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Research Journal of Agricultural Sciences
An International Journal

P- ISSN: 0976-1675
E- ISSN: 2249-4538

Volume: 12
Issue: 04

Res Jr of Agril Sci (2021) 12: 1437–1442

CARAS

Res. Jr. of Agril. Sci. (July-Aug 2021) 12(4): 1337–1442
www.rjas.org

Full Length Research Article

Status of Micronutrients and Heavy Metals in Some Selected Samples of Soil and Irrigation Water in Dayalbagh

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Received: 25 May 2021 | Revised accepted: 23 Jul 2021 | Published online: 21 Aug 2021

ABSTRACT

Knowledge of micronutrient availability in the soil is fundamental for suitable fertilization recommendations, to avoid deficiency or toxicity problems. Heavy metal contamination of soil is a threat to the quality and well-being of all components of the biosphere. Pb, Cu, Zn and As are the elements suggested to have the highest adverse effect on organisms. In an attempt to assess the concentration of these micronutrient and heavy metals, samples were collected from different locations of Dayalbagh and heavy metal analysis was done. To make a comparative detail of the soil, 16 sampling sites were selected for collection. Irrigation water was also collected from same sites to study the heavy metal load. A negative correlation has been observed between micronutrient and pH, whereas positive relationship exists between pH and organic carbon. However, there is no such correlation exists between pH and heavy metals. Lesser contamination was observed in these sites with negligible concentration of heavy metals.

Key words: Soil, Heavy metal, Micronutrient, pH, Correlation

Plant based food is very nutritious having a source of antioxidants, vitamins, and minerals hence played important role in human nutrition [1-3]. Edible parts of plants which are consumed without processing are the main source of heavy metals that can enter into the food chain and consequently in body. Although some of them are required for metabolic activities of plants as well as human body but these become toxic for the same at their concentration beyond threshold values [4-5]. Industrial and some agricultural activities have adverse effect on properties and quality of soil. Sustainable development demands preservation of soil quality and prevention of its deterioration. In recent decade it has been observed that heavy metals and their persistence have been increased in the atmosphere which is a major problem to be taken into consideration [6-8]. Anthropogenic activities have increased their concentration in the environment although, these metals are naturally present in stones and soils itself. Use of fertilizers and chemicals in agricultural activities are some human activities that causes contamination of heavy metal in soil [9]. Plant growth and development depends upon some elemental component of soil. Certain symptoms appear in plants to show deficiency of these elements. They exist as their respective complex forms. On the basis of plant requirement, two categories are there i.e., micronutrients and macronutrients. It has been observed that plants and microbes help in recycling of certain waste and are a source of detoxification of waste dumps [10]. By the analysis of soil and plant tissue certain facts about presence of each element in plant and their permissible limit in soil can be revealed. Plant as well as soil has beneficial effect of nutrient at their permissible limits while negative impacts have been observed at the range above or below the threshold. In such conditions soil amendment techniques proved to be beneficial. Availability of these nutrients in soil is regulated by soil pH, therefore special attention should be given to pH of the soil [11]. Micronutrient such as B plays a vital role in membrane-level functions of plants e.g., cell elongation, nucleic acid synthesis. This micronutrient is essential for the normal growth of plants and certain diatom species. Its deficiency causes anatomical changes with corresponding change in physiology and biochemistry of cell. Other possible roles of boron are sugar transport, The available concentration of Boron may vary from soil to soil, while it is reported in range of 20–200 mg/kg [12]. Rapid industrialization and urbanization causes negative impact on soil properties. It has adverse effects on the plant growth, crop production, and consequently can affect food safety. It is necessary to implement a simple, rapid and practical technique to assess heavy metal load in contaminated soil and also in edible plant parts [13]. It has been suggested that soil contamination by heavy metals can be estimated by bioavailability which is affected by metal species, their

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affinity to plants and some soil properties e.g., pH, Organic matter and anions and cations present in soil [14-15]. Therefore, availability of metal in soil can be predicted on the basis of soil properties and environmental factors. Correlation studies are being implemented for validation of data [16]. Soil properties influence availability of heavy metals therefore correlation varies among different soils [40], [17]. However, correlation once predicted can differ with the growth and developmental stages of plants [13]. In order to figure out complex connection between soil and heavy metals contents Principal Component Analysis (PCA) technique can be used based on analysis of eigenvalues of the covariance or correlation matrix. Variables are represented by loadings inferring importance of model components and also reflect variation or correlation in prescribed data set that can be used to detect patterns, groupings, similarities or differences [18-19]. In general, PCA is useful for selection of variable [20]. PCA can be used for reduction of a large data set and analysis of only two variables i.e., first two PCs having eigen values <1. The major focus of the present investigation were to understand the correlation of heavy metal concentration in soil and irrigation water in these areas and estimate predictable principal components for data set of heavy metal concentration of soil.

MATERIALS AND METHODS

Selection of sampling sites

Plants growing in this area were suffering from major damage in their growth. There were symptoms of mineral deficiency. Some species were drastically affected e.g., *Litchi chinensis, Cinnammomum verum, Magnolia champaca, Indopeptadenia oudhensis, Diospyos, Strychnos nux vomica* and some flowering plants. Therefore, to understand the deficiency of micronutrient and also if there is any heavy metal contamination in irrigation water and soil all the sections of the park were taken into consideration. Samples were collected for micronutrient and heavy metal analysis in soil and irrigation water. Possible source of heavy metal in this area is mainly fungicides and agrochemicals containing micronutrients.

Collection and analysis of soil and water samples

Soil samples were collected from each section (3 replicates per site) of the park and other regions of Dayalbagh following composite sampling patterns [17]. Surface soil (0-15cm) and irrigation water were collected during the month of August (2017). In order to represent the whole 12-acre land of the park each section was divided into 60 sampling sites, hence approximately 60 samples were collected from each section. Soil samples were air dried and homogenized to make a representative mean of all samples for each site [21]. However, soil samples were air dried and ground to fine powder for further analyses. Soil and water samples were processed immediately after collection for chemical analysis. The soil was analyzed for organic carbon content following the standard protocol [22]. Available micronutrient and heavy metal contents in soil were estimated using DTPA-$CaCl_2$-TEA method using ICP-OES (Agilent Technologies model-007) [23].

Statistics

Statistical technique involving (PCA) was employed to identify the effects of physicochemical properties of soil and irrigation water. Pearson correlations analysis was performed for studied variables with physicochemical properties to find out any existing relation between them. A computer code Statistical Package for Social Science (SPSS, version 16.0) was used in performing the statistical analysis.

RESULTS AND DISCUSSION

The soils of the nine sampling sites were slightly alkaline with pH 7.98 to 8.36 (Table 1). Organic carbon content as observed to be very low in these sections ranged from 0.002% to 0.346%. At succulent and gymnosperm garden, bougainvillea garden, birds and butterfly garden, palm plantation, arboretum 1 and arboretum 2, tropical garden and temperate garden and multigrafted and rare plants organic carbon content of soil were 0.002%, 0.093%, 0.195%, 0.346%, 0.165%, 0.237%, 0.297% and 0.346 respectively (Table 1). Irrigation water of these sites had pH 6.81 to 7.71 (Table 6). Soil samples collected from the sites showed marked variation in the level of micronutrient (Table 1). It has been observed that difference in heavy metal and micronutrient concentration of soil was due to the use of different quantity and quality of fertilizers and plants grown in particular sections. Depending upon the plant requirement for micronutrient differences were there. Furthermore, urbanization near the sampling sites, proximity of field from main road, and use of different types of agrochemicals [24-25] affect the chemical properties of the site. Various physico-chemical properties of soil are key factor for availability of micronutrient content. Organic matter in soil may chelate these metals and reduce their availability. Cationic metals such as Zn^{+2}, Cu^{+1}, Cu^{+2}, Pb^{+2}, Cd^{+2} may exist as adsorbed ion on clay-humus complex. Several studies have suggested strong relationships between soil pH and micronutrient. In general, the availability of micronutrient in soil decreased with increasing pH. A negative correlation exists between soil pH and available micronutrient. This could be due to the formation of insoluble complexes of micronutrients with their respective salts. Similar positive relationship exists between total B and Fe contents. But for As and Pb such relationship did not exist indicating that their availability depends upon soil pH rather than total contents in soil [23]. In earlier studies also pH was reported to be one of the important factors of heavy metal availability [26-28]. But clay content [29], ion interaction [30], redox potential [31] and organic matter content [32] are also significant. Additionally, heavy metal availability can be directly affected by plant itself [33]. The variation in metal load was due to the variation in quality of sewage used and background level of metal contamination. Slightly negative correlation found between As and pH (-0.503); strong negative correlation was observed between B and Mn (-0.792), Pb (-0.658) and Zn (-0.707). Similarly, Cu have weak positive correlation with Mn (0.587) and strong positive correlation with Pb (0.827) and Zn (0.788). Mn is positively correlated with Pb (0.814) and Zn (0.762). Pb has strong positive correlation (0.938) with Zn (table 2). The average As, B, Cu, Fe, Mn, Pb and Zn loads of irrigation water ranged between 0.001–0.015, 0.021- 0.627, 0.004–0.171, 0.004-0.399, 0.032–0.353, 0.036-0.158 and 0.033–0.106 ppm, respectively (Table 3). Water sample elemental analysis infer that Cu was positively correlated with Pb (0.995**) and Zn (0.848**). Mn is positively correlated with Zn (0.905). Pb has positive correlation (0.866) with Zn (Table 4).

Table 1 Micronutrient, heavy metal and pH of soil samples collected from Dayalbagh region

Sampling sites	ppm								
	As	B	Cu	Fe	Mn	Pb	Zn	pH	OC%
Bougainvillea garden	0.012	0.004	0.038	0.114	0.671	0.094	0.134	8.08	0.002
Succulent and gymnosperm garden	0.004	0.019	0.138	0.167	0.495	0.134	0.294	8.22	0.093
Birds and butterfly garden	0.002	0.068	0.08	0.119	0.337	0.085	0.118	8.27	0.165
Palm plantation	0.001	0.042	0.094	0.211	0.572	0.091	0.19	7.98	0.195
Multigrafted and rare plant	0.021	0.063	0.116	0.167	0.477	0.101	0.159	7.97	0.237
Temperate fruit garden	0.016	0.08	0.043	0.181	0.351	0.084	0.11	8.08	0.297
Arboretum 1	0.01	0.071	0.056	0.133	0.339	0.079	0.081	7.82	0.299
Arboretum 2	0	0.074	0.028	0.197	0.349	0.067	0.063	8.29	0.346
Tropical garden	0.013	0.079	0.004	0.229	0.142	0.055	0.035	8.05	0.346
Botanical garden	0.006	0.073	0.103	0.099	0.358	0.088	0.102	8.36	0.171
Seminar hall complex	0.009	0.082	0.078	0.072	0.273	0.076	0.085	8.06	0.003
Phal bagh	0.011	0.075	0.146	0.167	0.354	0.086	0.137	7.6	0.159
Herbal garden	0.002	0.069	0.082	0.141	0.302	0.081	0.088	8.08	0.159
Polyhouse 1	0.013	0.077	0	0.112	0.121	0.039	0.029	7.84	0.154
Polyhouse 2	0.026	0.079	0.003	0.157	0.112	0.051	0.03	7.86	0.154
Dairy	0.008	0.077	0.006	0.024	0.08	0.048	0.046	8.02	0.151

Table 2 Pearson correlation matrix; correlation between variables at p<0.05 level of significance

	As	B	Cu	Fe	Mn	Pb	Zn	pH
As	1.000							
B	0.207^{NS}	1.000						
Cu	-0.293^{NS}	-0.298^{NS}	1.000					
Fe	0.042^{NS}	-0.096^{NS}	0.126^{NS}	1.000				
Mn	-0.271^{NS}	**-0.792^{**}**	**0.587^{*}**	0.272^{NS}	1.000			
Pb	-0.269^{NS}	**-0.658^{**}**	**0.827^{**}**	0.221^{NS}	**0.814^{**}**	1.000		
Zn	-0.294^{NS}	**-0.707^{**}**	**0.788^{**}**	0.244^{NS}	**0.762^{**}**	**0.938^{**}**	1.000	
pH	**-0.503^{*}**	-0.198^{NS}	0.029^{NS}	-0.065^{NS}	0.212^{NS}	0.292^{NS}	0.185^{NS}	1.000

Table 3 Elemental and heavy metal analysis of irrigation water (W1=REI, W2=Phalbagh, W3=Botanical Garden, W4=Herbal Garden, W5= Dairy, W6= Seminar Hall Complex)

Sites of study	ppm								ds/m
	As	B	Cu	Fe	Mn	Pb	Zn	pH	EC
W_1	0.009	0.091	0.041	0.192	0.353	0.067	0.092	7.71	0.121
W_2	0.001	0.021	0.004	0.399	0.046	0.042	0.036	7.33	0.128
W_3	0.012	0.024	0.018	0.206	0.032	0.039	0.036	7.42	0.124
W_4	0.009	0.083	0.171	0.095	0.23	0.158	0.106	7.41	0.11
W_5	0.014	0.627	0.005	0.004	0.063	0.036	0.035	7.45	0.134
W_6	0.015	0.035	0.009	0.162	0.046	0.042	0.033	6.81	0.135

Table 4 Correlation matrix; correlation between variables (*p<0.05 and **p<0.01) of water

ppm	As	B	Cu	Fe	Mn	Pb	Zn
As	1.000						
B	0.395^{NS}	1.000					
Cu	-0.089^{NS}	-0.188^{NS}	1.000				
Fe	-0.790^{NS}	-0.693^{NS}	-0.299^{NS}	1.000			
Mn	-0.134^{NS}	-0.121^{NS}	0.545^{NS}	-0.154^{NS}	1.000		
Pb	-0.143^{NS}	-0.201^{NS}	**0.995^{**}**	-0.259^{NS}	0.576^{NS}	1.000	
Zn	-0.172^{NS}	-0.196^{NS}	**0.848^{*}**	-0.209^{NS}	**0.905^{*}**	**0.866^{*}**	1.000

It has been observed that there is a significant correlation (p < 0.01) for Cu and Zn in soil, these two elements may become toxic when present beyond their permissible limit in soil although the correlation observed was probably due to metabolic activities of the plant. Thus, results obtained can be verified the fact that the concentration of Cu and Zn in soils were not in the toxic range. Besides, it has also been inferred that the Cu or Zn can be strongly held by root tissues for the transport to shoots even under conditions of both Cu or Zn deficiency as well as Cu or Zn excess [34]. It has been suggested that organic matter can regulate the availability of heavy metals through chelation reaction, as these are not available to plants in their complex forms [35]. Negative relationships are seen between soil pH and As. These results suggested that the concentrations As could be lowered with increasing soil pH. The reason for this may be that increasing the soil pH could reduce the concentrations of heavy metal in the soil solution and consequently the uptake of Cd and Zn by crops.

Assessment of soil data by principle component analysis

Soil forms a linkage between different components of food chain i.e., it is the main source of nutrients for plants that subsequently provides food for animals and humans. However, soil can be a source of toxic elements such as heavy metals that can be absorbed by roots directly and through foliar absorption indirectly. PCA was a performed to identify the probable sources between the heavy metals when they were interrelated [36]. PCA was selected as the investigative method as it is a multivariate statistical technique commonly used to investigate variability in large geochemical data sets [37-39]. When using PCA only those PCs with Eigenvalues >1 is used as they account for the majority of the variance in the data. The first two PCs have eigenvalues >1 (Fig 1 and) are considered. According to Kaiser rule, the first two principal components have eigenvalues greater than 1. These two components explain variation in the data. The scree plot shows that the eigenvalues start to form a straight line after the second principal component. In these results, first principal component has large positive associations with B and As and negative association with Cu, Fe, Mn, Zn and Pb. The second component has large positive associations with Fe, Mn, Zn, Pb and As and negative with B and Cu. When original variables were compared with PCs similar results were obtained.

The soil, irrigation water samples collected from 16 sites showed lower level of contamination with heavy metal such as Cu, Zn, Pb and As. Most of the soil and irrigated water samples showed lower levels of Pb and As loads as compared to Cu and Zn loads. The level of contamination was negligible in these sites. However, correlation studies suggest that some of them are negatively correlated with pH e.g., As. PCA analysis reveals two principal components having maximum effect on variable. Agricultural activities such as fertilization, use of pesticides contributed the metal contamination of soil and water.

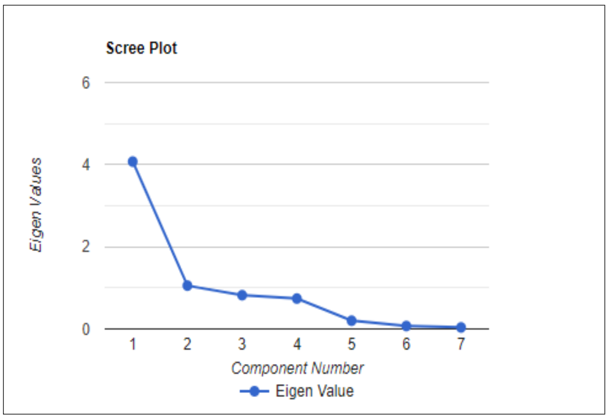
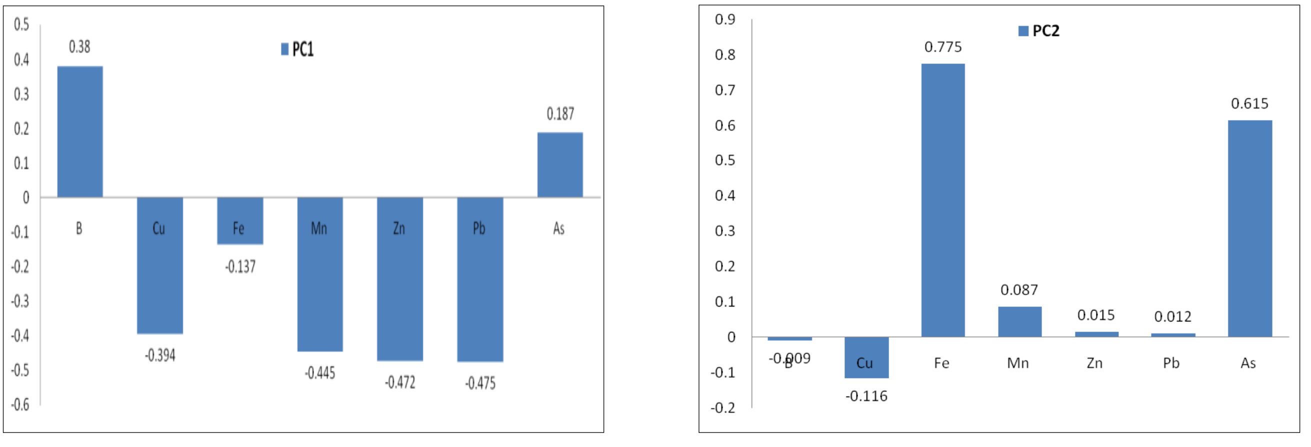


Fig 1 Scree plot for eigenvalues of first two PCs

Table 5 Eigen values of first two principal components

Component number	Eigen value
1	**4.074**
2	**1.055**
3	0.822
4	0.74
5	0.201
6	0.071
7	0.037



(a) (b)

Fig 2 Loadings of PC1 (a) and PC2 (b) of soil data

Table 6 Loadings (Eigenvectors) of correlation matrix

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
B	**0.380**	-0.009	-0.534	0.443	0.266	0.433	0.341
Cu	-0.394	-0.116	-0.302	0.577	0.177	-0.586	-0.181
Fe	-0.137	**0.775**	-0.520	-0.301	-0.072	-0.085	-0.088
Mn	-0.445	**0.087**	0.188	-0.211	0.772	0.109	0.327
Zn	-0.472	**0.015**	0.011	0.142	-0.536	0.078	0.680
Pb	-0.475	**0.012**	0.008	0.221	-0.088	0.666	-0.523
As	**0.187**	**0.615**	0.563	0.516	0.034	-0.028	0.030

Table 7 Correlation of principal components with original variables

	PC1	PC2	PC3	PC4	PC5	PC6	PC7
B	**0.767**	-0.009	-0.485	**0.381**	0.119	0.115	0.065
Cu	-0.795	-0.119	-0.274	**0.497**	0.079	-0.156	-0.035
Fe	-0.276	**0.796**	-0.471	-0.259	-0.033	-0.023	-0.017
Mn	-0.897	**0.089**	**0.170**	-0.182	0.346	0.029	0.063
Zn	-0.954	**0.015**	**0.010**	**0.122**	-0.241	0.021	0.131
Pb	-0.959	**0.013**	**0.007**	**0.190**	-0.040	0.178	-0.100
As	**0.378**	**0.632**	**0.511**	**0.444**	**0.015**	-0.007	0.006

CONCLUSION

Soil and water samples were collected from different sites of Dayalbagh and were analyzed for heavy metal and micronutrient concentration. It was observed that these elements were present within the optimum limits of their respective concentration. However, in these sites mostly organic farming is practiced. Therefore, lesser contamination is observed. Thus, this land may be utilized for growing fruits, vegetables and any other crop accordingly. These lands may be used for growing ornamental, timber plants, leafy, root and tuber vegetables. Similarly, water used in these areas showed very lesser amount of heavy metal concentration i.e., lower than optimum range with electrical conductivity in the range of 0.11-0.135 dS/m i.e., non saline, hence can be used for irrigation purpose. Although in present study water from sewage treatment plant is also taken into consideration but it was found that all heavy metals were within the range of permissible limits.

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