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Research Paper

Factorial analysis of trace elements of *Tamarindus indica* with reference to Bela ophiolite

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Abstract

A study of ophiolitic rocks, soils, twigs and fruits of *Tamarindus indica* have been carried out to evaluate elemental relationship. Soil of the study area revealed concentration of trace elements acquired from the bedrock. Its average abundance (mg/kg) in the soil was Mn (30), Fe (28), Pb (5.12), Cr (4.7), Ni (3.12), Cu (2.66), Zn (1.02), Co (0.97) and Cd (0.49). Fruit pulp presented: Fe (16.0), Cr (5.57), Zn (3.75), Mn (2.99), Cu (2.05), Co (0.92) and Ni (0.24). Twigs of *T. indica* showed Fe>Zn>Mn>Cu>Ni>Cr>Pb>Co>Cd trend of concentration. Elemental composition of rock-soil-twig-fruit of *T. indica* demonstrated similarities in the distribution pattern, reflecting common association between them. Correlation matrix (CM) and principal component analysis (PCA) revealed that elemental distribution of *T. indica* is influenced by the composition of rocks and soils of the study area.

Keywords: *PCA; Rock-Soil-Twig-Fruit Relation; Element Distribution; Geochemistry; Balochistan.*

1. Introduction

Tamarindus indica (Tamarind) is a well-known plant of the Pakistan. It is a large, evergreen and long-lived tree and widely planted in the study area. It belongs to Leguminosae/Fabaceae family [1]. Fruit of the plant is velvety cinnamon brown in colour and extremely sour in taste. It is mainly used for souring food items and pickles. The fruit has many health beneficial ingredients and is conventionally utilized as a raw material in eastern medicine [2, 3].
Several fruit farms are present in and around Winder town which is situated nearly 80 km NW of Karachi city along the RCD Highway, in southern Balochistan (Fig. 1). The area lies at the western margin of the Indian Plate [4]; forming southern part of the Mor range which comprises of sedimentary rocks (Ferozabad Group) of Jurassic age and Bela Ophiolite (BO) of Cretaceous age [5]. Rocks of BO were generated during Neotethyan tectonics showing supra subduction character [6, 7]. Majority of igneous rocks are amygdaloidal and vesicular porphyritic basalt in the area. Sedimentary rocks are comprised of clastic and carbonates and contains Pb-Zn-barite mineralization [8]. These rocks are enriched with appreciable quantities of Fe, Mn, Cr, Ni, Co, Cu, Zn, Pb and Cd.
During weathering processes, elements get concentrated in the soils of the study area [9]. Assessment of trace element content of soil is contingent to evaluating the sustainability of the agricultural ecosystem of an area for better crop production and reducing of trace elements intake through food chain [10]. The average water content and organic matter of the soils is 31% and 2% respectively. Soil shows Fe>Pb>Cr>Ni>Cu>Zn>Co>Cd abundance trend [8]; this shows relevance mainly with BO of Cretaceous age along with sedimentary rocks of Mor Range of Jurassic age.
The Cr, Ni, Cu, Co and Cd in the soil are mainly supplied by ophiolitic rocks while high Fe and Zn can be contributed both from ophiolite and sedimentary rocks of the area. Mineralogically, it contains high quartz and calcite along with variable proportions of clay minerals and iron oxides. Presence of clay fraction is responsible for mobilizing Cr, Cu, Zn and Cd [9]. Bio-available trace elements can be absorbed by the plants through their root systems and translocated to different parts of the plants, including the fruits. The accumulation of trace elements through food chain is probably responsible for the spread of diseases related to toxic elements among the consumers [11].

Present study has evaluated the relationship between trace elements assemblage of rocks-soils-twigs and fruits of *T. indica* of the study area with the help of CM and PCA. These are significant statistical methods used to reduce huge data and determine the association of trace elements [12]. It also assessed the amassing of trace elements through geological environment in the locally grown *T. indica.*

2. Material and methods

Representative composite samples of 21 igneous rocks, 14 sedimentary rocks, 49 soils, 19 twigs and 15 fruits of *T. indica* were collected from different fruit farms of Winder town. Igneous and clastic sedimentary rock samples were decomposed by flux method [13]. Carbonate rocks were digested using HCl (10%). The resulting solution was transferred to 100 ml volumetric flask [14]. Soil samples (2 mm) were soaked overnight in double distilled water. Shake on an electric shaker for 2 h. The content was filtered through Whatman No. 42 filter paper in a 100 ml volumetric flask [15]. The twigs were charred slowly at low flame till gray ash was formed in the china dish [16] and then digested with 5 ml concentrated HNO_3 [17].

Fresh fruit pulp was treated with HNO_3 and heated near to dryness [18]. The residue was treated with 10 ml of concentrated HCl and after heating for 30 min, 20 ml of distilled water was added and solution was further heated for 15 min. The final solution was filtered and made up to 100 ml [19]. Atomic Absorption Spectrometer was used to determine the concentration of the elements in the studied samples.

2.1 Statistical analysis

Multivariate analysis was performed using SPSS- 20.0 for Windows. PCA was interpreted in accordance to presence of trace elements combination [20, 21]. Varimax rotation was applied for data reduction and results have been shown in a 3D rotated space of PCA.CM computed through Pearson's technique with degree of significant level was $p<0.05$.

3. Results and discussion

The level of trace element in the fresh fruits of *T. indica* follows Fe>Cr>Zn>Mn>Cu>Co>Ni trend (Table 1). The Fe shows wide range of concentration, from 33 to 0.49 mg/kg with an average of 16.17 mg/kg. The average amount of Cr in the pulp of *T. indica* was 5.57 mg/kg while that of Zn was 3.75 mg/kg (Fig. 2A). All other trace elements were found to be < 3 mg/kg. The Ni displays lower levels of concentration among the trace elements (av. 0.24 mg/kg). The present work reveals higher Fe (16.17 mg/kg) and Cu (2.05 mg/kg) concentrations and lower Zn (3.75 mg/kg) and Mn (2.99 mg/kg), compared to the analytical result of [22] which shows 14.07, 0.76, 8.52 and 25.9 mg/kg respectively, for Fe, Cu, Zn and Mn. Twigs of *T. indica* illustrate Fe>Zn>Mn>Cu>Ni>Cr>Pb>Co>Cd trend of concentration (Fig. 2B). The concentration of Fe ranges from 1691 to 4415 mg/kg with an average of 2578 mg/kg (Table 2). Zinc is the second most abundant element (av. 410 mg/kg) found in the twigs of *T. indica* of Winder area. The average accumulation of Mn, Cu, Ni and Cr is 305, 152, 142 and 92 mg/kg respectively. Chromium (92 mg/kg) is much higher than the world average for all plants (9 mg/kg). Average concentration of Pb is 51 mg/kg, which is between the 70 mg/kg of [23] Brooks (1972) and 30 mg/kg of [24] for common plants. Cadmium is least recorded (av. 4.4 mg/kg) in the twigs of *T. indica*. It is a significant toxic element for plants because of its mobility and high solubility in water.

In the Winder area, rocks of BO are exposed and mainly consist of mafic tholeiitic pillow basalts. These rocks are rich in trace elements and display Fe>Mn>Cr>Ni>Cu>Zn>Co>Pb>Cd abundance trend (Table 3). These elements get dispersed in the soil after weathering. The arid climate of the area accumulates more immobile elements (as Fe and Mn) in the soil but the magnitude of concentration is low (Table 3 and Fig. 3). Despite the high concentration of Cr in the rocks (av. 694 mg/kg), it has been noted to be very low in the soil (av. 4.7 mg/kg).

Mutual relation among the trace elements composition of rocks, soils, twigs and fruits of *T. indica* has been illustrated in Figure 3. The diagram shows nearly similar distribution pattern, other than a few exception. The diversity is probably due to different in the nature of materials and the mechanisms of enrichment. Similarity in the distribution pattern reflects a pathway in the rock-soil-plant system, responsible for the accumulation of the trace elements in the soils and henceforth, transfers to the twigs and fruits of *T. indica* in the study area.

Ternary diagram (Cr-Ni-Co) illustrates mutual relation between them. Plots of average concentration in rocks, soils, twigs and fruits of *T. indica* were in the array, reflecting genetic association between them (Fig. 4A). Fruits had relatively high Cr, while twigs contained elevated amount of Ni. Iron along with Mn and Cr was valuable to infer inherited composition from the rocks and soils of the study area. Twigs, rocks and fruits have been found in close composition, while soils of the Winder area were found to be rich in Mn (Fig. 4B). Liaison of different segments of BO and *T. indica* has also inferred from Mn-Co-Ni triangulation variation diagram. Rocks, soils and twigs show variation in three components, having more Mn and moderate Ni. Soils demonstrate high Mn, medium Co and low Ni (Fig. 4C).

The impact of ophiolitic rocks of the study area can also be visualized from the results of CM. Pairs of trace elements in rocks, soils, twigs and fruits show good relation between them, reflecting close association and even generation from the same source (Table 4). The trace elements of ophiolitic rocks show good correlation between Fe-Cd, Cu-Cd, Zn-Cd, Mn-Zn, Mn-Cd (Table 4). Similarly, trace elements assemblage within the soil of the study area also demonstrates mutual relationship. The Fe shows good correlation with Mn, Cd and Ni; while Cd has good relation with Mn and Ni. Such geochemical relations are not unexpected in mafic rocks. The positive correlation among the important trace elements of the soils of the study area suggests similarity in composition. Negative relation of Pb with Mn, Ni and Fe (Table 4), indicate probable source of Pb from Sedex-type sedimentary rocks, which are widely exposed in the study area [25].

The rock-fruit relation is linked through twigs and is influenced by the composition of the soil. The mutual association between the elements also exists in the elemental composition of twigs. The young twigs of *T. indica* display strong to moderate correlation (Table 4). The fleshy part of *T. indica* shows strong CM (r = 0.842) between Cr and Co. In the current study Cr-Ni-Co-Mn-Cu positive relation indicates that the fruits of *T. indica* accumulate these elements with nearly equal ease from the soils.

Table 1: Concentration of Selected Trace Elements (mg/kg) In Fruits of *T. Indica*

Sample	Cu	Zn	Ni	Fe	Co	Mn	Cr
Sites							
SB	6.6	6	0.3	11	0	1.1	2.7
HC	5.6	5.5	0.3	25	1.6	2.5	8.5
AH	0.8	5.7	0.3	1.1	1.1	5.9	5.1
GD	0.8	1.7	0.2	33	1.1	2.2	5.2
QS	1.1	3.2	0.2	16	1.5	3.6	11
RB	1.1	5.6	0.3	30	0.9	3.8	4.5
GF	4.5	2.5	0.4	10	0.3	1.2	1.5
NS	4.5	3.2	0.2	14	0.3	2.4	1.8
WT	0.7	6.4	0.3	17	0.8	2.7	4.8
HG	0.7	2.5	0.2	6.1	0.6	3.1	4.9
HM	0.8	3	0.3	0.5	1.4	5	5.4
UG	0.8	1.9	0.3	24	0.6	2.1	4.9
KR	0.8	3.1	0.1	5	0.7	2.8	5.1
CF	1.1	3.3	0.2	28	1.6	2.8	7.2
MN	1	2.8	0.2	22	1.4	3.8	11
Mean	2.1	3.8	0.2	16	0.9	3	5.6

Table 2: Concentration of Selected Elements (mg/kg) In Twigs of *T. Indica*

Sample	Cu	Pb	Zn	Ni	Fe	Co	Mn	Cr	Cd
Sites									
SP	145	70	430	267	2004	2.1	479	93	7.5
SB	321	99	646	304	1691	2.8	320	106	9.5
GH	179	46	348	242	1878	1.5	272	72	4.5
HS	107	39	622	287	2286	1.4	250	88	5.2
AK	206	74	636	2.3	2303	2	560	111	5.9
HC	126	7.5	349	36	2601	1.6	301	57	0.4
AH	266	103	1043	281	2730	2.9	569	144	9.3
HF	124	97	551	322	2386	2.7	223	126	13
GX	130	64	232	161	2580	1.4	275	96	4.8
QS	112	15	2	148	2634	1.5	219	107	4.8
AR	113	46	288	85	3589	21	322	93	1.5
RB	218	46	401	88	2657	19	220	86	1.1
CU	139	51	268	44	3147	23	239	91	1.7
GP	90	49	156	68	2524	16	293	82	4.6
GF	137	57	361	77	4415	18	309	105	2
GE	88	59	444	70	2170	17	246	80	2.3
NS	128	16	310	154	2635	11	305	110	3.8
TA	168	23	296	30	2464	1.5	200	47	0.7
MN	93	12	403	33	2297	1.7	191	59	0.5
Mean	152	51	410	142	2578	8	305	92	4.4

Table 3: Concentration of Selected Elements (mg/kg) In Rocks and Soils of Winder Area

Rocks (n = 35)					Soils (n = 49)			
Elements	Min	Maz	Mean	SD	Elements	Min	Max	Mean	SD
Cu	2.6	422	245	132	Cu	0.03	8.8	2.66	2.73
Zn	2.2	141	79	35	Zn	0.03	16.7	1.02	2.67
Ni	5.4	1410	635	372	Ni	0.52	13.3	3.12	2.9
Fe	156	11984	5044	4,062	Fe	0.8	197	28	46
Co	12	103	62.8	24	Co	0.05	2	0.97	0.38
Mn	42	2252	907	511	Mn	1.23	140	30	39
Cr	12	3984	694	854	Cr	0.07	9.8	4.7	2.61
Pb	1.2	97	58	36	Pb	0.08	10.55	5.12	4.14
Cd	0.9	6	3.8	1.66	Cd	0.13	1.8	0.49	0.46

Table 4: Correlation Coefficient between Elements Concentration in Rocks, Soils and Plants (Twigs and Fruits) of T. Indica

Rock		Soil		Twigs (T. indica)		Fruit (T. indica)	
Fe-Cd	0.899	Fe-Mn	0.983	Ni-Cd	0.811	Cr-Co	0.842
Cu-Cd	0.871	Fe-Cd	0.911	Pb-Cd	0.775	Mn-Co	0.554
Zn-Cd	0.737	Mn-Cd	0.903	Cr-Cd	0.724	Mn-Cr	0.381
Mn-Zn	0.667	Mn-Ni	0.866	Cr-Pb	0.685	Ni-Cu	0.314
Mn-Cd	0.626	Fe-Ni	0.843	Zn-Pb	0.66	Ni-Zn	0.294
Cu-Zn	0.571	Cd-Ni	0.789	Zn-Cu	0.606	Mn-Cu	-0.569
Cu-Fe	0.541	Pb-Mn	-0.632	Fe-Co	0.606	Co-Cu	-0.373
Cr-Co	0.539	Pb-Ni	-0.568	Mn-Zn	0.605	Cr-Cu	-0.35
Co-Pb	-0.756	Pb-Fe	-0.567	Pb-Cu	0.575	Fe-Mn	-0.328

The average Cr content was considered to be high (5.57 mg/kg) as compared to 2.9 mg/kg of [26] for all native floras. Possibly, the high amount of Cr has due to the presence of extraordinarily high amount (~10%) of tartaric acid in the fruit [27]. Tartaric acid reduced Cr^{6+} (atomic size 0.75Å) to Cr^{3+} (size 0.58Å), which is compatible to many divalent ions, thus Cr is enriched in the fruit pulp.

Based on rotated component matrix, trace elements have been observed significant group combination in the rock samples. First combination consists on Fe (0.90), Mn (0.88), Ni (0.87) and Cr (0.81), while, Co (0.92), Cd (0.89) and Cu (0.87) has shown as second group of combination. Zn (0.70 and 0.61) associated among both combinations and its role can be defined as bridge (Fig. 5). Concentration of Pb in rock sample has depicted independent role, probably it is related to Sedex type of mineralization as referred before. Soil sample sites of *T. indica* were identified strongest group combination on the basis of selected trace metals concentration (Fig. 5). Closet group chain has been developed by Mn (0.98), Fe (0.97) and Cd (0.90) and associated character can be provided from Ni (0.88) and Zn (0.76). This combination also produced repels force against Pb (-0.67). The content of Cr, Cu and Pb can be defined as weak group due to their correlations (0.87), (0.74) and (0.51). The concentration of Co has identified as independent role in the soils which is most distinguished comparatively rock combinations (Fig. 5).

Three distinct groups of combinations have been observed in twigs of *T. indica* (Fig. 5). Cadmium (0.88), Ni (0.82) and Cr (0.80) concentration intake in twigs depict strong interaction among them in terms of injection while Mn (0.83), Zn (0.78) and Cu (0.77) were arranges as second combination in the twigs of *T. indica* although Pb concentration has distinct as associated member and bridge between both combinations with its correlation (0.69) and (0.57). Third group combination consists on Fe (0.89) and Co (0.85) which can be identified as closet with each other and Ni (-0.41) try to producing resistance against them.

Due to significance of factor analysis, various scholars have also utilized PCA in the assessment of fruit composition [28, 29]. In the fruits of *T. indica*, rotated component matrix, demonstrate three separate populations (Fig.5). In component 1, Co (0.95), Cr (0.87) and Mn (0.64) are strongly associated, but Cu (-0.51) has shown inverse trend while, second component has shown Zinc (0.82), Ni (0.75) and Cu (0.60) part of its members. Third combination of trace minerals consist on Fe (0.86) and Mn (-0.71) in which their opposite characters can be identified (Fig. 5).

4. Conclusions

Average elemental composition of *T. indica* fruits showed Fe (16.17), Cr (5.57) while Zn is 3.75 mg/kg. Rest of the elements (Mn, Cu, Co, Ni) is <3 mg/kg. Twigs of *T. indica* illustrate Fe>Zn>Mn>Cu>Ni>Cr>Pb>Co>Cd trend of distribution and their average concentration are 2578, 410, 152, 142, 92, 51, 8 and 4.4 mg/kg respectively. The amount of Cr (av. 92) in the twig is high then the average value of Cr (9 mg/kg) in the common plants of the world. In general, magnitude of concentration of elements in twigs is high in contrast to fruit values. The twig/fruit ratio of *T. indica* was noted minimum in case of Co (8.6) and maximum found in Ni (591.6), indicating restriction in the transformation of Ni from twig to fruit. *T. indica*, a local fruit plant is widely cultivated over the soil of the study area, which are derived mainly from the weathering of igneous (BO) and sedimentary rocks of Jurassic age. Average composition of the soil showed high Mn (30) and Fe (28 mg/kg); moderate Pb (5.12), Cr (4.7), Ni (3.12), Cu (2.66) and low Zn (1.02), Co (0.97) Cd (0.49 mg/kg). Elemental composition of rock-soil-plant on log scale and ternary plots displays near identical distribution pattern, reflecting mutual relation among them. Statistical analysis in terms of CM and PCA revealed that elemental distribution of *T. indica* is influenced by the composition of rocks, minerals and soils of the study area.

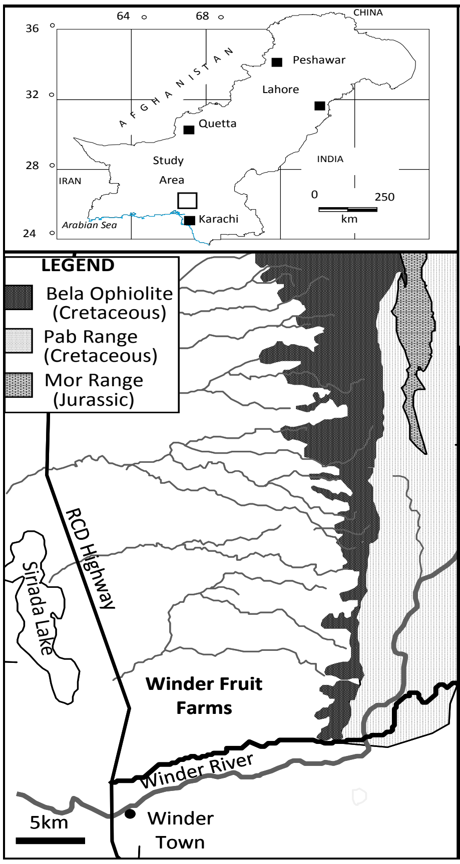

Fig. 1. Geological map of Winder and adjoining areas

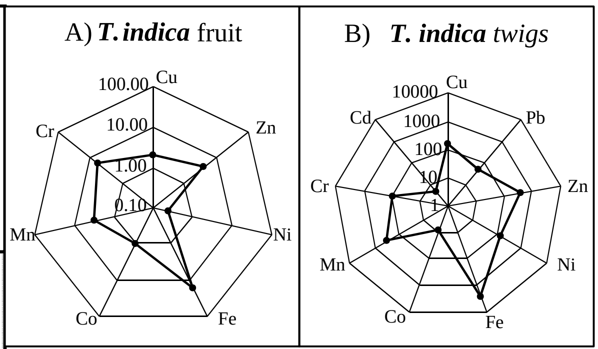

Fig. 2. Trace elements composition (mg/kg) in fruit (A) and in (B) twigs of *T. indica*. All values are in log scale.

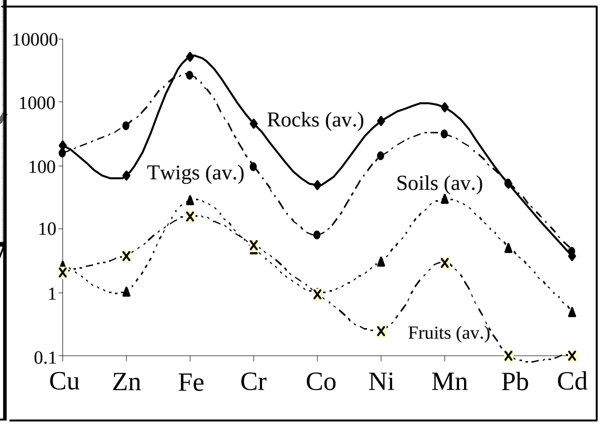

Fig. 3. Distribution of the studied elements (mg/kg) in rocks, soils, twigs and fruits of *T. indica* on log scale.

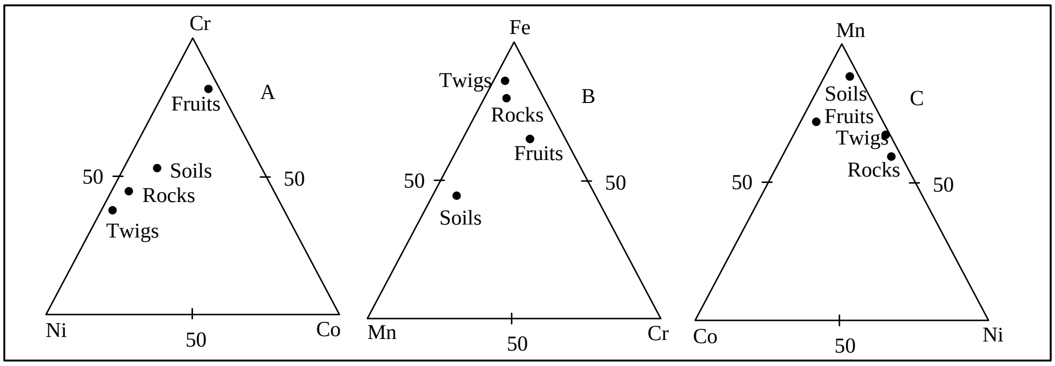

Fig.4. Relation between rocks, soils and plants (twigs and fruits) of *T. indica*

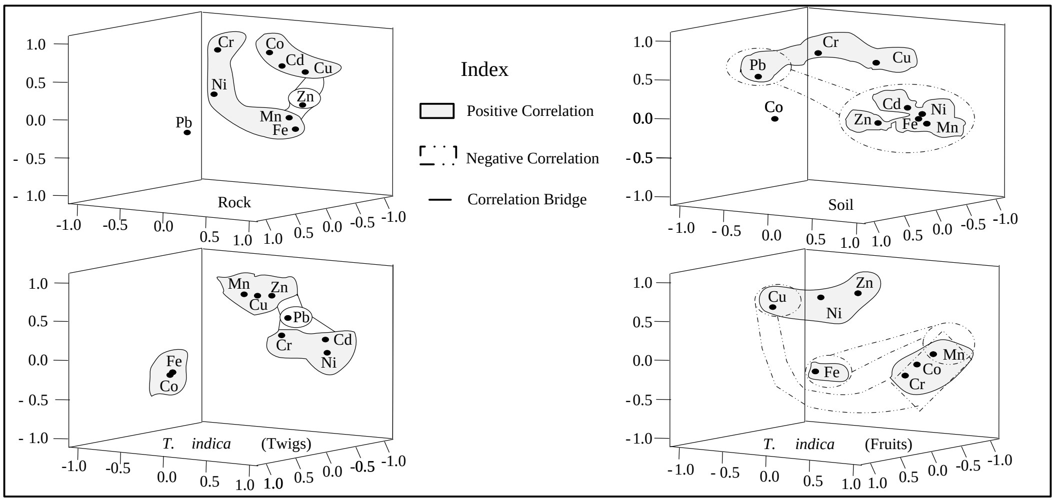

Fig. 5. Results of the PCA for rocks, soils, twigs and plants (twigs and fruits) of *T. indica*

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