TRANSPORTATION OF ELEMENTS FROM SOIL TO PLANTS IN PADERU AREA AND KAKINADA MANGROVE FOREST

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Abstract- Concentration of major and trace elements of soil samples collected from the Paderu agency area (at high altitude) and Kakinada mangrove forest of India have been evaluated by using SPECTRO XEPOS, EDXRF spectrometer and Si(Li) detector; and analyzed their role in the accumulation of elements present in the Paderu agency medicinal plants and also in the Kakinada mangrove plant species. Several analytical parameter(s) that provide information regarding pollution or quality of soil/sediment due to anthropogenic activity have been evaluated in the present studies. Accumulation factor, different quality indices namely geo-accumulation index; contamination factor; eco-toxicological risk, pollution load index etc. are evaluated besides Pearson's correlation analysis. Concentrations of Na, P, S, Cl, K, Ca, Zn, Se, Cu, Mn, Si, Fe, Ni, V, and Co have been determined and the quantities of these trace elements in different parts of present mangrove and medicinal plants are found to be varied leading to the conclusion that they are useful for specific purposes

Keywords – Medicinal plant, Therapeutic usage, EDXRF, Trace elements, Elemental analysis.

I. INTRODUCTION

Uptake of elements by plants usually depends on several factors namely type of plant species; its age; soil type; wastage disposal and atmospheric parameters such as temperature; humidity etc. Transport and accumulation of different elements in various parts of plants takes place based on their root to stem structure along with their leaf's nature besides corresponding physical properties. Physiochemical and geochemical properties of plants play key role in the transport of elements; element type also exhibit impact on its transport. Sediments are one of the important carriers of elements. Metals do not present as static one in the sediments. Their distribution and cycling of them depend on their chemical and biological agents.

Several factors like human activity; anthropogenic disposal; industrial effluents etc. show impact on the movement of different elements. These may become responsible for arise of pollution depending on the concentration values of the elements. These elements function as nutritious one up to certain values of their concentrations beyond which they become toxic turning into anti functional elements for the health management causing responsible for the arise of health diseases. Some of the heavy metals; which called as potential toxic elements (PTE) accumulation take place due to pollution. Hence determination of these elements concentration in the soil/sediment is important as these transpose to different parts of plant species those useful for health management.

Earlier an investigation on soil physical parameters of Paderu location on the lines mentioned above was carried out to analyze the fertility of soil to understand its suitability for agriculture purpose [1]. It concluded that pH of the soil varies in the range 4.8 to 7.5 showing 83% of the study area is acidic in nature having electrical conductivity values in the range 0.04 – 0.87 ds/m in association with non-saline condition. A similar type of investigation by Prakash et al [2] was carried out on transfer of trace elements from soil to plants belonging to Mangalore city of Karnataka state in India. It concluded that uptake of some elements found to be negligible even though they contain largely in the soil. Hence; aim of the present work is to understand the impact of soil on the concentration of elements present in the plant species.

II. EXPERIMENTAL DETAILS

Soils as well as different plant species have been collected from two places namely; Paderu division (high altitudes-medicinal plants) and Kakinada Coringa forest (Mangroves) covering four different locations. Elemental analysis of plant species related to the above mentioned two places has been reported elsewhere [3]. Soil samples were collected from the superficial layer of the soil and also at 20cm depth. For each site the soils were collected from three points; a few meters apart from one another and then mixed in order to prepare homogeneous samples. These soil samples and the respective plant samples were collected on the same day. Polythene bags used for the sample collection were cleaned by soaking and rinsed with distilled water. The soils were dried in oven at 60^0C for 30 hours. The samples were thoroughly ground and homogenized in an agate mortar. The risk of contamination during the sample preparation procedure was kept to a minimum.

The experimental measurements were carried out at NCCCM, Hyderabad by using Energy Dispersive X-ray Fluorescence Spectrometry. Approximately 4 g of a powder ground well was poured into a cuvette. The bottom of the cuvette was covered by a 4 μm Prolene foil. After pouring, the powder was slightly pressed with a pistil to form a good surface avoiding any cavities or pores at bottom. These powder samples were exposed to X-rays by using SPECTRO XEPOS spectrometer and the fluoresced X-rays emitting from the sample were collected and displayed with energy dispersive detector systems. The spectra were analyzed by SPECTRO XRF Analyzer Pro operating software; an inbuilt one with the system. Further elemental profile of these two places soil or sediments have been evaluated to understand the affinity of the elements present in the soil and respective plant species along with plant and element specific in association with dynamic behavior of elements. Validity of the EDXRF set up was performed by analyzing standard reference materials such as Apple leaf (SRM1515) and Oriental Tobacco leaves (CTA-OTL-1) those obtained from National Institute of Standards and Technology (NIST).

III. RESULTS AND DISCUSSION

The values of major and trace elemental concentrations of the present studies related to soils of Paderu division are shown in the table 1. As there are no industries; pollution and its impact on the variation of elemental concentration may be considered as negligible. Change of elemental contents may be due to anthropogenic activity of local habitants and varying environmental parameters. Besides bio and geo chemical properties; pH; biological activity of soil microorganisms [4] also contribute to the change of soil elemental concentrations leading to the nutrient cycling. The observed variations of elemental concentration values from one location to other can be attributed to the change of environmental conditions; different patterns of land usage; soil erosion and practice of shifting cultivation by local people. Organic carbon and pH of soil will influence largely on soil fertility and its elemental concentrations. Earlier Naik et al [5] reported that the present under taken locations pH values lie in the range 5.7 to 6.4. It helps to assess the acidity and alkalinity of soil [5] that shows impact on the growth of plant species. They also observed [5] that among major nutrients N, P, K of soil; nitrogen found to exhibit highest concentration while lowest concentration by phosphorous. In the present studies also, potassium found to show higher concentration relative to phosphorous following the same order of elemental concentration as mentioned above and nitrogen is not detected due to experimental limitation of EDXRF.

Table 1 shows the highest concentrations of potassium and sulfur in the soil belong to Minumaluru location while lowest of potassium and sulfur obtained at Seribayalu and Thumpada respectively. In the case of secondary nutrients highest level of calcium and sulfur found to exist in the soil belong to Thumpada while highest chlorine found to be in the soil of Seribayalu location. Lowest concentrations of calcium and sulfur are obtained at Seribayalu and Minumaluru locations respectively while chlorine lowest level observed at Vanthadapalli. Among the obtained micro nutrients silicon found to be the highest concentration relative to the all other elements obtained in the present studies. After that iron and manganese are observed as 2^{nd} and 3^{rd} highest elements. The decreasing order of the elemental concentration is Si > Fe > Mn > V > Cr > Zn >Ni > Cu > I > Mo > Se. The observed highest concentration of silicon found to be 99500ppm at Thumpada while lowest 95810.0 ppm obtained at Minumaluru. Iron and chromium highest levels are obtained at Vanthadapalli and lowest of both the elements observed at Thumpada location. Similarly, highest concentration of manganese; zinc; nickel and vanadium are observed at Seribayalu while lowest found at Minumaluru for Mn; Ni and Thumpada for Zn and V. Further Iodine concentration found to be in the range 0.4 ppm to 3.0 ppm while molybdenum (1.0 ppm) and selenium (0.5ppm) values observed to be constant for all the locations. The obtained values of I; Mo and Se show very small quantities assuming no much impact of them.

Table 1: Major and trace elemental concentrations (ppm) of the soils collected at Paderu (18.08330^{0}N & 82.66670E; altitude 904m i.e. 2966 ft.) agency area

Element symbol	Vanthadapalli 17.4000^{0}N 78.4800^{0}E 1000m (3000ft)	Thumpada 18.0670^{0}N & 82.7017^{0}E 904m (2996ft)	Minumaluru 18.0249^{0}N & 82.7088^{0}E 904m (2996ft)	Seribayalu 18.0653^{0}N & 82.6930^{0}E 914m (2990ft)
P	223.2±19.4	175.6±15.3	230.1±21.4	195.2±16.8
S	1.4±0.3	2.0±0.8	2.6±0.2	2.0±0.3
Cl	143.1±11.3	153.8±10.2	146.4±9.6	157.6±12.4
K	1430.0±128.4	1698.0±115.5	2915.0±198.2	1343.0±112.2
Ca	1543.0±125.4	1763.0±148.6	997.6±95.4	934.4±89.9
Zn	32.8±2.6	25.4±1.9	31.4±2.6	33.6±1.9
Cu	26.8±2.4	39.4±3.6	13.1±1.8	20.6±1.7
Mn	859.3±78.2	843.8±45.6	761.3±65.2	970.7±94.3
Si	98380.0±8542.8	99500.0±6582.0	95810.0±5897.2	96380.0±8562.3
Ni	24.6±2.6	23.2±2.1	21.9±1.8	28.5±1.9
V	115.1±10.2	74.3±6.7	101.4±9.8	1070.0±98.6
Fe	35650.0±3126.0	27040.0±1982.5	30560.0±2854.6	33360.0±3560.1

The highest concentration is obtained for calcium element followed by potassium; phosphorous and chlorine. The observed Sulfur concentration seems to be very small that required for different growth functions of plants. It plays key role in the process of photosynthesis; synthesis of amino acids and also proteins. The major nutrients namely nitrogen; phosphorous and potassium besides organic carbon are required for proper growth of the plants [4]. As the nitrogen and magnesium are low atomic number element; these could not be detected in the present studies due to limitation of the experimental technique. The other two elements are detected at considerable level. The secondary nutrients such as calcium, magnesium and sulfur are also necessary for vegetation of plants. These elements required quantities are relatively higher when compared with the micro nutrients. But lower quantities of them is enough if these compared with the primary nutrients (NPK). Calcium concentration is found to be higher relative to other nutrients; which are useful for reducing salinity of soil and improvement of water absorption supporting longer wetness for plants. Chlorine also observed at considerable level in the present studies as it needed for opening and closing of leaves stomata (pores) enabling to take in and send out of oxygen and carbon dioxide during photosynthesis. It improves disease resistance nature too.

Twelve medicinal plants collected from the above mentioned four locations of Paderu division were analyzed for elemental concentrations and presented elsewhere [3] as mentioned above. Based on this data and the obtained present results related to soils; elemental transfer coefficient/ratio; which also called as accumulation factor for major and essential nutrients have been evaluated and displayed in the table 2. It indicates that highest value (2,365.00) of accumulation factor (AF) for sulfur is obtained for the plant *Alstonia venenata*. It belongs to Vanthadapalli location while sulfur lowest (239.45.00) AF is observed for *Rhaphidophora decursiva* related to Seribayalu location. Potassium shows lower values relative to all other elements exhibiting its lower value (3.15) for the plant species *Ardisia solanacea* that collected from Minumaluru location and its highest value (24.06) belong to the *Rhaphidophora decursiva* plant that procured from Seribayalu location. The highest values of calcium (31.39) for *Alstonia scholaris* and chlorine (59.45) for *Curculigo orchioides* belong to Vanthadapalli and Thumpada locations respectively. Lowest values of Ca (3.45) and Cl (1.07) are observed for *Rambano* and *Cassia fistula* respectively; which belong to Vanthadapalli location. In the case of phosphorus, lowest AF (6.95) is observed for *Ardisia solanacea* and highest found in *Aristolochia indica*; which belong to Minumaluru and Thumpada respectively.

In the present studies among all the elements; sulfur and chlorine have significance relative to other elements due to the macroscopic parameter; which integrates several factors namely soil physical; soil chemical and plant physiology process; hydrological and biological causes for exhibition of large variability corroborating the obtained results in the present work. Many external factors like climatic conditions; agricultural practices also influence the accumulation of elements in the plant species. As mentioned in the earlier studies [6] not only the elemental concentration of soil responsible for the presence of elemental concentration /quantity in the plant; micro and macro nutrients also influence it. The obtained higher values of transfer factor/ accumulation factor can be ascribed to the contaminant redistribution within the soil profile. This contaminant redistribution of soil changes for deep root

plants as the time increases or passes. Therefore, the obtained higher variability of accumulation factor is a complex process depending on variety of factors. Uptake or absorption of elements from soil to plant or soil to vegetation usually influenced by the physical and chemical properties of soil along with chemical form of element in the soil. The locations that under taken in the present studies are also influenced by the plugging and fertilizers as these exposed to shifting cultivation; locally called as podu cultivation [5]. Sabine et al [7] discussed about environmental processes affecting plant root uptake of radioactive trace elements and variability of transfer factor. They have mentioned based on the literature that concentration of radionuclide in a soil is not only the cause for transfer of elements from soil to plant i.e. absorption of element by plant and referred several factors responsible for the said process.

Table 2 Accumulation factors (AF) of major and trace elements for Agency medicinal plants

Scientific name	Soil location name	P	S	Cl	K	Ca	Zn	Cu	Mn	Si	Ni	Co	V	Fe	Pb
Alstonia scholaris	**Vanthadapalli**	**7.76**	**332.21**	**1.59**	**17.87**	**31.39**	**0.42**	**0.16**	**0.02**	**0.00**	**0.10**	**0.19**	**0.20**	**0.00**	**0.05**
Alstonia venenata	**17.40000N**	**12.65**	**2,365.00**	**57.65**	**22.99**	**16.33**	**2.52**	**0.69**	**0.06**	**0.03**	**0.14**	**0.19**	**0.22**	**0.01**	**0.05**
Cassia fistula	**78.48000E**	**15.71**	**368.64**	**1.07**	**8.90**	**17.62**	**0.71**	**0.19**	**0.08**	**0.02**	**0.11**	**0.19**	**0.13**	**0.00**	**0.05**
Rambano	**1000m (3000ft)**	**12.85**	**782.86**	**9.26**	**9.61**	**3.45**	**0.64**	**0.25**	**0.14**	**0.11**	**0.20**	**0.19**	**0.37**	**0.04**	**0.04**
Aristolochia indica	**Thumpada**	**24.27**	**2,163.00**	**36.43**	**19.05**	**14.73**	**1.02**	**0.39**	**0.29**	**0.05**	**0.33**	**0.19**	**0.23**	**0.01**	**0.02**
Stemona tuberosa	**18.06700N &**	**17.85**	**532.00**	**52.63**	**12.20**	**4.13**	**0.94**	**0.26**	**0.05**	**0.03**	**0.18**	**0.29**	**0.38**	**0.01**	**0.08**
Curculigo orchioides	**82.70170E 904m (2996ft)**	**23.58**	**1,446.50**	**59.45**	**18.86**	**15.84**	**6.18**	**0.55**	**0.27**	**0.03**	**0.28**	**0.24**	**0.42**	**0.03**	**0.04**
Clematis gouriana	**Minumaluru**	**13.47**	**3,555.00**	**22.41**	**9.16**	**19.91**	**1.15**	**0.95**	**0.13**	**0.04**	**0.18**	**0.19**	**0.20**	**0.00**	**0.05**
Ardisia solanacea	**18.02490N & 82.70880E 904m (2996ft)**	**6.95**	**588.33**	**17.53**	**3.15**	**12.17**	**0.16**	**0.31**	**0.05**	**0.01**	**0.15**	**0.23**	**0.23**	**0.01**	**0.07**
Arisaema tortuosum	**Seribayalu**	**11.37**	**2,056.67**	**16.42**	**10.66**	**31.06**	**5.00**	**0.82**	**0.08**	**0.03**	**0.15**	**0.15**	**0.16**	**0.01**	**0.20**
Rhaphidophora decursiva	**18.06530N & 82.69300E**	**11.50**	**239.45**	**24.26**	**24.06**	**15.76**	**9.60**	**0.38**	**0.35**	**0.02**	**0.13**	**0.19**	**0.03**	**0.00**	**0.00**
Rubus	**914m (2990ft**	**11.83**	**296.30**	**8.01**	**3.92**	**6.35**	**0.53**	**0.50**	**0.06**	**0.02**	**0.11**	**0.19**	**0.02**	**0.01**	**0.06**

3.1 QUALITY INDICES (ESTIMATION OF POLLUTANT IMPACT)

Number of analytical parameters that provide information regarding pollution or quality of soil/sediment due to anthropogenic activity have been evaluated in the present studies. Enrichment factor (EF) is intended to estimate pollution due to human induced changes in a particular region. It can be computed for a specific metal/element concentration of a soil/sediment against concentration of that particular metal/element of uncontaminated background [8-9]. The method of EF evaluation involves the normalization of measured metal content with respect to the reference metal namely iron (Fe) or aluminum (Al) [10]. These reference metals (Fe & Al) are considered as proxy elements for the soil content [9]. By following the similar procedure; EF values were computed on taking manganese as reference metal for marine sediment [11]. Later Matthai et al [12] used cobalt as reference element for normalizing element for determining pollution due to anthropogenic activity. However, for normalization some investigators [13-14] considered iron as reference or standard element due to its distribution that do not depend on other heavy metals by having relatively high natural concentration. The enrichment factor (EF) is computed by using the following equation that reported earlier [9].

$$EF = M_x . Fe_b / M_b . Fe_x \quad \text{----------(1)}$$

M_x and Fe_x are heavy metal and iron concentrations present in the soil/sediment sample; M_b and Fe_b are concentrations of heavy metal and iron concentrations present in a suitable reference material. The evaluated values of EF related to the four different locations of Paderu agency area are presented in the table 3.

In the present investigations EF values of six metals have been computed. Iron found to be fixed or constant value (1.00) for all the four locations. Lead; manganese and chromium are found to show the values in the range 1.28 to 2.29; 1.90 to 2.45 and 1.09 to 1.23 respectively.

Cobalt also has the range values 0.75 to 1.54 contributing its impact towards pollution. Nickel and zinc are showing EF values less than one having the range 0.46 to 0.60 indicating pollution due to these two metals can considered as negligible. Copper also showing smaller values except at Thumpada where it found to be 1.53. Among all the four locations as per the obtained values given in the table 3, Thumpada seems to be higher polluted area relative to the other locations as all the observed metals show higher values of EF when compared with others.

Geo-accumulation index (I_{geo}) that introduced by Muller [15] is useful to assess the pollution level due to enrichment of metal content with reference to baseline concentrations. This method is useful to classify the extent of pollution in

terms of seven enrichment classes of geo-accumulation index (I_{geo}). Following is the formula that reported by earlier investigators [9] for computation of I_{geo} values.

$$I_{geo} = \log_2 C_n / 1.5\ B_n \qquad \text{----------(2)}$$

Table 3 Enrichment factor, Geo-accumulation index, Contamination factor for soils collected in the Paderu Agency area and Eco-toxicological risk, Pollution load index and PERI of sampling locations of Paderu agency

	Area Name	Vanthadapalli	Thumpada	Minumaluru	Seribayalu
EF	Mn	1.9	2.45	1.96	2.29
	Fe	1	1	1	1
	Ni	0.48	0.6	0.5	0.59
	Cu	0.79	1.53	0.45	0.65
	Zn	0.46	0.47	0.51	0.5
	Pb	1.62	2.29	1.28	1.3
I_{geo}	Mn	-0.07	-0.09	-0.24	-0.11
	Fe	-0.99	-1.39	-1.21	-14.37
	Ni	-2.05	-2.14	-2.22	-1.84
	Cu	-1.33	-0.78	-2.37	-1.71
	Zn	-2.12	-2.49	-2.18	-2.08
	Pb	-0.3	-0.2	-0.85	-0.71
C_f	Mn	1.43	1.41	1.27	1.62
	Fe	0.76	0.57	0.65	0
	Ni	0.36	0.34	0.32	0.42
	Cu	0.6	0.88	0.29	0.46
	Zn	0.35	0.27	0.33	0.35
	Pb	1.22	1.31	0.83	0.92
E_r	Cu	2.98	4.38	1.46	2.29
	Zn	0.35	0.27	0.33	0.35
	Pb	6.1	6.55	4.15	4.6
PLI		1.1	1.1	0.96	0.44
PERI		11.23	12.61	7.48	8.78

C_n and B_n are concentration of the element in the soil/sediment and geo-chemical background of the element. The evaluated values of I_{geo} are displayed in the table 3. These values are showing compliance with the obtained values of enrichment factor (EF). Except for cadmium and mercury; the remaining all the elements geo-accumulation index (I_{geo}) values are found to be negative indicating their uncontaminated status due to these elements in all the four locations undertaken in the present studies.The extent of contamination due to each element in the soil/sediment can be estimated by a parameter called contamination factor (C_f) [16]. It is calculated with the following equation

$$C_f = M_x / M_b \qquad \text{----------(3)}$$

Where M_x = Concentration of pollutant element in the contaminated soil/sediment and M_b = Concentration of element in the geochemical background [17-18]. In the present studies contamination factor (C_f) values have been evaluated and presented in the table 3. Values of C_f for all the elements are found to be less than 1 except for manganese and lead for which C_f value ranges 0.83 to 1.62. Therefore, these locations are considered as uncontaminated areas with reference to Fe; Co; Ni; Cu; Zn and Cr. Based on the Mn and Pb values of C_f the present undertaken locations are considered as uncontaminated to moderately contaminated category [8].

In the present studies eco-toxicological risk (Er) that describes potential risk of individual element and pollution load index (PLI) of all the locations have been computed by using the following equations reported by earlier investigators [9]. The PLI is an important parameter to estimate contamination of a particular region [19].

$$PLI = (C_{f1}.\ C_{f2}.\ C_{f3.\ \text{---------}}\ C_{fn})^{1/n} \qquad \text{------(4)}$$

Where C_f is the contamination factor; which already given above. Eco-toxicological risk (Er) of the elements calculated; which explains as the quantitative expression of risk degree based on some common PTEs of ecological importance [16]

$$E_r = T_r.\ C_f \qquad \text{--------(5)}$$

Er is a measure of potential risk due to individual element; T_r gives toxic response factor (TRF) for a given metal or element [16] and C_f represents contamination factor. Potential ecological risk index (PERI) is nothing but sum of potential risk of individual elements/metals. It has been computed with the following equation [16]

$$PERI = \sum_{i=1}^{n} E_r^i \qquad \text{---------(6)}$$

For the locations undertaken in the present studies Er; PERI and PLI values are evaluated and given in the table 3. The evaluated PLI values are observed to be in the range 0.44 to 1.10 indicating increasing trend of contamination

i.e. deteriorating quality of habitant locations. The increasing order of PLI is 1-A = 2-A >3-A >4-A. The Eco-toxicological risk (E_r) values are found to be in the range 1.46 – 4.38 for Cu; 0.27 – 0.35 for Zn and 4.15 to 6.55 for Pb. The highest values of E_r for two elements namely copper and lead are observed at Thumpada while for zinc it is observed at Vanthadapalli and Seribayalu. The obtained Potential ecological risk index (PERI) values are also showing highest at Thumpada (12.61) followed by Vanthadapalli (11.23) indicating observed risk found to be within the low level but higher relative to other two locations.

IV. RESULTS AND DISCUSSION (MANGROVES)

As mentioned above besides agency medicinal plants; mangroves also undertaken for elemental analysis work as a part of plant species investigation on their nutritional and medicinal usage. Experimental results pertaining to the plants species collected from the present study areas in the Coringa mangrove forest (Lat. $16^0\ 44^1$ to $16^0\ 53^1$ N and Long. $82^0\ 14^1$ to $82^0\ 22^1$ E) that situated on south side of Kakinada Bay having distance about 150 km from south of Visakhapatnam city; AP was reported elsewhere [3]. Coringa is named after the river Corangi. Mangroves of Coringa receive freshwater from Coringa and Gaderu rivers, distributaries of Godavari River and its back waters from Kakinada bay. Numerous creeks and canals traverse to this ecosystem.

For understanding soil/sediment contribution towards elements presented in the plant species; soil samples are collected from the four different locations at which plant species (*Excoecaria agallocha; Rhizophora Mucronata; Ceriops Decondra; Avicennia Officinalis*) were collected. These soil samples used for elemental analysis and the obtained results of major and micro elements are presented in the table 4 as performed in the case of soil samples of medicinal plants.Among the obtained elements potassium found to have highest concentration (6423 – 7335) followed by calcium concentration (2549 – 5311). Phosphorous shows lowest values relative to all other elements having the range 223.2 – 1937.0. The trend of elemental concentration in the decreasing order is K > Ca > Cl > P > S. Among these four locations, Thogara location contains highest concentrations of three elements namely P; K and Ca while highest sulfur and chlorine occurred at Nallamada. Among trace elements iron found to be the highest concentration followed by manganese and vanadium respectively. The trend of elemental concentration in the decreasing order is Fe > Mn > V > Zn > Cu > Sr > Rb > Ni > Pb. Among these four locations Thogara shows highest concentrations of majority elements as observed in the case of major elemental concentrations followed by the location at which Aalbi plant was collected that contain next order of highest concentration of elements.

Table 4 Major and trace elemental concentrations (ppm) of soils collected at Coringa mangrove forest

Soil Location	MTS-1 (Thilla)	MTS-2 (Uppuponna)	MNMS-3 (Thogara)	MTS-4 (Nallamada)
Na	100.0±0	100.0±0	100.0±0	100.0±0
P	255.5±20.5	1826.0±150.2	1937.0±152.3	223.2±16.4
S	210.8±15.8	203.9±12.3	261.9±18.5	299.3±16.8
Cl	1955.0±168.5	2113.0±140.3	2038.0±180.6	2215.0±130.2
K	6423.0±520.6	7073.0±618.4	7335.0±512.3	6572.0±475.2
Ca	4658.0±268.9	4486.0±226.7	5311.0±451.3	2549.0±168.3
Zn	44.0±3.2	57.7±4.7	59.7±3.6	42.5±2.8
Cu	46.1±3.2	56.2±4.6	55.9±3.5	44.9±2.6
V	114.2±10.3	151.0±13.5	156.4±13.7	112.7±9.7
Mn	838.6±75.8	1216.0±118.4	1416.0±121.6	521.7±48.6
Fe	35850.0±2450.2	42650.0±3625.9	45980.0±3678.4	33760.0±2456.3
Ni	36.7±3.4	46.3±3.6	47.0±3.4	35.8±2.4
Co	14.3±1.2	27.6±1.5	30.1±2.4	11.6±1.1

Earlier also some of the investigators studied heavy metals distribution and pollution impact of the mangrove plant species [8-9, 20]. Abrahim et al [8] investigated about degree of contamination and heavy metals enrichment factors of marine sediments belong to Tamaki Esturay, Auckland, New Zealand. Madhurima et al [9] studied on sediment quality and elemental bioaccumulations of mangroves belong to Indian Sundarban. Heavy metals distribution in mangrove sediments along the mobile coastline of French Guiana was carried out by earlier investigators [20]. The observed minimum concentrations of all the minor elements are presented in the table 4. Presence of P and Ca can be understood on the lines as reported by Marchand et al [19] in which it mentioned that *Avicennia* (local name - Nallamada) contain exclusion of excess metals through leaves. Age and biomass production of a mangrove plant influence the retaining of metals [21] and thus the observed higher concentrations of elements at Thogara can be interpreted on these lines. To estimate the impact of elemental contents present in the soil/sediments on the uptake or absorption of elements by the mangrove plant species related to the respective locations; bioaccumulation and

enrichments factors have been evaluated following the procedure that mentioned above in the case of agency medicinal plants. Therefore, the evaluated values of bio-accumulation factors related to mangrove plants are given in the table 5. As shown in the table 5 sodium shows higher AF values particularly for leaf relative to bark of a plant species indicating higher levels of elements absorption by plant (s) leaves. Some of the plants bark part showing AF values as unity (one) reflecting concentration of respective elements contained in the soil and absorbed by the bark with equivalent value. The obtained AF values for P are in the range 0.39 to 1.67 while for S the AF values range 0.73 to 7.83. Further the AF values for Cl; K lie in the ranges 0.63 to 3.87 and 0.05 to 0.26 respectively. In the case of minor elements AF values seem to show < = 1 for all the

Table 5 Accumulation factors (AF) of major and trace elements belong to Mangrove plants

Scientific name	Xylocarpus Granatum (Leaf)	Xylocarpus Granatum (Bark)	Rhizophora Mucronata (Leaf)	Rhizophora Mucronata (Bark)	Excoecaria agallocha (Leaf)	Excoecaria Agallocha (Bark)	Bruguiera gymnorhiza (Leaf)	Bruguiera Gymnorhiza (Bark)
Na	50.4	1	39	30.1	55	1	51.7	1
P	0.47	1.37	0.39	0.35	0.53	1.58	0.42	1.67
S	3.64	1.08	1.85	0.73	2.59	6.32	3.32	7.83
Cl	3.53	0.63	3.09	2.53	3.87	1.54	3.3	3.04
K	0.07	0.21	0.06	0.05	0.08	0.24	0.07	0.26
Ca	2.91	8.59	2.39	4.79	1.32	6.8	2.93	5.03
Zn	0.14	0.13	0.07	0.07	0.23	0.22	0.19	0.16
Cu	0.05	0.08	0.31	0.04	0.06	0.05	0.42	0.33
V	0.06	0.09	0.1	0.07	0.07	0.12	0.1	0.14
Mn	0.01	0.01	0.35	0.06	0.1	0.05	0.1	0.04
Fe	0	0	0	0	0	0	0	0
Ni	0.04	0.06	0.06	0.04	0.04	0.05	0.07	0.09

elements except for strontium that has the AF values in the range 0.82 to 5.03. On the other hand, for Bryopsis Penneta; Zn (3.11) and Cr (5.20) also show higher values. Earlier Madhurima et al [8] reported bio-accumulation factor values of K; Ca; Mn; Fe; Cu and Zn for mangroves of Indian Sundarbans. These values found to be < = 1; thus, as the present AF values are also < = 1; these can be understood on the same line and the observed variation of values may be attributed to the biological effects of the elements besides several influencing physical and chemical parameters. The obtained higher values of AF for Ca; Cl and P for Dalbergia Horrida and Bryopsis Penneta may be interpreted on the basis of integration of several macroscopic parameters like soil chemical; biological; hydrological and plant physiological processes etc. [2] as discussed above in the case of agency medicinal plants.

To estimate soil quality belong to mangroves; its indices parameters namely enrichment factor (EF); Geo-accumulation Index (I_{geo}); contamination factor and pollution load index along with potential ecological risk index (PERI) are computed and their values are displayed in the table 6. Earlier observed [8] EF values found to be < = 1 for most of the elements except for Cr (range 1.08 to 1.23) and Cu (range 1.36 to 1.47) that related to mangroves of Indian Sundarbans. The present EF values of Cr (range 1.03 to 1.09) and Cu (range 1.28 to 1.39) that belong to Coringa mangrove plants shows compatibility with the EF values of Indian Sundarban mangroves. The obtained present EF value of Zn seems to be slightly lower than the earlier observed Zn (0.94 to 1.00) EF values; contrary to this Mn and Pb values are improved relative to earlier observed EF values of Mn (0.59 to 0.90) and Pb (0.28.to 0.50). Ni values seem to be almost nearer to the earlier values (0.66 to 0.85). The observed negative geo-accumulation (I_{geo}) values corroborating their uncontaminated profile of the four locations. The positive I_{geo} values are obtained for Mn at two locations (Aalbi; Thogara) while for Co at one location (Thogara) reflecting these areas as uncontaminated to moderately contaminated due to these elements as per the Muller classification [15].

The contamination factor (C_f) values for chromium; iron; nickel; zinc and lead as shown in the table 6 are found to be < = 1 as obtained earlier for Sundarban mangroves [7] reflecting as low contamination due these elements. On the other hand, the C_f values for Mn; Co and Cu ranges 0.61 to 2.36 suggesting these locations as moderate contamination [16]. Majority of elements are showing their highest concentrations at Thogara location following the next highest concentrations to occur at Aalbi indicating contamination order of locations. The contamination order of locations has been evaluated by computing values of eco-toxicological risk (Er) and pollution load index (PLI along with potential ecological risk index (PERI) that provide suitable information about contamination or pollution. The values are calculated by following the procedure mention above in the case of agency medicinal plants. The PLI values range 1.05 to 1.53 is found to be higher when compared with the earlier observed [8] PLI values range 1.08 to 1.30 of Sundarban mangroves. The decreasing order of PLI is 4-A > 2-A > 1-A > 3-A. Thogara and Aalbi locations found show higher PERI values 12.52 and 12.19 respectively; which supporting pollution order obtained in

the results of other quality parameters. The evaluated eco-toxicological risk (Er) values are also found to be higher at Thogara and Aalbi locations authenticating the results obtained in the measurements of other physical parameters. The obtained E_r values show degree of contamination and risk level associated due to accumulation of different elements such as Cu, Zn, Cr and Pb.

Table 6 Enrichment factor, Geo-accumulation index, Contamination factor, for soils collected in Coringa mangrove forest and Eco-toxicological risk (Er), pollution load index (PLI) and PERI of sampling locations of Coringa mangrove forest

	Sample code	MTS-1-A (Thilla)	MTS-2-A (Aalbi)	MNMS-4-A (Thogara)	MTGS-3-A (Nallamada)
EF	Mn	1.84	2.24	2.42	1.22
	Fe	1.00	1.00	1.00	1.00
	Co	0.99	1.61	1.63	0.85
	Ni	0.71	0.75	0.71	0.74
	Cu	1.35	1.38	1.28	1.39
	Zn	0.61	0.67	0.65	0.63
I_{geo}	Mn	-0.1	0.43	0.65	-0.79
	Fe	-0.98	-0.73	-0.62	-1.07
	Co	-0.99	-0.05	0.08	-1.3
	Ni	-1.47	-1.14	-1.12	-1.51
	Cu	-0.55	-0.26	-0.27	-0.59
	Zn	-1.7	-1.3	-1.26	-1.75
	Cd	2.74	2.74	2.74	2.74
	Hg	1.74	1.74	1.74	1.74
C_f	Mn	1.4	2.03	2.36	0.87
	Fe	0.76	0.9	0.97	0.72
	Co	0.75	1.45	1.58	0.61
	Ni	0.54	0.68	0.69	0.53
	Cu	1.02	1.25	1.24	1
	Zn	0.46	0.61	0.63	0.45
	Cd	10	10	10	10
	Hg	5	5	5	5
E_r	Cu	5.12	6.24	6.21	4.99
	Zn	0.46	0.61	0.63	0.45
	Pb	2.65	3.45	3.68	2.48
PLI		1.16	1.46	1.53	1.05
PERI		9.88	12.19	12.52	9.41

V. PEARSON COEFFICIENT

From two categories of samples namely agency medicinal plants and mangroves undertaken in the present studies; for one of the specimens i.e. agency medicinal plants are chosen for their results analysis by doing computation of Pearson coefficient values of them. These values are given below in the table 7.

Table 7 Pearson correlation coefficients between soil and plant elements of Paderu Agency

P	S	Cl	K	Ca	I	Zn	Cu	Cr	Mn	Si	Ni	Co	V	Fe	Pb
-0.546	0.203	0.352	0.036	0.252	-0.115	0.086	0.452	0.396	0.395	0.266	-0.245	-0.552	0.007	-0.015	-0.216

Analysis of Pearson's correlation has been carried out for the important elements detected in the soil samples of four different locations belong to Paderu agency area in association with the corresponding same element taking as pair those detected from the plant species collected at those locations. The obtained Pearson coefficient values show positive association for S; Cl; K; Ca; Zn; Cu; Cr; Mn; Si and V while negative association is reflected for the elements P; I; Ni; Co; Fe and Pb as shown in the table 7. These values show linkage between soil elements and elements of plant species collected at corresponding site. As S; Cl; K; Ca; Zn; Cu; Cr; Mn; Si and V elements are showing positive association the variation of these elemental concentration i.e. either increase or decrease in the soil specimens show impact on their concentrations in the plant species by increasing or decreasing concentration value. The highest positive correlation is observed for Cu (0.452) followed by Cr; Mn and Cl having the values 0.396; 0.395 and 0.352 respectively. These values reflect medium level of strength between those elements present in the soil and the respective plant species. For the remaining elements such as S; K; Ca; Zn; Si and V having Pearson's coefficient values less than 0.3 indicate small level of strength for those elements. Similarly, highest negative association is observed for Co (-0.552) while P (-0.546) and Ni (-0.245) show 2nd and 3rd highest values. Thus, Co

and P show large level of negative association between them those present in the soil and plant as they are > 0.50. For the remaining element Ni; I; Fe and Pb show small level of strength as their Pearson's coefficient values less than 0.3. Therefore, if the concentration of these elements increases or decrease in the soil specimen then their concentration in the corresponding plant species decrease or increase takes place. Hence soil – plant association is established only for few elements while for other majority of elements; no proper association established as observed earlier for Sundarban mangroves [8].

The nutritional elements play significant role in the body functions namely metabolic; enzymatic and tissue process. Immunity also depends on the role of these elements showing impact on several diseases [22-23]. These plant species are used to develop and manufacture variety of cosmetics and drugs due to their valuable nutritious elemental contents. The present results show the presence of some important elements namely Fe; Ca; K; P; Cu; Zn and Mn are useful and thus local habitants are using to combat with some pathogenic diseases and thus they are using for manufacturing Ayurvedic medicine or drug preparation; which has long history in India. These can be used particularly for stomach ache; skin irritation; allergy; inflammation; and diarrhea etc.

V. CONCLUSIONS

1. To estimate soil quality of mangroves and tribal medicinal plants; their indices parameters namely enrichment factor (EF); Geo-accumulation Index (I_{geo}); contamination factor and pollution load index along with potential ecological risk index (PERI) are computed.
2. Analysis of Pearson's correlation has been carried out for the important elements detected from soil samples of belong to Paderu agency area in association with the corresponding same element taking as pair those detected from plant species collected at those locations.
3. The obtained Pearson coefficient values show positive association for S; Cl; K; Ca; Zn; Cu; Mn; Si and V while negative association is reflected for the elements P; I; Ni; Co; Fe and Pb. These values show linkage between soil elements and elements of plant species collected at corresponding site.
4. S; Cl; K; Ca; Zn; Cu; Mn; Si and V elements are showing positive association; The highest positive correlation is observed for Cu (0.452) followed by Mn and Cl having the values 0.396; 0.395 and 0.352 respectively.
5. Highest negative association is also observed for Co (-0.552) while P (-0.546) and Ni (-0.245) show 2nd and 3rd highest values. Thus, Co and P show large level of negative association between them those present in the soil and plant as they are > 0.50.
6. Hence soil – plant association is established only for few elements while for other majority of elements; no proper association established as observed earlier for Sundarban mangroves.

REFERENCES

[1] R.N. Desavath; A.R. Nadipena; J.R. Peddada, Egypt. J. Remote sensing space sci., (2017) 1
[2] V. Prakash; Y. Narayana; M.K. Saxena; S.B. Deb; B.K. Nagar; K.L. Ramkumar, J. RadioanalNuc Chem **209** (2011) 103
[3] D. Ch. Rajubabu; Ph.D. Thesis; Trace Elemental Analysis of Seaweeds, Mangroves and Medicinal Plant Species by Nuclear Analytical Techniques (EDXRF); Andhra University, 2019, Visakhapatnam, INDIA.
[4] M.K. Basavaraj; R.R. Chavan; S.R. Kaladagi; M.B. Kalashetti, IOSR J.Envi.sci., Toxicology & Food Tech., **9(2),** (2015) 30
[5] D.Ramprasad Naik; N. Appala Raju; P. Jagadeswara Rao, Egypt J. Remote Sensing Space Sci., xxx (2017) xx
[6] M.S. Mokolobate; R.J. Haynes, Eur.J. soil sci., **53(3)** (2002)481
[7] E. Sabine; K. Gerald, J. Envi.Radioactivity**58** (2002) 97
[8] B. Madhurima; G. Somdeep; S.S. Ram; M. Sudarsan; A. Chakraborty; B. Jayant Kumar; S.M. Shaheen; N. Nabeel Khan; J. Rinklebe; P. Chaudhuri, Environ Geochem Healthhttp://doi.org/10.1007/s10653-018-0145-5 (2018)
[9] G.M.S. Abraham; R.J. Parker, Environ Monit Assess, **136** (2008) 227
[10] M.Ravichandran; M. Baskaran; P.H. Santschi; T. Bianchi, Envi. Sci. & Tech., **29** (1995) 1495.
[11] C.Stewart; Ph.D. thesis, University of Canterbury; Chrischurch; Newzeland
[12] C.Matthai; G. Birch, Marine pollution Bulletin, **42** (2001)1055
[13] J.M. Deely; J.E. Fergusoon, The Sci. of the total Environ., **153** (1994) 97.
[14] L.F. Niencheski; H.L. Windom; R. Smith, Marine pollution Bulletin, **28** (1994) 96
[15] G. Muller, Geojournal, **2** (1969)108
[16] L.Hakanson, Water research, **14** (1980)975
[17] M.S. Islam; M.K. Ahmed; A.M.M. Habibullah; M.F. Hoque, Environ Earth Sci., **73(4)** (2015) 1837
[18] S.M. Shaheen; M.S. Shams; M.R. Khalifa; A. Mohamed; J. Rinklebe, Ecotoxicology & Environmental safety, **142** (2017) 375
[19] V.Antoniadis; S.M. Shaheen; J. Boersch; T. Frohne; G. DuLaing; J. Rinklebe, **186** (2017c) 192
[20] C.Marchand; E. Lallier-Verges; F. Baltzer; P. Alberic; D. Cossa; P. Baillif, Marine Chemistry 98 (2006) 1
[21] N.F.Y. Tam; Y.S. Wong, Hydrobiologia, **352** (1997) 67
[22] R. Gowrishankar; M. Kumar; V. Menon; S.M. Divi; M. Saravanan; P. Magudapathy, Biological Trace elements Research, **133(3)** (2010) 357
[23] J. Emsley, "Nature's building blocks: an AZ guide to the elements; Oxford University press (2011)