Assessment of Physico-Chemical and Heavy Metals in the Soils of Tirupati Urban and Tirumala, A.P, India

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Abstract: ***In the present study, assessment of physico-chemical and heavy metal contaminants in soil samples from various localities of Tirupati and Tirumala was undertaken. Pollutants of heavy metals like Cd, Pb, Zn, Cu, Cr, and Ni have been studied and soil characterization was carried out like pH, electrical conductivity (EC), nitrogen, phosphorous and potassium etc. The studied metal concentration in soil samples ranges from 0.46 to 69.16 µg/g. The results showed that Cd, Pb, Zn and Cr concentrations were relatively higher in tirupati urban soils. The concentrations of Cd, Pb, Zn, Cr and Ni were found to be high at Alipiri forest than the other forest regions, which was contributed mostly by anthropogenic sources whereas, Tirumala forest samples were similar to their acceptable limits. The results indicate that the soil samples were moderately polluted when compared to SEPA and Indian standards and there is a dire need to implement reduction strategies to reduce land pollution for fast industrialization and urbanization.***

Keywords: Heavy metal contaminants, physico-chemical characterization, anthropogenic sources, land pollution

1. Introduction

Tirumala Sri Venkateswara Swamy Temple (also known as Thiruvengadam) is a famous Vedic temple in the hill town of Tirumala, near Tirupati in Chittoor district of Andhra Pradesh, India. It is very important to understand the physico-chemical properties of the soil which provides a basis for careful soil management that limits as far as possible. Heavy metal pollution can be defined as an undesirable change in the physical, chemical or biological characteristics of land, water and air that may harmfully affect animals and plants (Odum, E.P., 1971. Assessing soil fertility is difficult because most soil chemical properties either change very slowly or have large seasonal fluctuations. This decline includes; nutrient depletion, nutrient mining, acidification (decline in pH and or an increase in exchangeable Al), loss of organic matter and increase in toxic elements (e.g., Al, Mn) (Hartemink, 2006).). Heavy metals enter into the environment mainly via three routes; (i) Deposition of atmospheric particulate (ii) Disposal of metal enriched sewage sledges and sewage effluents and (iii) By-products from metal mining process. Traces of heavy metal concentration in the soils are a major concern because of their toxicity and threat to human life and the environment (Bangalore Metropolitan Road Transport, 2006). Heavy metal contents of soil are of major significance because of their non-degradable nature and ability to accumulate for long period of time (Gallego *et al*., 2002; Wu and Zhang, 2010). A few metals, including copper, manganese, cobalt, zinc and chromium are, however, essential to plant metabolism in trace amounts. It is only when metals are present in bio available forms at excessive levels; they have the potential to become toxic to plants (Nagajyoti *et al*., 2010).

Soil serves both as sink and a source for trace metal contaminants in the terrestrial environment. Excessive accumulation of heavy metals in urban soils may result not only in heavy metal contamination in soil but also in increased human exposure to heavy metals due to their close proximity to human activities. In particular, heavy metal pollution of surface soils due to intense industrialization and urbanization has become a serious problem in many developing countries (Mireles *et al*. 2012; Wei and Yang 2010; Yaylal- Abanuz 2011). Moreover, heavy metals can be transferred into the human body as a consequence of dermal contact absorption, inhalation and ingestion. Therefore, they may cause toxic effects on human health, especially children (Ljung *et al*. 2006; Poggio *et al*. 2009). Cheng *et al*. (2006) stated that among heavy metals, cadmium (Cd), arsenic (As), chromium (Cr), nickel (Ni), and lead (Pb) are commonly considered as toxic to both plants and humans. Health risk due to heavy metal contamination of soil has been widely reported (Eriyamremu *et al*. 2005; Muchuweti *et al*. 2006; Satarug *et al*. 2000). In the present study, physico-chemical characterization of soils namely pH, organic carbon (OC), Electrical conductivity(EC), Available nitrogen (N), Available phosphorus(P), Available potassium(K) and heavy metal contents from different sampling sites in and around Tirupati was studied. The specific objectives includes (i) to make a detailed characterization of some selected Industrial and Forest soils of Tirupati and Tirumala (ii) to identify the heavy metal concentrations of the study area.

2. Materials and Methods

2.1 Study area

The present work has been carried out in and around Industrial areas of Tirupati and Forest regions of Tirumala during the summer season. The climate of the study areas is hot and semi-arid. The maximum, minimum and mean temperatures are 44.4. 15.5 and 27.5 °C respectively. The sampling sites were mainly divided into two major groups viz., Industrial areas of Tirupati (Sampling site 1 to 5) and Forest regions of Tirumala (Sampling site 6 to 9). Forest region is located on the longitudes of 79° 07" and 79°'24" E and latitudes 130 38" and 130 55" N covering an area of 2675 hectors.

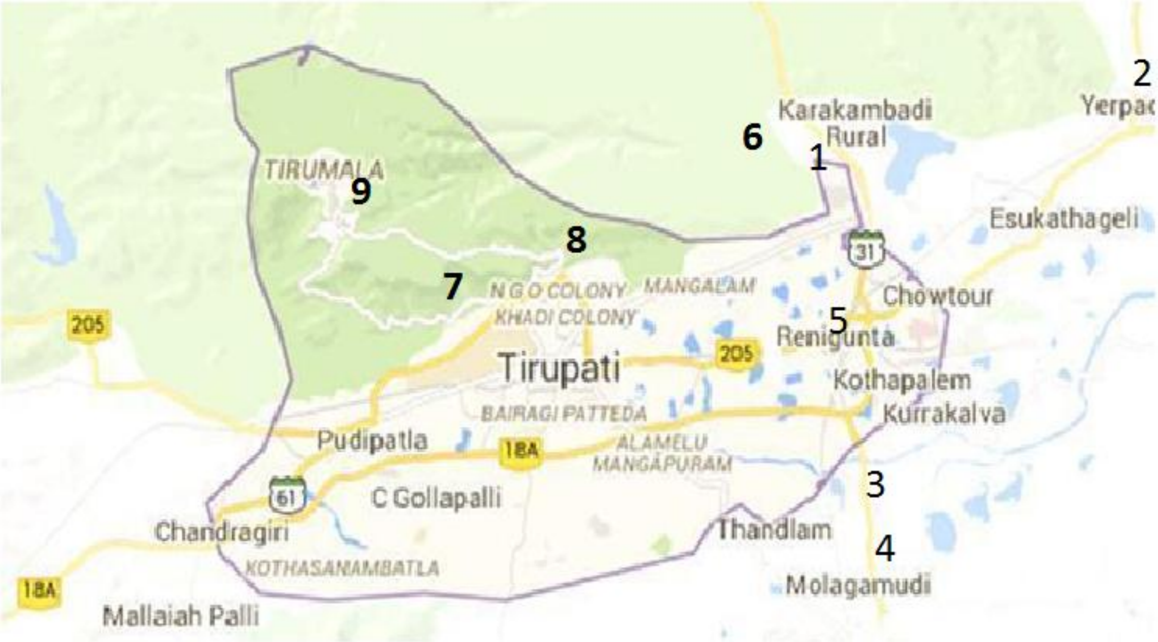

Figure 1: Geographical map of Tirupati

2.2 Collection of soil samples

The soil sample of 500 grams was collected from nine sampling sites from a depth of 0-15 cms with the help of Auger and stored in zip lock covers to prevent the contamination, brought to the laboratory for experimental studies. Physico-chemical parameters were analyzed by standard methods (Chaturvedi and Sankar (2006) and heavy metals were analyzed by using FAAS.

2.3 Analysis of metals

The soil samples were air dried at room temperature and sieved to a particle size of 2 mm, digested with HNO3: HCL: H_2O_2:HF (4:1:3:2) and evaporate to dryness to remove HF. After digestion, all samples were filtered through Whatmann No. 42 filter paper made up to 100 mL. Heavy metals such as cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), chromium (Cr) and nickel (Ni) concentrations were determined by flame atomic absorption spectrometry (FAAS, Perkin Elmer).

2.4 Estimation of Physico - Chemical Characteristics

Soil pH value as a measure of the hydrogen ion activity of the soil water system and expresses the acidity and alkalinity of the soil. It is a very important property of soil as it determines the availability of nutrients, microbial activity and physical condition of soil. The pH of soil water suspension was determined using Equiptronics pH meter as described by Jackson (1967). 20 g soil sample was mixed with 40 ml distilled water in 1: 2 ratio. The suspension was stirred intermittently with glass rod for 30 minutes and left for one hour. The electrode was inserted into supernatant and pH was recorded .The electrode was washed with distilled water every time to record the other new reading of the soil sample.

Electrical conductivity (EC) as the measure of the concentrations of soluble salts in the salts in the soil at any particular temperature. The electrical conductivity of a soil samples were determined on an Equiptronic's digital electrical conductivity bridge. In a 20g soil, 40 ml of distilled water was added. The suspension was stirred intermittently for half an hour and kept it for 30 minutes without any disturbances. Conductivity cell was inserted in solution and EC was recorded.

Organic matter acting an important role in provides nutrients and water and gives good physical conditions to the plants. The quantity of organic carbon of the soil was estimated by the method of Walkey and black (1934) described by Jackson (1967). 1g finely ground soil sample passed through 0.5 mm sieve without loss was taken into 500 ml conical flask, to which 10ml of 1 N potassium dichromate and 20 ml Conc. H_2SO_4 were added with measuring cylinder. The content was shaken for a minute and allowed to set aside for 30 minutes and then 200 ml distilled water 10 ml orthophosphoric acid and 1 ml diphenylamine indicator was added. The solution was titrated against std. ferrous ammonium sulphate (FAS) or ferrous sulphate, till colour flashes from blue- violet to green. Simultaneously, a blank is run without soil.

Available phosphorus was estimated by Olsen's method (Olsen, *et al.*, 1954) modified by Watanbe (1965). The reagent for Olsen's P was 0.5 M $NaHCO_3$ (pH 8.5) prepared by dissolving 42 g NaHCO3 in distilled water and made up to 1 lit. The pH was adjusted at 8.5 with 20 % NaOH solution. 2.5 g of air dried soil was weighed into 150 ml Erlenmeyer flask, 50 ml of Olsen's reagent (0.5 M $NaHCO_3$ Solution, pH 8.5) and little of activate charcoal were added. The flasks were shaken for 30 minutes on the electrical shaker and contents filtered immediately through Whatman filter paper No.41. 5 ml of the filtrate was pipette out into 25 ml of volumetric flask and was neutralized with 1: 4 H_2SO_4 using paranitrophenol as indicator. The volume was made up by adding distilled water. Colour developed when few crystals of stannous oxalate were added. The solution was shaken well and intensity of blue colour was read in photoelectric calorimeter within 10 min. at wavelength of 730 to 840 µm. A blank was run without soil.

The flame photometric method (Jackson, 1958) was employed to estimate available potassium of samples. 5g of air dried sample was taken in 100 ml flask and 25 ml of 1 N ammonium acetate was added to the flask. The contents were shaken for 5 minutes on a mechanical shaker and filtered through a dry filter paper (Whatman No.1). Measure potassium in the extract using flame photometer and note the reading.

Alkaline potassium permanganate method (Subhaiah and Asija, 1956) was followed to estimate available nitrogen of soil samples. In 1000 ml round bottom distillation flask (Kjeldahl flask), 20g soil was taken. To this 20ml distilled water was added. Then 100ml each of 0.32 % potassium permanganate and 100 ml 2.5% NaOH solution were mixed and immediately connected it to kelplus assembly. The froth during boiling was prevented by adding liquid paraffin (1ml) and bumping by adding a few glass beads. The contents were distilled in a kjeldahl at a steady rate and liberated ammonia collected in conical flask (250 ml), containing 20 ml of 2 % boric acid solution with methyl red and bromocresol green indicator. With the absorption of ammonia, the pinkish colour turns to green. After 30 minutes it was titrated with 0.02 N H_2SO_4 till the original shade (pinkish) starts appearing. Blank (without soil) was run simultaneously

3. Results and Discussion

Physicochemical properties of Tirupati urban and Tirumala soils

The experimental results of physico-chemical parameters were presented in Table 1 and graphically represented in the Figures 1-6. The pH of soil samples in industrial areas ranged from 6.7 to 9.0, which shows that the soil of these areas of Tirupati and Tirumala is slightly alkaline due to excessive evaporation of water in dry areas, which bring salts to the surface. High pH can affect the availability of nutrients in the soil and plant growth is limited in alkaline medium and also high soil pH is a stabilizing factor for toxic metals in soil (Kabata-Pendias, 2000) as shown in Figure 1. Electrical conductivity showed maximum (2.17 ds/m) at karakambadi industrial area because of the improper discharge of the effluent. Electrical conductivity signifies the amount of total dissolved salts (Singare P U et al, 2010) as represented in Table 1. The soil organic carbon is recorded for all locations and its value ranges from 0.25 to 1.50 percent. The location Lanco industrial area recorded maximum value 1.50 percent and the location (Tripathi *et al*., 2014). Karakambadi industrial area recorded minimum value 0.25 percent. Among soil fertility indices, the concentrations of macronutrients N, P and K in both industrial and forest soils were low (Fig. 1), as compared to acceptable ranges of 15 000, 2 000 and 10 000 mg kg^{-1} for N, P, and K respectively, as recommended for agricultural soils (HSE-ENV 2004).

Heavy metal analysis

The results of the heavy metal analysis are presented in Table 2.The heavy metals Cr, Cu and Zn, which are required for plants in low quantity for their growth and developmental activities. These are micronutrients for plants (Sinha *et al*, 2006: Jolly *et al*, 2013) ranged from 4.05-59.1 µg/g, 1.53-42.63 µg/g and 7.43-69.1 µg/g respectively. The level of cadmium was below the permissible level in all the samples collected at forest areas and exceeds in all the samples collected at industrial areas except Renigunta industrial area compared to the standards prescribed by Awasthi, 2000. In the present study, highest concentration of cadmium was found in Lanco Industrial area 12.93 µg/g. Cadmium above the acceptable limit can potentially cause liver, bone and blood damage from a lifetime exposure (Budhadev Basumatary *et al.*, 2012). Karakambadi and Lanco industrial area soils contained significantly higher concentrations for all analyzed heavy metals (Cd, Pb, Zn, Cu, Cr, Ni) in comparison to Tirumala forest soils.. The metals Lead, Zinc, Copper, Chromium and Nickel were all below the permissible levels recommended by Awasthi, 2000, Council of European Community (CEC) 1986 and Strategic review of organic waste spread on land, SEPA (1998). Overall results showed that the samples collected at various forest areas showed lesser accumulation of metals than the samples collected at industrial zones. In order to minimize these accumulations, industries should properly treat their effluents within the premises before the disposal into the nearby soil and water bodies.

4. Conclusion

It was concluded that, the soil samples collected from two different sampling areas and nine different sampling sites and analyzed for the physico-chemical properties and heavy metals contents on it. High pH and low concentrations of macronutrients N, P and K in both industrial and forest soils were effect the plant growth. The high concentrations of heavy metals at the present study area elevate serious alarm for environmental quality and human health. There is clearly a high risk of surface and ground water pollution through industrial discharge and atmospheric deposition of pollutants in the contaminated soils. It is concluded that the soil quality of the Tirupati urban areas is not support for the agriculture and other activities. Therefore, suitable protective measures were suggested for soil health and there is need for remediation of this environment.

Table 1: Physicochemical properties of soil samples collected from different locations of Tirupati urban area.

Sampling sites	pH	E.C. ds/m	OC %	P mg/kg	K mg/kg	N mg/kg
Karakambadi Industrial Area	9.0	2.17	0.25	5	43	75
Lanco Industrial Area	6.7	0.10	1.50	25	101	110
Gajula Mandyam Industrial Area Phase-I	7.3	0.28	0.75	154	55	78
Gajula Mandyam Industrial Area Phase-II	7.7	0.48	0.63	134	216	64
Renigunta Industrial Area	8.0	1.23	0.43	15	55	121

Karakambadi Forest	7.78	0.32	0.51	40	58	82
Alipiri Forest	7.32	0.23	0.69	145	65	91
Jeevakona Forest	6.55	0.19	1.29	38	110	95
Tirumala Forest	5.5	0.23	1.05	19	78	125

Table 2: Total heavy metal contents of soil collected from different locations of Tirupati urban (µg/g)

sampling sites	Cd Mean± SD	Pb Mean ± SD	Zn Mean± SD	Cu Mean± SD	Cr Mean± SD	Ni Mean± SD
Karakambadi Industrial Area	8.9±0.16	58.93±0.61	68.43±0.32	31.4±0.37	53.23±0.28	43.9±0.45
Lanco Industrial Area	12.93±0.20	48.7 ± 0.43	69.16±0.36	42.63±0.24	59.1±0.16	44.5±0.21
Gajula Mandyam Industrial Area Phase-I	9.4±0.29	52.33±0.36	50.26±0.28	28.33±0.26	44.26±0.13	30.33±0.36
Gajula Mandyam Industrial Area Phase-II	7.1±0.16	39.46±0.28	48.03±0.16	20.26±0.33	39.33±0.20	24.7±0.16
Renigunta Industrial Area	4.13±0.04	42.63±0.65	42.33±0.26	22.33±0.24	28.6±0.16	26.66±0.20
Karakambadi Forest	2.56±0.33	42.63±0.65	21.85±0.14	12.33±0.41	11.46±0.12	16.9±0.16
Alipiri Forest	2.7±0.16	20.43±0.46	14.13±0.16	15.13±0.28	9.56±0.16	11.16±0.20
Jeevakona Forest	0.46±0.16	8.13±0.20	7.43±0.24	1.53±0.26	7.6±0.29	5.9±0.16
Tirumala Forest	0.8±0.08	4.5±0.28	9.13±0.16	3.93±0.20	4.05±0.18	5.3±0.21
Permissible limit(a)	3-6	250-500	300-600	135-270	-	75-150
Permissible limit(b)	1-3	50-300	150-300	50-140	100	30-75
Max.accptable concentrations(SEPA)*	3	270	630	300	55	30

Data represent mean ± SD of three replicates.
a=Permissible limits of Indian standards (Awashti, 2000.)
b=Permissible limits described by Council of European Community (CEC) 1986.
*Source- SEPA (1998) Strategic review of organic waste spread on land, SEPA

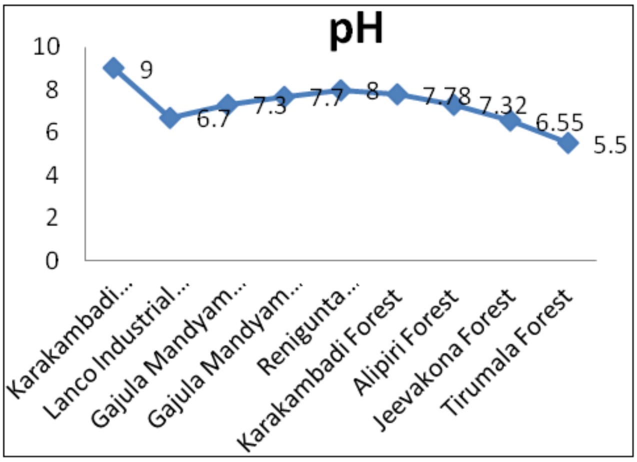

Figure 1: Variation in pH of different soil samples

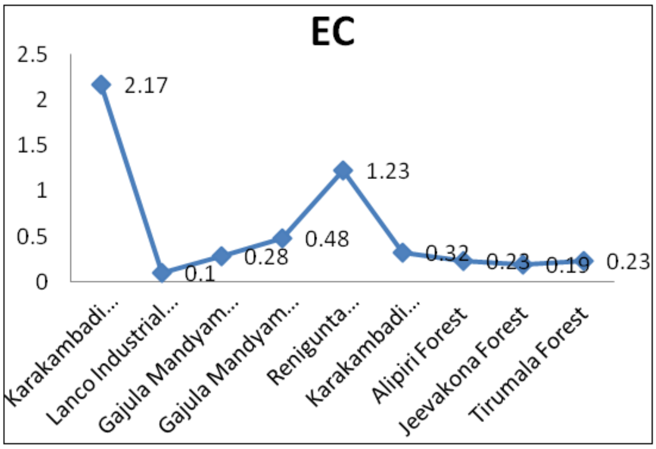

Figure 2: Comparison of electrical conductivity of different soil samples

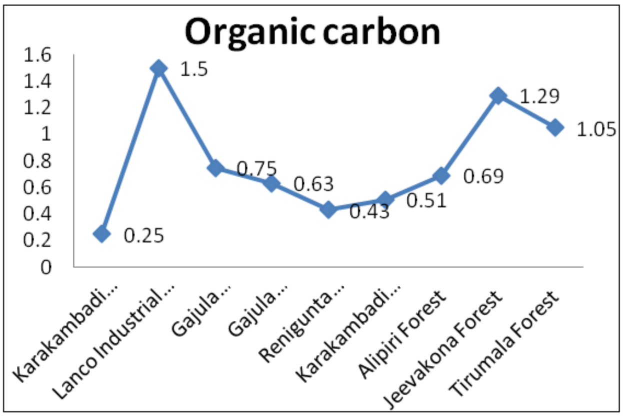

Figure 3: Comparison of soil organic matter.

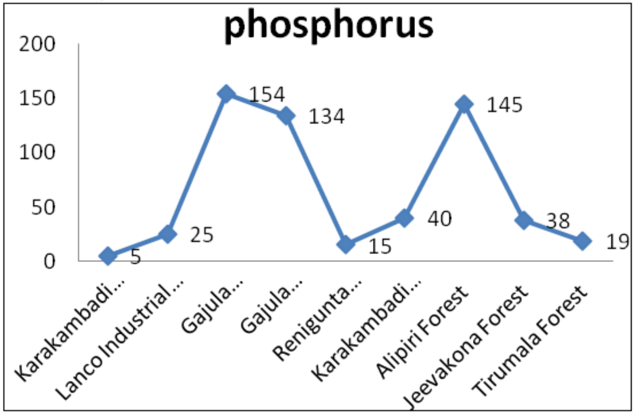

Figure 4: Variation of available phosphorus in different soil samples.

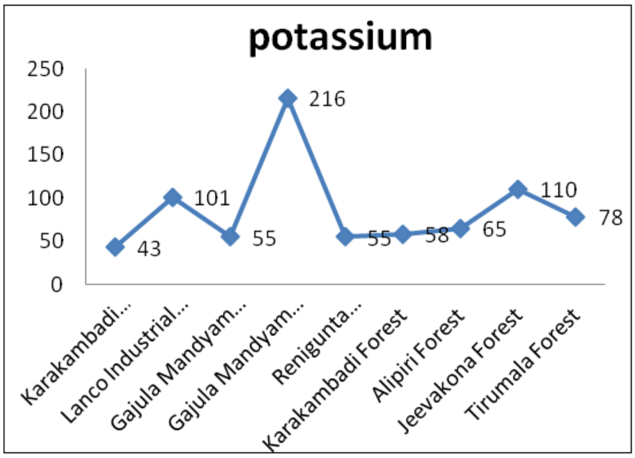

Figure 5: Variation of available potassium in different soil samples.

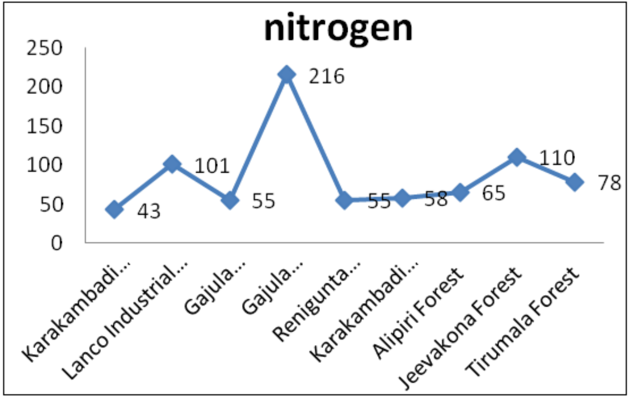

Figure 6: Comparison of available nitrogen in different soil samples.

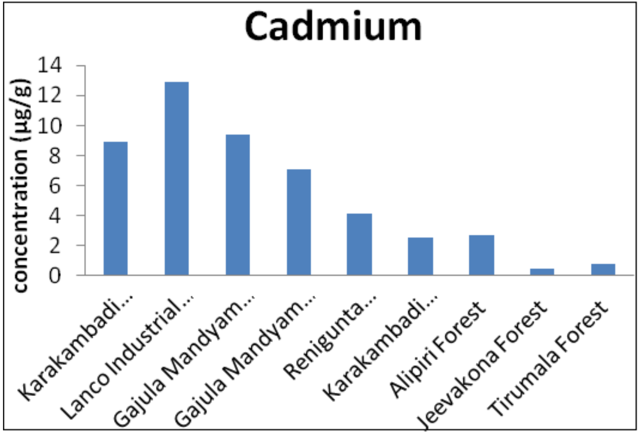

Figure 7: Variation of Cadmium levels in different soil samples

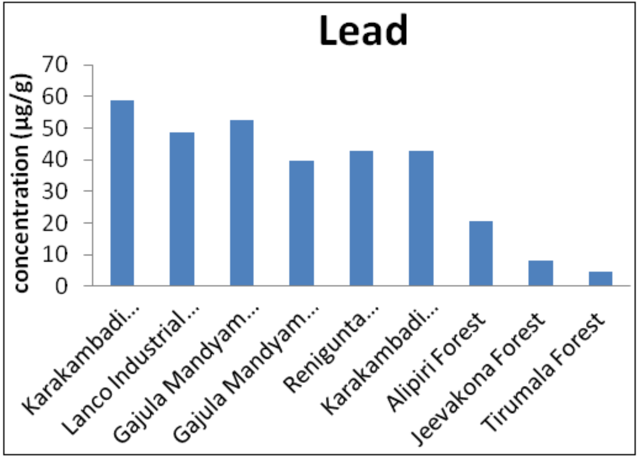

Figure 8: Variation of lead levels in different soil samples

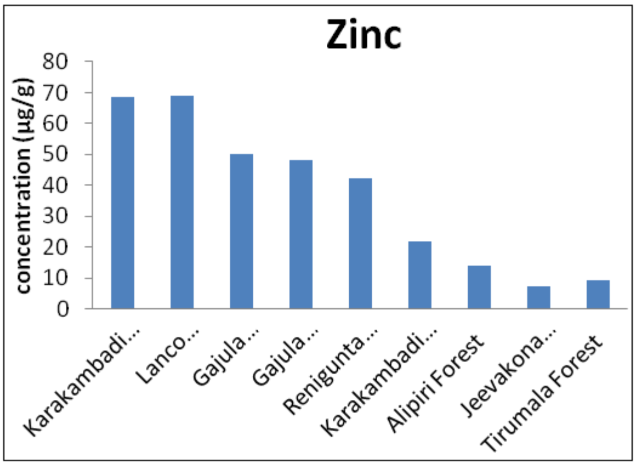

Figure 9: Comparison of zinc levels in different soil samples

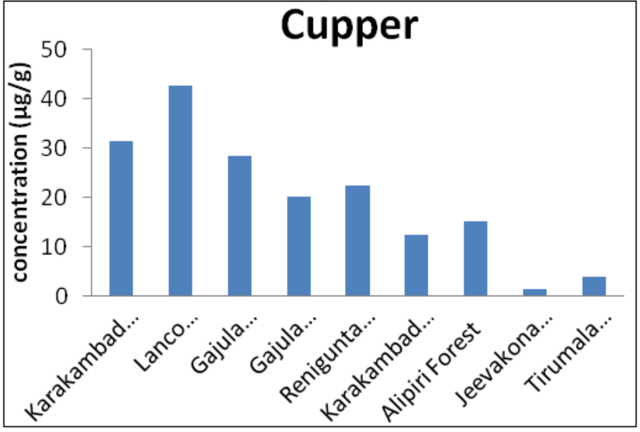

Figure 10: Comparison of cupper levels in different soil samples

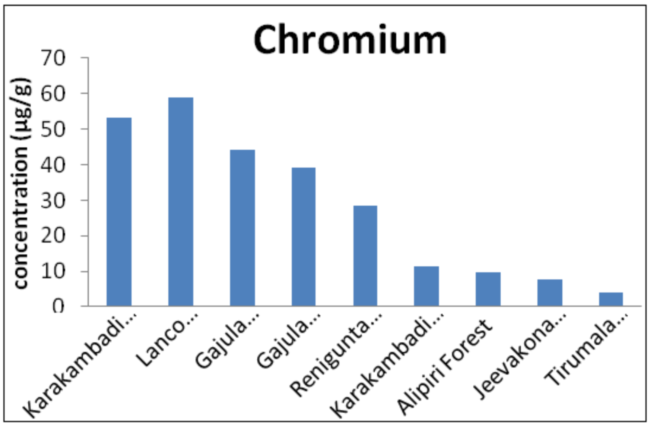

Figure 11: Variation of chromium levels in different soil samples

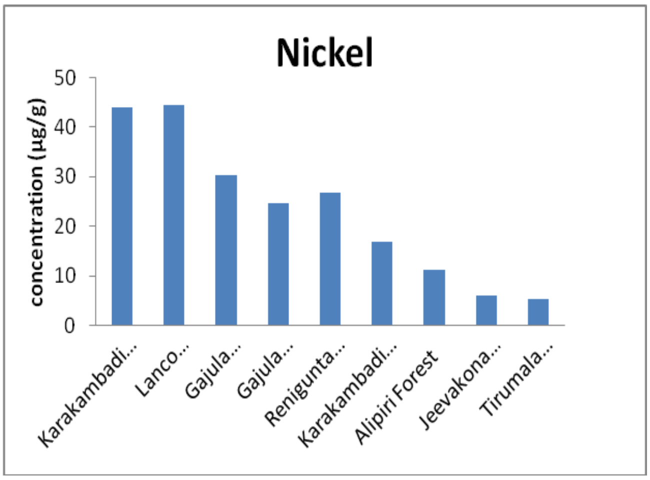

Figure 12: Comparison of nickel levels in different soil samples

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