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## RESEARCH ARTICLE

# PRESENT-DAY POSITION OF HEAVY METAL ADULTERATION IN TOP SOIL AFFECTED BY TANNERY ACTIONS, VANIYAMBADI, VELLORE DISTRICT

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## ABSTRACT

This research was aimed to reveal the Present-day heavy metal pollution in top soil by tannery activities. This research was done at the site of the Tannery, Residential and normal rural zone areas in two layers of the top soil samples at Vaniyambadi, Vellore district. We investigated only four heavy metals (Cr, Pb, Cd, Zn) adulteration in the top soil samples of study area. Flame AAS (Atomic Absorption Spectrometer) technique was used to determine these four heavy metals concentration. This result showed that heavy metals concentration is significantly higher in top soil at the site of the tannery region than in the normal rural zone and residential areas and also these four metals strength was found to be not very much significant changes in top soil at the site of the normal rural zone and residential areas. These metals adulteration in the top soil is answerable for the support of harmfulness in farming crops and underground water.

***Key words:*** Metal adulteration, Tannery region, Rural zone, Housing region, Vaniyambadi.



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## INTRODUCTION

In latest years, environment and health associated problem by heavy metal has turn into a main anxiety. As top soil is a vital constituent of village and urban environments, the function of heavy metals in the top soil structure is more and more becoming an issue of worldwide anxiety. The pollution of heavy metals in top soil undesirably suffers its physicochemical criteria vital to sterility and minimum yield of crops due to their toxicity. Present days, with the growth of the worldwide economy, top soil pollution by trace metal has gradually enlarged, ensuing in the deterioration of the environment. This top soil fertility is contaminated by heavy metals through the modern irrigation system; resulting toxicity is received into tropical food chain which affects the food quality and protection (Del Mar López, 2001; Maria *et al.,* 2017). Adulteration of top soil by heavy metal due tannery wastes and effluents becoming a universal problem.

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Wastewater from tanneries, other industries or additional sources carries a huge amount of toxic metals such as Fe, Ni, Mg, As, Cr, Pb, Zn, Cd etc. which are answerable for the pollution of farming top soil (Rahaman *et al.,* 2016; Bollikolla *et al.,* 2016; Su *et al.,* 2014). In India, Tannery is a very important foreign money sector. There are more than 600 tanneries in Vellore district and among them, 150 are situated in Vaniyambadi, Vellore district close to the Palar River, covering an area of 48haand the rest of them are situated in further Towns of Vellore district. The tanneries in Vellore district are posing a heavy risk to the surroundings. Throughout tanning process, lots of chemicals such as NaCl, $Ca(OH)_2$, $Cr(SO_4)_3$,$H_2SO_4$ and dyes are widely used. During tanning raw skin takes only 50% - 60% of the functional chemical and rest of them discharge as effluents. Most of the tanneries in Vellore district do not have effluent treatment facilities. These tanneries disposed of their untreated wastes and tannery effluent directly to open drain which will be

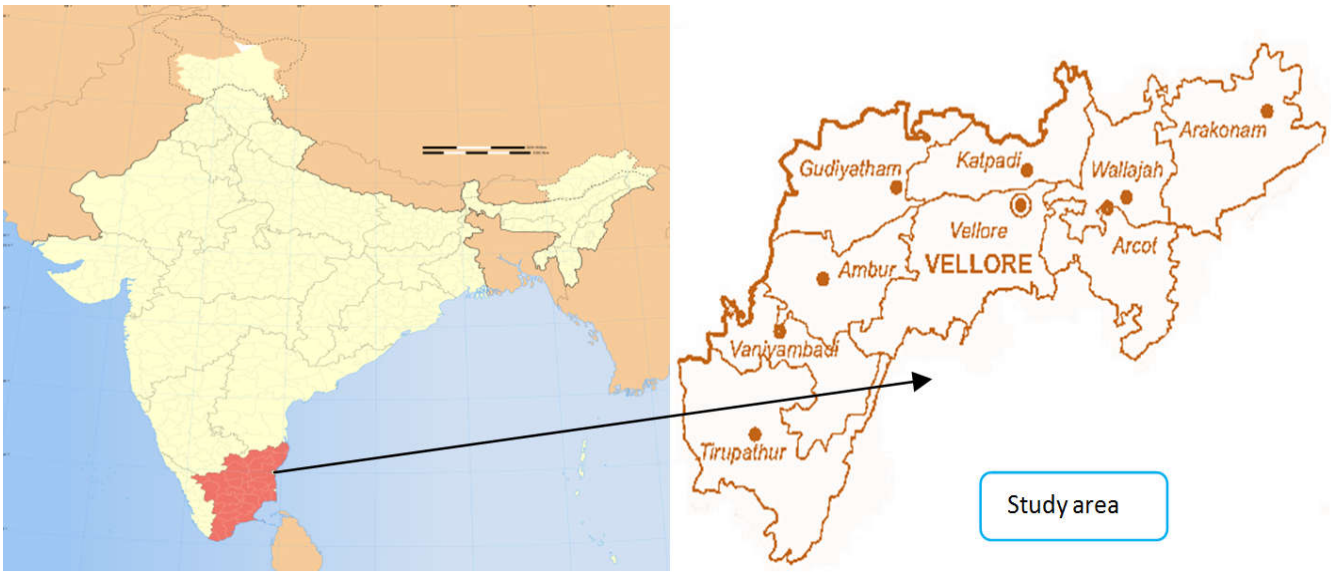


**Fig. 1. Study area Vaniyambadi – Vellore district**

finally connecting to the Palar River and discharged minimum 10,000 $Ld^{-1}$raw effluents (Mohan *et al.,* 2006; Subramanian *et al.,* 2001; Muchuweti *et al.,* 2006; Ong *et al.,* 2013). A few workers confirmed that during peak stage about 14,950 $Ld^{-1}$, off-peak stage about 9300 $Ld^{-1}$ effluent discharged from tanneries (Anda, 2012). Accordingly, distribution of heavy metals has taken from the untreated effluent to rivers, top soil, water and crops (Huq, 1998). Heavy Metals content in top soils may go into the body directly through ingestion, skin contact etc. Heavy Metals in farming top soils are accumulated and absorbed through vegetables and fruits etc. Ingesting heavy metals through top soil-crop structure is a chief way of destructing human physical conditions (Afzal *et al.,* 2014; Metalsgivianrad, 2014). The focus of this research was Present-day status of abundant metals (Cr, Pb, Zn, Cd) in tannery effluent-affected top soil and compared the results with the adulteration of abundant metals in unaffected top soil such as rural zone and residential areas of Vaniyambadi, Vellore district, Tamil Nadu which were not compared in the past studies (Chowdhury *et al.,* 2014; Singh, 2014). This research was carried out using the Flame atomic absorption spectrometer to estimate the concentration of Cr, Pb, Cd and Zn.

The Flame atomic absorption spectrometer (Model Varian Spectra A240) used in this research which was very simple operating spectrometer, less time required to do experiments, can get precision results, easy to handled, and can be used to estimate other heavy metals also. From this research it has been explained that heavy metals contagion in top soil has now a day's become a major concern. In a developing country like India, the situation is not better due to deficient of technological improvement. It is clearly evident that the top soil in the tannery region of Vaniyambadi, Vellore district is moderately to extremely contaminated with Cr, whereas Cd, Pb and Zn are very slightly to uncontaminated. This is due to being exposed to a huge amount of untreated wastes and effluents from the nearby tanneries day by day. This kind of metal adulteration can be suppressed by using some low cost adsorbent which are easily available such as coconut shell, rice husk carbon, fly-ash, charcoal etc. before discharging effluent into surface water body these adsorbent should be used in order to suppress metal adulteration.

## MATERIALS AND METHODS

### Study area

Vaniyambadi is one of the towns in Vellore district as shown in Fig 3.2. Vaniyambadi town is situated along national highway which is connecting to Bangalore. It has longitude between 78o 34'17" and 78o 45'0" East, and latitude between 12° 36'25" and 12° 42'51"north (Figure.1). The town is surrounded by Udayandram on north, Nekkanamalai on East, Ckikkanankuppam on West and Govindapuram on south total area of about is 22.5 Sq. km. It has the length of about 7.35km and a breadth of about 4.75km. Palar river is flowing in the study area. It is coming from Karnataka and enters in to the Vellore district near Vaniyambadi. Basically it is non-perennial and flow in the river depends on precipitation. There are nearly 93 tanneries in the study area in those 85 tanneries in Kachiarpet, 3 tanneries near the trunk road and 5 tanneries in Conamedu area. They produce 3,122 kilo litres of effluent per day. Most of the tanneries discharge their effluent into the Palar River. These tanneries are polluting the Palar River, causing environmental degradation and health problems (Krishna and Govil, 2004; Thangarajan, 1999).

### Geology of study area

Geologically the research region is enclosed by crystalline rocks of Achaean age consisting of Granites and a few essential intrusive bodies. The alluvium consisting of small to coarse sand and clay occurring in the region is of a fluviatile origin and controlled to the course of Palar River and most important streams (Arora *et al.,* 2008). Examination of the sample was completed by Atomic Absorption Spectroscopy. In this method, the photo energy due to exact wavelength gets absorbed while the electrons of the constituent metals of the sample gains energy from a lower to a higher energy level. The intensity of light passing through the sample is compared with that of the standard solutions of the element to be estimated. Their corresponding absorbance is measured and their concentration is calculated through calibration curves plotted with concentration against absorbance values (Beer-Lambert's law).The top soil samples (Figure 1) were collected from seven different points of different sites in the locality of tannery on

the rural zone area and housing region is a densely populated area of Vaniyambadi, Vellore district where about many registered tanneries discharge their vast amount of unprocessed solid and liquid waste straightly into the Palar River and other water bodies. So this area was chosen as a study area to compare the level of heavy metals with other non-tannery area. Four different points in the tannery vicinity were marked as TA-1 which is the discarding point itself, and TL-2, TL-3, TL-4, TL-5, TL-6, TL-7which are located at 0 -50 m, 75 - 150m, 250 - 300m, 400 – 500m, 550 – 600m, 750 – 850m and 1000-1200m distance respectively from the discarding point. Vaniyambadirural zone area was marked as AA and Residential areas marked as RA.

**Sampling**

In the month of May 2017, the top soil samples were collected from the sampling sites with the help of a Steel Trenching hoe and transferred to pre cleaned plastic bottles. The samples were collected from two different layers of different depth at al sample points. The first layer is the shallow layer (0 - 15 cm) and the other is 25 - 35cm below from the surface level by measuring with 100 cm wood scale. After collecting the top soil samples were washed, weighed and dried in an electric hot oven at 110˚C until become constant weight then cooled in desiccators with fused Calcium chloride. Then all the top soil samples were grinded by stone top soil grinder (figure. 2) and thoroughly homogenized. The crushed top soil samples were lastly stored in cleaned dry closed glass bottles and well-maintained in desiccators for further Examination.

**Fig.2& 3: Top soilsamples preparation**

**Ingestion of Top soil Samples**

For the quantitative Examination of Cr, Pb, Cd and Zn top soil samples were digested following ISO 11466 thermal heating methods. According to this method, first 5 g of each crushed top soil samples were weighed and taken into pre cleaned 100ml glass beakers. Then the weighed samples were humidified with 2 ml of deionized water. After that 24 ml, of HCl and 8 ml of HNO3 were poured drop by drop and then 18 ml of dilute HNO3 (0.5 M) was poured to every beakers and the samples were permitted to position at lab temperature (27-$30^0$C). Every mixture was then refluxed on a heating not plate for 2hrs and was filtered through filter paper (Whitman no 42) after cooling and kept at room temperature for further Examination.

**Heavy Metals Absorption Measurement**

After top soil samples digestion, Cr, Pb, Cd and Zn metals were analyzed by using Flame atomic absorption spectrometer ( FAAS - Model Varian Spectra A240), (Sample volume – 10 mL/min. Burner – Air/Acetylene, $N_2O$/Acetylene burner/ Gases hallow cathode – Acetylene and nitrous oxide) at Technology Business incubator Lab, Department of Science and Technology, VIT-university, Vellore, Tamil Nadu. Cd (Wavelength 228.8 nm), Cr (Wavelength 357.9 nm), Pb (Wavelength 283.3 nm), and Zn (Wavelength 213.9 nm) specific hollow cathode lamp was used to analyze the samples. The instrument having a minimum detection limit of 0.01 mg/L for Cd, 0.10 mg/L for Cr, 0.20 mg/L for Pb and 0.01 mg/L for Zn in the flame method. Samples were aspirated through Nebulizer and absorbance was measured with a blank solution (Deionized water) as reference. Calibration curve was obtained using standard samples (containing 0.1, 0.2, 0.3, 0.4, 0.5,.0.6mmg/L for Cd; 0.4, 0.8, 1.2, 1.6 and 2.0 mg/L for Cr; 0.2, 0.4, 0.6, 0.8 and 1.0 mg/L for Pb and 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 mg/L for Zn).

## RESULTS AND DISCUSSION

After this survey, it was cleared that Cr adulteration of top soils in the locality of tannery is honestly high in all seven tannery location samples and observed that Cr was exceeded the permissible limits (Table. 1). The outcome recorded maximum values of heavy metal concentration at the tannery effluent discharging point and lowest values in the top soil of Agriculture area and housing region. These heavy metals concentration was found highest abundantly in the shallow layers of the top soil and the concentration of heavy metals reduced with the increase of depth and distance (Table. 1, 2 & 3 and Figure 4 & 5). It is accepted that in the case of Tannery region top soil samples, Cr content was found more abundant (1524.28 mg/kg) in 0 – 10 cm depth (surface layer) of TA-1 (effluent discharging point) and least abundant (59.45 mg/kg) in 25 - 35cm depth of TA-7. In the shallow layer of top soil samples, the values for Cr concentration ranged from 1408.66 to 104.22 mg/kg, in 0 - 15 cm depth, it ranged from 470.02 to 34.12 mg/kg in25 - 35 cm depth ( Table.1). The case of Rural zone and residential areas top soil, Cr content in surface layer, 0 - 15 cm and 25 - 35 cm depth is found 79.71 - 51.09 (Table.2) and 41.71, - 30.10 mg/kg (Table.3) Correspondingly. From the end result, it is obvious that Cr content in the Tannery surrounding area of same layers reduced with increase of distance from the tannery effluent discharging point and also with the increase of depth at each point (fig. 4&5).

**Table 1. Heavy metal Examination of tannery regiontop soil samples**

| Sampling points | Distance from dumping of tannery wastes(m) | Depth of layers from surface level (cm) | Cr (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Zn (mg/kg) |
|---|---|---|---|---|---|---|
| TR-1 | 0 – 50 | 0 - 15 | 1408.66 | 90.55 | 6.80 | 252.32 |
| | | 25 - 35 | 470.02 | 78.61 | 2.18 | 122.24 |
| TR-2 | 100 – 150 | 0 - 15 | 1112.29 | 66.26 | 3.26 | 197.31 |
| | | 25 - 35 | 238.29 | 58.42 | 1.90 | 99.40 |
| TR-3 | 200 – 300 | 0 - 15 | 674.70 | 42.29 | 2.82 | 183.5 |
| | | 25 - 35 | 206.70 | 29.50 | 1.61 | 67.39 |
| TR-4 | 350 – 400 | 0 - 15 | 444.00 | 38.73 | 2.02 | 117.23 |
| | | 25 - 35 | 130.33 | 17.37 | 1.14 | 61.05 |
| TR-5 | 500 – 600 | 0 - 15 | 270.84 | 28.45 | 1.85 | 120.52 |
| | | 25 - 35 | 114.33 | 16.06 | 1.08 | 81.69 |
| TR-6 | 700 – 800 | 0 - 15 | 256.61 | 16.76 | 1.87 | 73.36 |
| | | 25 - 35 | 88.36 | 9.68 | 1.04 | 57.57 |
| TR-7 | 900 - 1000 | 0 - 15 | 104.22 | 14.00 | 1.82 | 54.59 |
| | | 25 - 35 | 34.12 | 5.28 | 0.62 | 40.37 |
| | Maximum | | 1408.66 | 92.58 | 5.86 | 282.32 |
| | Minimum | | 34.12 | 5.28 | 0.66 | 46.48 |
| | Mean | | 404.84 | 36.64 | 2.04 | 109.18 |
| | Standard deviation (SD) | | 410.59 | 26.19 | 1.025 | 63.96 |
| | Maximum permissible level recommended by EC (1986) [13] | | 50 | 300 | 3 | - |

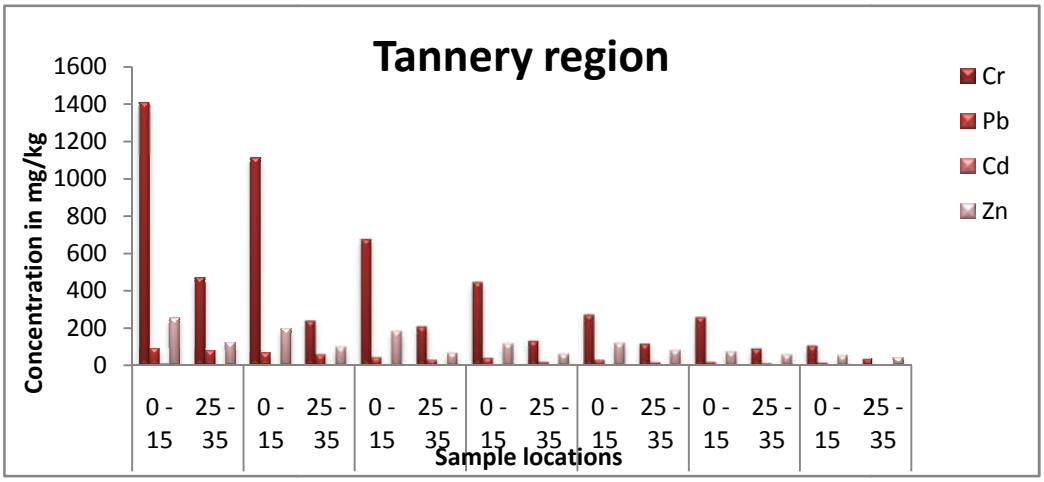


**Fig. 4. Heavy metal examination in tannery region soil samples**

**Table 2. Heavy metal Examination of rural zonetop soil samples**

| Sampling points | Depth of layers from surface level (cm) | Cr (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Zn (mg/kg) |
|---|---|---|---|---|---|
| AA | 0 - 15 | 80.54 | 29.28 | 1.84 | 52.02 |
| | 25 - 35 | 50.28 | 28.47 | 3.04 | 36.94 |
| | Mean | 65.41 | 28.88 | 2.44 | 44.48 |
| | Standard deviation (SD) | 10.80 | 2.26 | 0.09 | 3.82 |
| | Maximum permissible level recommended by EC (1986) | 50 | 300 | 3 | - |

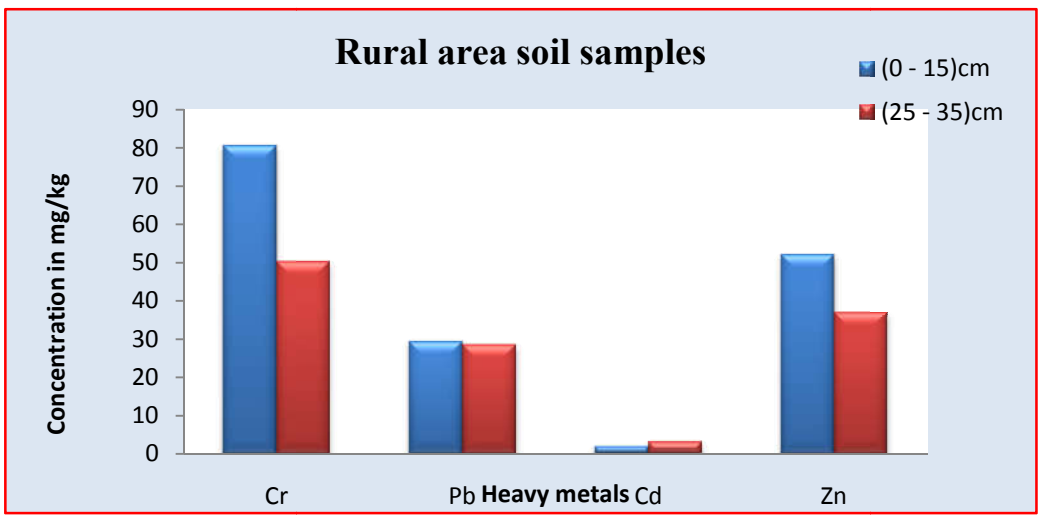


**Fig. 5. Heavy metals concentration in rural area soil samples**

**Table 3. Heavy metal Examination of housing region top soil samples**

| Sampling points | Depth of layers from surface level (cm) | Cr (mg/kg) | Pb (mg/kg) | Cd (mg/kg) | Zn (mg/kg) |
|---|---|---|---|---|---|
| HR | 0 - 15 | 46.10 | 48.54 | 1.07 | 17.17 |
| | 25 - 35 | 25.72 | 26.60 | 2.06 | 16.72 |
| Mean | | 35.65 | 38.29 | 0.48 | 16.94 |
| Standard deviation (SD) | | 9.80 | 11.98 | 1.56 | 1.38 |
| Maximum permissible level recommended by EC (1986) | | 50 | 300 | 3 | - |

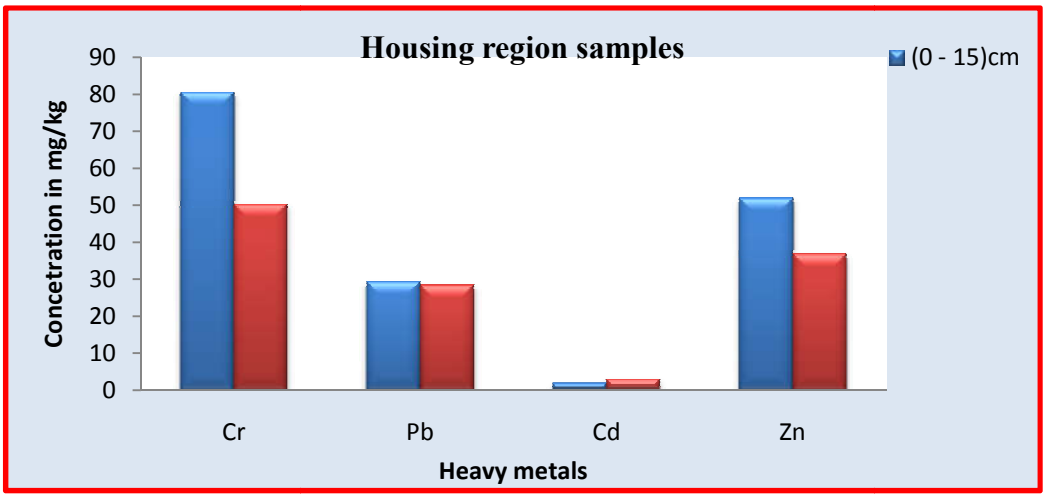


**Fig. 6. Heavy metals in housing regiontop soil samples**

In the shallow top soil layer (0 -15cm), the rate of decreasing Cr concentration with distance was higher than other depth layers (25 - 35cm) (Fig.4, 5& 6). In all cases Cr concentration in the tannery location top soil samples were found higher than that of the rural zone and residential areas (Fig.4, 5& 6). In Tannery surrounding area, in the shallow layer of each point, the value of Cr content exceeded the permissible limit that is 50 mg/kg (Table. 1) (Aelion *et al.,* 2008). But rural zone Area top soil slightly exceeded and Residential top soil samples did not exceed that limit (Table. 2&3). The high concentration of Cr in the shallow layer of tannery surrounding area top soil samples might be due to pollution from different industrial wastes such as Cr pigment and raw tannery wastes, leather industrialized wastes, and municipal sewage mud etc (Alshammary *et al.,* 2014). Cr pollution in the top soil might be due to waste consisting of Lead-Chromium batteries, colored plastic bags, surplus plastic materials and unfilled paint containers (Council Directive, 1986). Cr is toxic and carcinogenic and long-term contact to Cr can cause liver and kidney impairment (Jung *et al.,* 2006). Chromium could also modify genetic materials and cause for cancer. Additional health troubles are Skin diseases, Stomachs upset, Respiratory problems, ulcers problems ,damaged immune systems, change of Hereditary material, Lung disease and Death that area used by Chromium (Mondol *et al.,* 2011). Lead is the next common metal in this study. In the case of Tannery surrounding area, Lead content was found more abundant (90.55 mg/kg) in the shallow layer of point TA-1 (waste discharging point) and minimum quantity abundant (5.28 mg/kg) in the depth layer(30 -40 cm) of point TA-7. In the shallow layers (0-15cm), the concentration of Pb ranged from 90.55 to 14.00 mg/kg, whereas in the depth layer (25 - 35 cm) of top soil, Pb concentration varied from 78.61 to 5.28 mg/kg (Table.1& Fig. 4, 5)). While in the case of Rural zone and Residential area top soil, Pb content in the shallow layer (0 - 15cm) and depth layer (25 - 35cm) was found 29.28–28.47 mg/kg and 48.54 – 26.60 mg/kg respectively (Table.2&3).

Also Pb content in the Tannery surrounding area top soil of similar layers, the values decreased with the increase of distance from the putting spot and also with the increase of depth at each point. In the shallow layer (0 – 15cm), the rate of Pb adulteration decreased with distance but higher than other layers of 25 – 35 cm depth (Fig. 4&5). Neither Tannery surrounding area top soil nor Rural zone Area top soil at any layer in this study exceeded the allowable limit for Pb that is 300 mg/kg (Korotkova *et al.,* 2017). The high content of Pb content near the discarding point may be due to the discharge of Pb-containing untreated tannery effluent. The presence of Pb in top soil can happen due to the release of Pb by automobiles using leaded petrol and other industries in this study area. This Pb content may be deposited on top soil and water, thus reaching humans by way of the food chain. Pb in the top soils might also be from vehicle exhaust smoke as well as dry cell batteries, sewage effluents, runoff of wastes and atmospheric depositions (Järup, 2003). Pb exposure has effects like disruption of the biosynthesis of red blood cell in blood and anemia, Miscarriages, Kidney damage, and subtle abortions, Disruption of nervous methods, enhance in blood pressure (BP), Brain grievance, Declined fertility of men through sperm impairment, decreased schooling abilities of children, Behavioral disruptions of kids, such as aggression, hyperactivity and imprudent behavior (Adaikpoh, 2013).Also Cd was taken into consideration for this study; the Cd content was found more abundant (6.80 mg/kg) in the top layer of TA-1 (dumping point) and smallest amount abundant (0.62 mg/kg) in 25 - 35 cm depth of TA-7 in case of Tannery region. In top layer, values for Cd content varied from 6.80 to 1.82 mg/kg, in the depth of 25 - 35cm the Cd concentration range was from 2.18 to 0.62 mg/kg (Table. 1). Whereas in the case of Rural zone and residential area stop soil, Cd concentration in shallow layer (0 - 15 cm) and depth layer (25 - 35 cm)was found 1.84 – 3.04 mg/kg and 1.07 – 2.06 mg/kg respectively (Table 3 & 4). At the sample TA-4, TA-5, TA-6 and TA-7 the concentration of Cd was more or less similar (Table. 1). In the shallow layer

(0 -15 cm) of tannery area top soil adulteration of Cd decreased with the increases of distance from the discarding point (Fig.4&5). The result was not same when 25 - 35 cm depth layer was considered as such regularity in the values was not found there. Like Cr and Pb, the concentration of Cd also decreased with the increase of depth at all points in the tannery region (Fig 4&5). Other than this was not the case for agriculture and residential areas top soil samples as the result was reverses there. For shallow layers, Cd content in each point of the Tannery surrounding area was found slightly higher than that of rural zone and residential areas (Table. 1, 2&3). But unlike Cr and Pb, Cd content in depth layers (25 - 35 cm) of Rural zone and residential areas top soil was found slightly lower than that of each point in the Tannery vicinity top soil (Fig.4, 5 &6).At any layer of any point in all Tannery region, Rural zone and residential areastop soil samples, Cd content did not exceed the maximum acceptable limit (3.0 mg/kg) (Table 1,2&3).The Cd was brought to top soil with the application of phosphoric fertilizers. Application of a lot of phosphate and compound fertilizers increases Cd in top soils continuously. Additional sources of Cd might be ceramics plastics, paint and glass production industry. The Cd is extremely toxic and even at very small amount; chronic contact to this metal can major to insomnia, anemia, cardiovascular diseases as well as hyper-tension (Rahaman *et al.,* 2016; Sharma *et al.,* 2006; Rao *et al.,* 2001).

Similarly for Zn, In the case of Tannery region, the Zn concentration was found more abundant (252.32 mg/kg) in the shallow layer (0–15 cm) of sample point TA-1 (waste discharging point) and minimum abundant (54.59 mg/kg) in the depth layer(25-35cm) of at the sample point of TA-7(Table.1). In shallow layer (0-10cm), values of Zn concentration varied from 122.24 to 40.37 mg/kg, in the depth layer (25 - 35cm), the Zn concentration varied from 124.24 to 46.48 mg/kg (Table. 1 & Fig. 4,5). While in the case of Rural zoneand residential area stop soil, Zn content in the surface layer, 0 - 15 cm and 25 - 35 cm depth was found 52.02 – 36.94 mg/kg and 17.17 – 16.72 mg/kg correspondingly (Table.2,3& Fig. 6). It is also noticed that in the case of the shallow layers (0-15cm) and depth layers (25 - 35 cm) of Rural zone Area and residential area stop soil possess lower Zn concentration than Tannery region top soil samples at each point (Table. 1, 2&3). The major sources of Zn pollution is industries as well as the use of liquid fertilizer, composted materials and agrochemicals like fertilizers as well as pesticides in agriculture's is an necessary trace metal for the growth plants, animals and human being other than is potentially hazardous for the earth planet when it is abundant in more concentrations. Heavy doses of Zn show toxic, carcinogenic effects and effect in neurologic as well as hematological complications, hypertension, liver and kidney function disorders (Rahaman *et al.,* 2016; Aelion *et al.,* 2008).

**Conclusion**

Weighty Metal adulteration in top soil has now become a most important concern. In growing countries like India, the condition is worst due to lacking of technological improvement. From this revise, it is obviously the evident that the top soil in the tannery region of Vaniyambadi, Vellore district is exceedingly contaminated with Cr not with other Pb, Cd and Zinc. This is due to being exposed to an enormous amount of raw tannery wastes from the nearby Tanneries day after day. A considerable quantity of Cadmium (Cd), Zinc (Zn) and Lead (Pb) has also been found in the top soil of this area which were not exceedingly contaminated but very slightly contaminated in only few sample points of this study area. These metals might store and placed in top soil and uptake by vegetables and fruits through route of plants and other crop grown in this area which eventually gets into animal and human body through the tropical food chain. This results in different unpleasant effects on animal and human health as Cr, Pb and Cd are extremely toxic and carcinogenic in environment. So authority concerned need to take direct measures for these problems to prevent such infectivity by these heavy metals.

**Remedy**

In order to avoid the above complications, heavy metal can be suppressed from effluents and waste of tanneries and other industries, some low cost adsorbent can be recommended such as coconut shell carbon, rice husk carbon, fly-ash, charcoal etc. before discharging effluent into surface water body these adsorbent should be used which will be very useful to destroy metal adulteration.

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