.5	500	-	500

It suggests that the groundwater is in hydraulic connection with surface water. High pH generally exacerbated the soil Zn deficiency problems (Alloway, 2009). The activity of Zn ion in soil is directly proportional to the square of the proton activity; therefore the solubility of Zn will decrease with increasing values of soil pH (Kiekens, 1995). The pH of water sample of location 4 is bit high 8.34 the reason might be alkaline mineral or rock. Alkalinity comes from rocks and soils, salts, certain plant activities, and certain industrial wastewater discharges (Dirisu, 2016).

2) Redox Potential (Eh)

The distribution of redox potential of ground and surface water has been listed in Table 3. The data reveal that the Eh of water is oxic which varied between +158 to +210 millivolts with mean of +158mV Table 3, and in compliance with WHO limits of 500mV. The Eh of water indicates prevalence of relatively low oxic environment. Since the study area's soil is naturally alkaline, Eh decreases with alkalization as microorganisms consume oxygen for respiration, this leads to a rapid decrease in Eh of water and soil (Flessa and Fischer 1992; Lambers et al, 2008). Relatively low but oxic Eh suggests the fresh infiltrate of water in aquifers due to rainfall.

The oxic condition at lower extreme conditions (<+350 mV) is a limit for water for many plants. The Eh is a factor that strongly influences the mobility of many micronutrients in complex chemical and biological environment (Gambrell and Patrick 1978; Kanbroek, 1990).

3) TDS

The TDS ranges between 436-1010mg/kg with a mean of 574mg/Kg in Table 3. The pH of water is alkaline which is attributed to the water rock interactions that add metals (Na, K, Ca, and Mg) to the water. TDS indirectly impact zinc availability by altering soil pH and Eh (Roba et al., 2016). Changes in water into alkaline pH due to carbonate and bicarbonate ions dissolution often occur in water flowing out of the mouth of the cave by passing carbonate rocks that contain calcium. It is caused by the presence of carbonate minerals (calcium and magnesium) dissolved by water sources in study area on its journey through the ground in this area. It is consistent with the occurrence of limestone rock units of Nari and Gaj.

TDS can affect the availability of various plant nutrients including zinc. The TDS contents of water in study area is found to be above 436mg/Kg, the concentration of ion in the water also increased, which led to compete for absorption sites and reduced zinc uptake by plants and negatively impact plant growth and development (Ondrasek et al, 2022).

4) Temperature

The temperature measured at all the locations was 27° C, slightly increasing the carbonate to bicarbonate ratio (Green, 1949).

The increase temperature affects the solubility of carbon dioxide. When water gets a lot of heat intensity from sunlight, the surface temperature will rise. When the surface temperature of the water rises, the solubility of carbon dioxide will decrease so that the pH will rise and the water is alkaline. An Increase in water temperature, decrease solubility of oxygen and increases dissolution of basic salts such as bicarbonate which makes the water alkaline (Mafiana, 2016).

5) Zinc in Water

The water samples Groundwater = 5, surface water = 1, analyzed for zinc determination are found to be deficient in this micronutrient. The World Health Organization stated a legal limit of 5 mg Zn^{2+}/L in water (WHO Geneva, 1996). The water samples of Gadap town are devoid of zinc. Groundwater recharge up source (Thaddo river) is also free of any zinc content. When the pH is fairly neutral, the zinc in water is insoluble. Conversely, solubility of micronutrients increases with increasing acidity. Zinc can enter the environment from both natural (e.g. weathering and erosion) and anthropogenic (e.g. zinc production, waste incineration, urban runoff) processes (CCREM, 1987).

In natural surface water the concentration of zinc is usually below 100 microgram/liter and in groundwater, 10-40 microgram/liters in tap water the zinc concentration can be much higher as a result of leaching of zinc (WHO Geneva, 1996). Drinking water usually makes a negligible contribution to zinc intake unless high concentration of zinc occurs (WHO, 1996). Generally, pH 6.0-7.5 is acceptable for most plants as most nutrients become available in this pH range (Mafiana, 2016).

Grain Size Analysis

The physical properties of collected sample of soil from all four locations were analyzed for the grain size and mineral composition.

The grain size distribution results of soil samples (n=11) collected from the field sites is summarized in Table 4. The grain size analysis reveals that the soil samples distribution varies from retained as coarse sand (>80%) to medium sand (>49-57%), fine sand (>32%), silt (8.17%), and clay (5-3.82%). The minimum, maximum, and mean values of soil samples on mesh 60, 90, 100, and 170 (Pan) are found to be (79.68% min, 163.19% max, and 89.53% mean), (15.70% min, 67.15% max, and 49.86% mean), (12.39% min, 60.90% max, and 32.00% mean), (4.76% min, 16.78% max, and 8.17% mean) and (3.82% min, 14.32% max, and 5.00% mean) respectively.

Table 4. Table of sieved soil sample weight retained in each mesh no. and their mean values.

Sample	Retained	Mesh 60	Mesh 90	Mesh 100	Mesh 170 (Pan)
L1S1	80.53	63.79	33.14	6.24	9.42
L1S2	81.23	61.36	43.64	7.17	5.00
L1S3	79.68	64.72	43.37	5.80	4.84
L2S4	89.00	57.79	24.16	4.74	6.92
L2S5	68.37	67.15	56.09	4.27	3.82
L3S1	93.19	26.70	60.90	8.17	9.76
L3S2	161.6	15.70	13.24	16.78	5.11
L3S3	122.39	30.00	38.15	5.39	4.50
L4S1	119.54	20.58	44.02	4.84	10.00
L4S2	91.51	57.83	32.00	4.76	14.32
L4S3	163.19	49.86	12.39	7.23	10.43
Min	79.68	15.70	12.39	4.76	3.82
Max	163.19	67.15	60.90	16.78	14.32
Mean	80.53	49.86	32.00	8.17	5.00

Textural Characteristics

The soil samples collected from Gadap town field sites are comprised of a large proportion of sand size and a medium distribution of silty grain size and very low contents of clay particles. A large number of soil samples was retained between mesh 60-90 (85%-49.86%) resulted indicating sandy soil, while a very low amount of soil samples were retained between 100-170 mesh indicating the occurrence of silty to clayey soil.

According to the textural soil classification system was developed by the U.S. Bureau of Soils (Figure 3). The triangular chart consists of different groups of soil indicating different percentages of sand, silt, and clay-sized particles. The samples are classified into sandy loam soils due to the high percentage of sandy grain size. They are relatively infertile, owing to their poor retention of fertilizer nutrients and low available water capacity, so they tend to be less important in world cropping than many of the soil types associated with secondary deficiencies of Zn (Alloway, 2009).

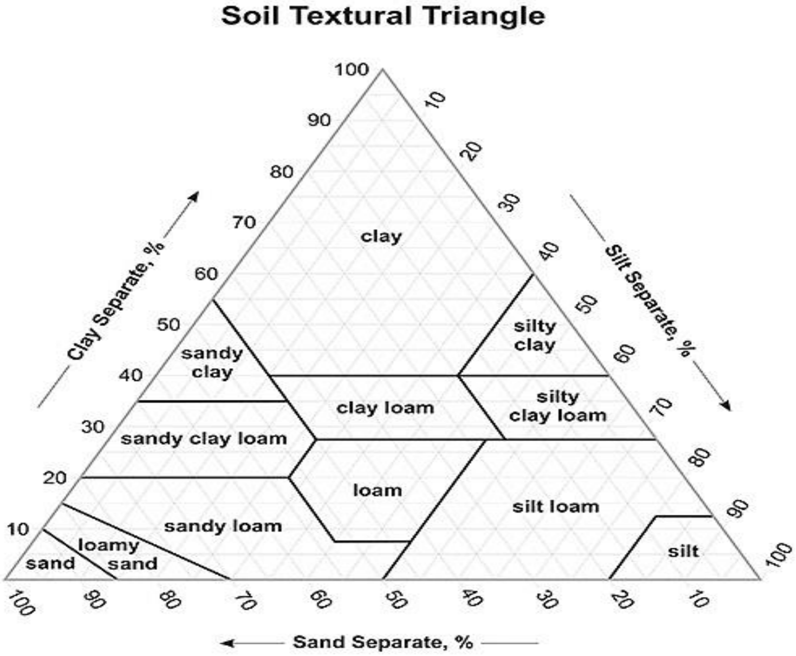

Figure 3. The textural soil classification system was developed by the U.S. Bureau of Soils.

Sandy loam soils generally contain moderate to high levels of sand, a small amount of silt, and a small to moderate amount of organic loam (Cochran, 2022). Sandy loam does not hold many of the minerals and nutrients needed by plants. The micronutrient zinc cannot be held by sandy soil. Sandy loam soils are often deficient in specific micronutrients and may require additional fertilization to support healthy plant growth (Thompson, 2018).

Sandy loams or on loamy sands that are moist, fertile, and deep, but it also does well on soils ranging in texture from sands to clays and on soils of relatively low fertility (Ambayeba, 2018). The low total Zn contents are found primarily in sandy soils and strongly leached tropical soils developed on highly weathered parent materials. Sandy textured soil has at least 65% sand-size grains and less than 18% clay in the top 100cm of the soil profile (Alloway, 2009).

Sieve analysis of Soil for zinc concentration in different grain size

Zinc concentration was determined from the sieved soil samples Table 5. It is observed that a large fraction of zinc (29.75%) in soil passes from mesh No 170 which is clayey soil, the percentage of zinc in mesh 60 (18.06%) is showing the lowest percentage of zinc in sandy loam texture. The zinc concentration is increasing followed by mesh no 60<90<100<170mm, which is more in number from 100mm to greater amount in mesh No 170mm, the zinc percentage values followed by 18.06%<22.38%<27.36%<29.75% of zinc high in clayey soil and low in sandy loam soil. Thus clay holds a high number of zinc micronutrients than sand. Clay soils are tightly packed, allowing very little water drainage or airflow, this soil is often packed in essential plant minerals such as zinc. Crop response to fertilizer zinc takes place mostly on fine-textured soils (Thompson, 2018).

Table 5. Table of sieved soil sample for each concentration of zinc in each mesh

Sample Zn	Mesh 60	Mesh 90	Mesh 100	Mesh 170
	Zn(mg/L)	Zn(mg/L)	Zn(mg/L)	Zn(mg/L)
S1 L1 Zn	0.498	0.560	0.649	0.892
S1 L2 Zn	0.589	0.549	0.627	0.835
S1 L3 Zn	0.573	0.671	0.837	0.980
S1 L4 Zn	0.656	0.824	1.010	1.082
Mean % Zn	18.06%	22.38%	27.36%	29.75%
Soil texture	Sandy Loam	Fine Sand	Silt	Clay

Mineral composition of soil (Petrography of soil)

The petrographic results of soil samples data reveal the occurrence of feldspar-quartz composition. There is a huge number of quartz that is a major sandy soil content. Sandy soils contain a high proportion of sand particles, with little silt or clay to modify the grainy nature of the soil (Breeman, 1987).

The agricultural soil of Gadap town is lacking clayey soil content in the soil which results in less amount of zinc present in the soil because sandy loam soil does not hold micronutrients (Dovikovskii, 1969).

Figures 4 and 5: Showing a Petrographic image of Gadap Town's Basin Agricultural soil sample, which reveals a large number of quartz in soil forming a sandy loam soil.

The minerals, chemical structure, amount of organic matter, and pH of the soil all affect the availability of Zn (Wang et al., 2017). The soil of the study area is sandy in nature. Zn availability is influenced by soil structure; sandy loam and organic soils are more prone to Zn deficiency than clayey or silty soils (Gong et al., 2020). If the soil composition is very light (e.g. sand), the micronutrients are easily washed away from the soil by rain. Conversely, denser clay-rich soils can retain micronutrients better, but they can also bind some of the nutrients with minerals in the clay. Clay soil requires slightly more fertilizer, while sandy soil requires less.

Physiochemical Parameters of Soil

The soils from four locations were also determined for their quantitative characterization of physiochemical parameters of soil which have been summarized in Table 6. The physiochemical properties of soil affect the metal solubilization processes, among the chemical properties oxidation and reduction-oxidation status (Eh) and pH are important for the solubility of heavy metals in soil (Reddy and Patrick, 1977).

Table 6. The list of soil samples' physical parameters and zinc concentration amount with permissible limits of Zn content in agricultural soil, by Alloway (1990) is 50mg/kg.

Code	pH	Eh(mv)	T	TDS(mg/L)	Zn (mg/Kg)
S3L4	**8.24**	**132**	**24.2**	**264**	**32.65**
S2L4	**8.44**	**120**	**24.1**	**267**	**40.1**
S1L4	**8.24**	**125**	**24.3**	**265**	**44.45**
S3L3	**8.25**	**124**	**24.6**	**214**	**31.25**
S2L3	**7.88**	**134**	**24.1**	**322**	**31.6**
S1L3	**8.16**	**125**	**24.3**	**206**	**35.41**
S5L2	**8.06**	**130**	**24.9**	**289**	**29.5**
S4L2	**8.07**	**130**	**24.9**	**278**	**24.75**
S1L1	**7.9**	**130**	**24.9**	**179**	**35.05**
S2L1	**8.08**	**130**	**24.9**	**170**	**41.85**
S3L1	**8.08**	**130**	**24.9**	**166**	**23.41**
Mean	**8.1**	**125**	**24**	**206**	**32.65**

1) pH

The pH of soil varies between 7.8-8.4 with a mean of 8.1. The ideal pH range of soil for growing fruits and vegetables is 6.0 - 7.0. Due to high pH, nutrients become less available to plants even if they are abundant in the soil (Hoidal, 2021). Most cultivated soil has a pH between 4-9 but a pH below 3 and above 10 can be measured in acid sulfate soil or sodic soils respectively (Husson, 2012). Soil pH is a characteristic that describes the relative acidity or alkalinity of the soil (Jensen et al, 2010).

The study area has soil pH above 6.5 resulting in decreased extractability and availability of zinc in soil and plants. The majority of plant nutrients are found to be most readily accessible to plants in the pH range of 6.5 to 7.5 (Jensen et al, 2010). Zinc in alkaline soil may become less soluble and available to plants due to precipitation with positively charged ions in the soil. pH has been referred to as the "master variable" due to its significant impact on soil zinc adsorption (Msaky et al, 1990).

Increase in pH over time without rainwater to wash nutrients through the soil, they can build up over time, increasing the alkalinity of the soil. This tends to drive the pH up as well (Hoidal, 2021). Soils that have received excess compost, especially composted manure, tend to have a higher pH due to the build-up of base cations.

2) Redox Potential (Eh)

The Eh result of soil samples varies between +120and132mV with a mean value of 125mV from Table 6. The soil Eh fluctuates normally between +300 and +900 mV (Husson, 2012). The change in redox potential (ORP) is the result of combined effects between many chemicals, physical and biological processes in soil.(Nemecek et al., 1990). Interestingly, pH and Eh are indirectly related that showing on soils results in the increasing pH with a decrease in Eh of the soil. The alkalinity and pH of soil and water tend to increase with chemical reduction and decrease with oxidation (Breeman, 1987).

As the soil of the study area is alkaline in nature, soil Eh decreases with alkalinization as microorganisms utilize the oxygen which decreases the oxygen value from the soil and increases the rate of reduction which automatically increases the basicity of the soil. When the acidic medium increases Eh also increases to reducing conditions and conversely decreased when Eh rose under oxidized conditions (Husson et al., 2001).

3) TDS

The Total dissolved solids TDS of soil samples varies between l66 mg/Kg-322 mg/Kg with a mean value of 206 mg/Kg. The distribution of soil TDS is shown in Table 6. TDS of soil refers to the concentration of all inorganic and organic substances dissolved in soil water. The Major factor responsible for this is a high content of bicarbonate ions because it has been found that the uptake of Zn and its transport within the plant from roots to shoots is inhibited by a high concentration of bicarbonate (15-40 mM) in Zn efficient varieties. In Zn inefficient variety, es even 5-10mM bicarbonate inhibits growth (Marcher, 1993).

The TDS of soil is in great amounts which results in high salinity of soil, followed by high pH of soil. An excellent indicator of soil salinity is TDS describing the inorganic salts and small amounts of organic water that are present in water (Pozdnyakowa et al., 2001). Watertable depths indicate salinity risk. The risk is greatest where groundwater can reach the soil surface by capillary rise and evaporation concentrates salts on the soil surface. TDS indirectly impacts zinc aimpactsility by altering soil pH and Eh (Roba et al., 2016). High TDS levels can increase soil pH and make it more alkaline leading to reduced zinc availability. Additionally, high TDS levels can also increase the soil Eh, making it more oxidizing and reducing zinc availability for plant uptake.

4) Zinc in Soil

The zinc result for soil varies between 29.5-44.45mg/Kg with a mean of 33.65mg/Kg. According, to Alloway (1990) zinc concentration amount with permissible limits of Zn content in agricultural soil is 50mg/Kg. The results reveal the deficiency of zinc in the agricultural soil of the study area.

Zinc mobility and uptake in the soil are dependent on many factors such as soil acidity, zinc total value in the soil, organic matter, and soil type (Alloway, 2009). The total Zn content in soil depends upon the parent rock, weathering, organic matter, texture, and pH (Husson, 2012). Zinc concentration in soil solution is highly dependent on soil pH, decreasing to very low levels at high soil pH (Jeffery and Uren, 1983; Brummer et aI., 1986). The zinc shows less concentration in water as well as in soil samples due to high alkaline pH because the nature of soil samples is calcareous Alloway, 2009), also due to high TDS of soil measured and low Eh value results in a reduction process in soil the availability of several micronutrients as Zn is strongly influenced by soil Eh and pH (Shams, 2022).

The fewer amounts of clayey mineral contents which hold zinc is also less available in the soil. There is a evidence for direct or indirect biological alternation in availability, solubility or oxidation reduction state of Zn (Reddy et.al 1988).

The main soil factors affecting the availability of Zn to plants are low total Zn contents, high pH, low redox potential, high calcite and organic matter contents and high concentration of Na, Ca, Mg, bicarbonate and phosphate in the soil solution or in labile form (Alloway, 2009).

While some fertilisers are less accessible to plants in alkaline soils, it’s crucial to note that the pH of the alkaline soil might also affect the fertilizer’s efficiency. This problem can be solved by bringing the soil pH into the ideal range for plant growth by adding acidic additions, such as sulphur or iron sulphate. Alkaline soil is less soluble than acidic soil, making it more difficult for plant roots to soak up necessary nutrients (Shams, 2022). High pH levels typically hinder plant growth and development (Alloway, 2009).

Zinc Interrelationship with physical parameters of soil

Table 7. Correlation of soil physical parameters with zinc in soil

	pH	*Eh(mv)*	*T*	*TDS(mg/L)*	*Zn(mg/Kg)*
pH	1				
Eh(mv)	**-0.799498172**	1			
T	**0.505464699**	**-0.501516101**	1		
TDS(mg/L)	0.052922643	0.123319416	0.090453616	1	
Zn(mg/Kg)	0.079575264	-0.076883763	-0.109049509	-0.342429482	1

This table shows a correlation between physical parameters of soil samples and with Zinc concentration of soil samples. The first negative value -0.799498172 shows the relationship of pH and Eh is indirectly proportional that is resulting in the increasing of pH and decreasing of Eh. Soil pH is one of the most important factor controlling Metal solubility in soil (B.R Singh, 2000). The result of (low eh- high pH) indicating the presence of alkaline material. The Eh of soil is decreasing due to microbial activity that is decomposing the organic matter (manure) present in soil, due to which the oxygen is breaking out from the organic chains that is forming gaseous bond and liberating from soil results in high reduction rate.

The soil pH and Eh plays important role in reducing heavy metal solubility in paddy soil (Reddy and Patrick, 1977). Soil Eh and pH can greatly vary at very short distances (Hinsinger et. Al, Yang, 2009).

The correlation between pH and temperature value is 0.50546499. The increase temperature led to significantly increase in soil pH, with greater the temperature increase the greater the increase of pH (Guoju, 2012). The correlation indicates direct relationship as the temperature is increased which is a support the process of evaporation due to which high amount water evaporates leaving behind the dissolved salts and alkaline contents in the soil, which automatically increases the pH of soil. The increase temperature significantly increase soil total salt, the greater the temperature raise the greater the increase in soil total salt (Alloway, 2009).

The Eh and temperature show an indirect correlation with a progressive reduction under high temperature. The Eh decreases due high reducing condition of soil due absence of oxygen. The increase in temperature increases the rate of biological, chemical activities of soil which releases gases that decomposes from the organic matter present in soil due to which Eh decreases. Eh factor influenced the mobility of many nutrients in complex chemical environment (Gambell and Patrick, 1978/ Kanbroek 1990).

Whereas, correlation of other physical parameters do not show any hugh influence on zinc deficiency of soil because the correlation values are below 0.5 that has no effects on zinc availability.

Zinc in Plants

The plants from all four locations were tested to determine zinc which results in zinc values varies between 10.71mg/Kg-21.35mg/Kg with a mean of 14.22mg/Kg in plants samples (Table 8). In plants, Zn acts as a functional, structural, or regulatory cofactor of a large number of enzymes and metabolism process (Brown et al., 1993).

The crops results in low zinc value according to FAO/WHO the standard zinc value is (60mg/Kg) and in normal plants zinc range falls between (20-100mg/Kg) but these samples from studied area shows low values of zinc than standard.

Table 8. List of plant sample from 4 locations and their zinc concentration, FAO/WHO guidelines for metals in food and vegetables.

Sno	Plants samples	Zinc (mg/Kg)	FAO/WHO (mg/Kg)	Normal Range in plants
1.	Hyacinth plant	21.35	60	20-100
2.	Bush plant	17.67	60	20-100
3.	Papaya plant	14.22	60	20-100
4.	Lemon plant	10.71	60	20-100

From table 8, at location 2, the Sem crops were collected which results in 21.35mg/Kg that is under the standard of (20-100mg/Kg) by FAO/WHO. The Sem crop consuming a better amount of zinc among other crops from studied area. From location 3, the Choriyaan crops results in less amount of zinc 17.67mg/Kg which is below the standard. From location 4, the crop of lemon and papaya also results in less zinc consumption in plants due highly alkaline pH of soil and water. Jones (1991) suggested that the average concentration of Zn in plants is 20 mg Zn/kg and that the critical deficiency concentration (CDC) is about 15 mg/kg. However, plant species differ in their sensitivity to Zn deficiency (for example Jones, 1991; Martens and Westermann, 1991).

Zinc is taken up by plant roots as Zn2+ or as Zn (OH)2 at high pH. As a result of low concentrations of zinc in the soil solution, uptake is mainly by direct root contact and is metabolically controlled (Alloway, 2009).

Most essential plant nutrients are soluble at pH levels of 6.5 to 6.8, which is why most plants grow best in this range. If the pH of soil is much higher or lower, soil nutrients start to become chemically bound to the soil particles, which makes them unavailable to your plants. Plant health suffers because the roots are unable to absorb the nutrients they require (LaLiberte, 2022).

Plants are unable to absorb the necessary amount of zinc because of the alkaline pH of the soil. Even though there is an adequate amount of zinc in the soil, it may convert into complex forms or interact with other nutrients. Additionally, because of the high pH, plants may not be able to absorb the necessary amounts of zinc, leading to deficiencies in people who consume this crop.

Scatterplot Correlation

Table 9. List of average zinc in soil and plant from SL2, SL3, and SL4 for correlation.

Locations	Soil Zn(mg/Kg)	plants Zn(mg/Kg)
SAL2	27.125	21.35
SBL3	39.066	10.71
SCL4	32.753	17.67

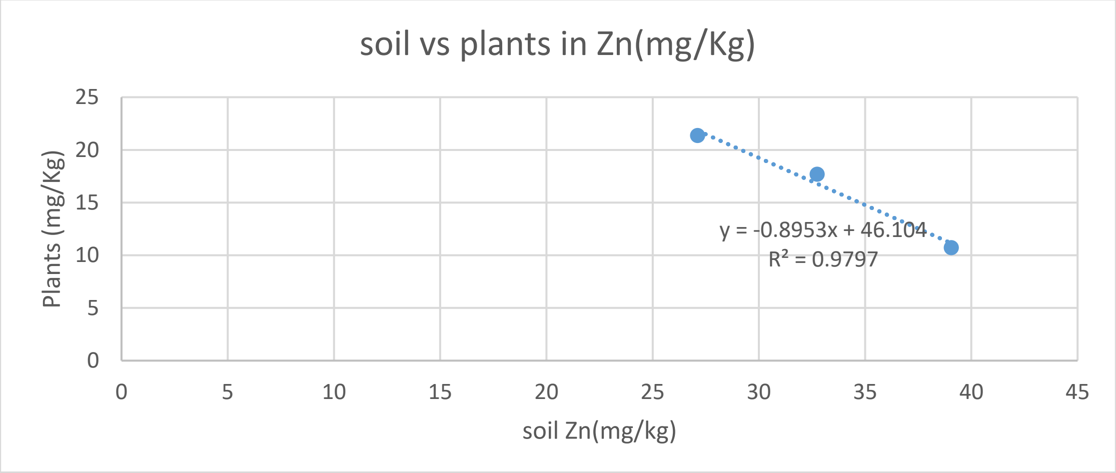

Figure 6. A scatterplot correlation between Zinc in soil and plants.

Scatter plots were generated to compare the Zn concentrations in soils ann crops at each site, S_L2 vs S_L3 vs S_L4, which showed a high positive correlation at the field site level (Figure. 6). The positive correlation shows the synergistic effect of Zn deficiency levels between soil and plant at all sites.

A scatterplot correlation result reveals a 97% strong relationship as all points near form a straight line. This reveals that number of zinc is retained in soil than absorbed by plants due to the highly alkaline pH of the soil with water. Although the soil is also deficient in zinc due to the high pH of the soil, the water is unable to absorb the zinc from the rom soil and transport it to the plants.

The solubility of Zn will decrease with increasing values of soil pH (Kirkens, 1995). This is due to the greater absorption capacity of the soil solid surfaces resulting from an increased pH-dependent negative charge, the formation of hydrolyzed forms of Zn (Alloway, 2009).

Conclusion

The Gadap Basin is a significant source of agricultural products which supplies fruits and vegetables for the city of Karachi for generations. It has been observed that agricultural operation in this peri-urban area has been declining over the past few decades. Zn is a crucial nutrient for plants and is involved in a number of their bio-physicochemical responses (Noman et al., 2019; Zaheer et al., 2022).

The present study revealed that pH has a stronger impact on zinc availability. Zinc deficiency in water, soil, and plants is caused by the high alkaline pH. Sandy loam soil is also contributing soil's zinc deficiency. Sandy soils are considered poor for plant growth because it they are loose and quick-draining, sand is often mixed with other soils to enrich it for plant growth.

Many methods have been employed all around the world to lower soil pH and make zinc available for plant absorption. Zinc deficiency can be decreased using a variety of fertilizers and techniques.

High pH Solution

When soil pH is too high, it can pose problems for plant health and growth. For many plants, soil that is high in alkalinity makes it harder for plants to drink in nutrients from the soil, which can limit their optimal growth (Noman et al., 2019; Zaheer et al., 2022).

The correlation between pH and TDS leading to the high amount of alkaline metals inside the soil with is positively increasing the pH within increase of TDS. High pH soil range from calcareous to alkaline saline and sodic soils (pH 8 and higher) (Bennett et. al, 2000).

Crops sensitive to Zn deficiency, calcareous soils, and soils having alkaline pH require higher fertilizer application rates (Alloway, 2008). As Soil of study area have alkaline pH so, application of Gypsum is required because it decreased the soil pH and thus enhanced the availability of soil Zn (Takkar and Singh, 1989).

Alkaline soil is less soluble than acidic soil, making it more difficult for plant roots to soak up necessary nutrients (Shams Tabrez Khan, 2022).

Soil pH can be reduced most effectively by adding elemental sulfur, aluminum sulfate or sulfuric acid. Aluminum sulfate is faster acting than elemental sulfur because it is very soluble.

The advantage of elemental sulfur is that it is more economical, particularly if a large area is to be treated.

Lowering the pH of alkali soils will dissolve zinc precipitates and increase the specifically absorbed Zn, well known for its low desorbability (Gupta, 1987). An increase in soil pH increased the negative charge of soil particles and also increased the exchangeability of sorbed Zn.

Correction of Sandy soil

Gypsum is easily applied to the soil surface with a regular lawn spreader. It's an ideal amendment for improving soil structure and relieving compaction which immediately to help compacted sandy soil, increase water penetration and improve drainage, correcting soil conditions to allow for better plant root growth (Cakmak et al., 2010, Rashid et al. 2019).

Addition of clay soil to sandy soil could be an option to increase water and nutrient holding capacity of sandy soils, but the effect of clay soil addition may depend on the form in which the clay soil is added and the addition rate (Shermeen, 2017).

Application of Zinc fertilizers

The correction of zinc deficiency in crops has considerable effects on yield and quality of crop production. However these yield responses can suffer from a number of edaphic and climatic factors (Watts, 2012). Zinc application and proper balancing of zinc with other nutrients in soil are all important to increase the yield and quality of crops production, quality of grain, and uptake of zinc in deficient soil.

Some soils are capable of supplying adequate amounts for crop production; addition of zinc fertilizers is needed for others. Zinc is a recommended micronutrient in fertilizer programs for crops production (Apurba, 2016).

Moreover source, rate, formulation, time, and method of zinc application and proper balancing of Zn with other nutrients in soil are all important to enhance crop productivity (Ahmad, 2012). Cakmak has reviewed that Zn fertilization increases the grain yield up to 5.7% in studies undertaken in China, India, Pakistan, and Zambia (Cakmak et al., 2010, Rashid et al. 2019).

Zinc sulphate is the most commonly used source around the world and is available in both the crystalline monohydrate and heptahydrate form (Alloway, 2009). Zinc sulfate (35%

of zinc) is usually used to supply the needed amount of zinc when dry fertilizer materials are used. This material can be either broadcast and incorporated before planting, or used in a starter fertilizer. It blends well with other dry fertilizer materials (Apurba, 2016). The ZnSO4 complex may increase the solubility of Zn2+ in soils and accounts for the increased availability of zinc when acidifying fertilisers, such as ammonium sulphate (NH4 (SO4)2) are used (Alloway, 2009).

The use of increase amount of nitrogenous and phosphatic fertilizers with high yielding hybrid varieties of crops often causes or exacerbate the zinc deficiency where the plant available zinc levels in soils are marginal (Apurba, 2016). Zinc deficiency in crops often occurs due to heavy Phosphatic fertilizers, as it is often found that enhance uptake of P causes deficiency of zinc but does not affect the total Zn content in the plant (Alloway, 2009).

A zinc-ammonia complex (10% of zinc) can be used to supply zinc when fluid fertilizers are used. This material mixes easily with other fluid fertilizers (Apurba, 2016). Zinc oxide (78-80% zinc) can correct a zinc deficiency but is slowly soluble and not effective in a granular form. To effectively correct a zinc deficiency, zinc oxide must be finely ground (Apurba, 2016).

Foliar applications of zinc have not been consistently effective in correcting deficiencies of this nutrient. This method of application should be used on a trial basis only. For foliar applications, powdered zinc sulfate can be dissolved in water and applied to the leaf tissue. The amount dissolved should supply 0.5 to 1.0 lb zinc per acre when a rate of 20 gallons of water per acre is used. Micronutrient applications through the foliar are preferable to soil applications because they quickly address deficiencies, are simple to employ, avoid toxicity from buildup, and prevent elements from fixing in the soil (Mousavi et al., 2011).

Application of poultry manure can add considerable amount of zinc to the soil. Because zinc content is variable in manure, it is suggested that manure sources be tested for zinc content before application (Apurba, 2016).

Many investigations have shown that Zn fertilization improves the amount of Zn in the plant's edible parts, increases grain yield, and enhances the overall health of the entire plant (Aghili et al., 2014, Phattarakul et al., 2012). Research has shown that all sources of zinc (except granular zinc oxide) have an equal effect on crop production. Consider cost before choosing a source of zinc for the fertilizer program.

The zinc deficiency can be reduced if the measurements are taken properly to enhance the yield of healthy crops for the population. As Gadap Town Basin serving the people of Karachi for decades, to overcome the zinc deficiency in Karachiits the quality of water and soil should be taken care of accordingly. There should be an assessment of water, soil, and crops every year to create a healthy Agricultural ground for the welfare of future generations.

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