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Study of changes in properties of calcareous soil at industrial disposal site of tannery industry in Bela, Muzaffarpur

Sonal Rani and Ashok Kumar Singh

Abstract
The present paper put forwards to see the potential change in soil characteristics due to disposal of industrial effluents emerging from tannery industry in surrounding areas of Bela at Muzaffarpur district of Bihar. Altogether, 15 soil samples from various sources were collected from different locations from the vicinity of the discharge point of the tannery effluents at every 100 m interval. The data obtained from the investigation revealed very interesting facts related to soil characteristics that there was 230% increase in organic carbon, 183% increase in Nitrogen content, 121% increase in Phosphorus, 72% increase in Iron and 318% increase in Chromium in surface soils at discharge point of the effluent water as compared to the farthest point (1400m) from the disposal site. Along with these, acidic soil pH was observed in close vicinity of disposal site and free $CaCO_3$ was lowest in soil where effluents were disposed.

Keywords: industrial effluents, tannery industry, chrome-based tanning, spatial variation, hazards, potential changes

Introduction
In present scenario the application of industrial effluents and town wastes disposed in agricultural land and has become common practices for better production of the crop during the past decades. These organic wastes, when added to soils, also impart influences in modifying the activity of most of the trace metal cations in soil solution. A long-term disposal these substances in agricultural land may cause the accumulation of non- essential and potential toxic heavy metals in soils and ultimately also degrade the quality of soil.

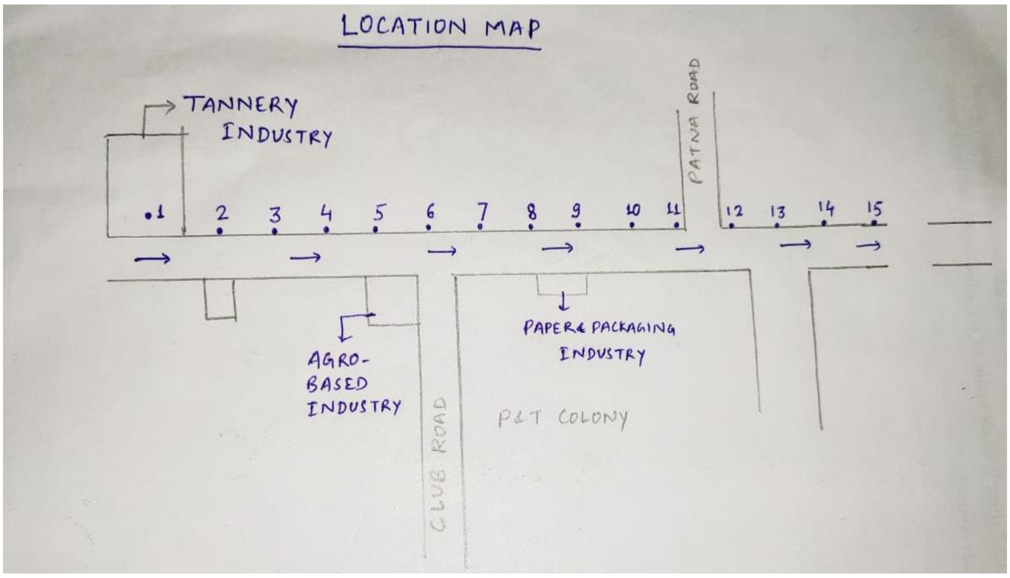
We know that water is the most valuable natural resource on the planet; however, global fresh water reserves are just around 3%. In the case of India, it has 2.45% of the world's land area and 4% of the world's water supply, but it has 16% of the world's population. The growing world population and decreasing supply of clean water are causing serious concern these days. Rapid industrialization and population development are resulting in massive amounts of wastewater production, which seems to be an ideal solution for today's agricultural needs. The use of drainage has both positive and negative effects on soil, impacting the ecosystem and human health in the end. The use of sewage water for irrigation increased the soil's chemical properties and fertility. The increased pressure on water resources can be attributed to climate change, population growth, and the rising demand for water in industrial sectors. The exploitation of water for irrigation in the agricultural sector accounts to 80% of the global water consumption and is the limiting factor in food production in many countries (Hanjra and Qureshi 2010) [12]. Innovative approaches are therefore, needed to attain both water and food security, particularly in developing countries (Finley *et al.*, 2009; Hanjra and Qureshi, 2010; Rodda *et al.*, 2011) [11, 12]. The increasing population, industries and agricultural activities required a greater attention towards continuous research.

While irrigation of treated waste water can help to save natural water supplies, it can also cause environmental issues. A number of disadvantages are associated with the reuse of wastewater for irrigation of developing crops. Wastewater irrigation possess both positive and negative impacts on soil characteristics. Positive side includes it has considerably high amount of primary nutrients viz., available Nitrogen, Phosphorus and Potassium, along with high organic carbon which is beneficial for plant growth and development. It also cuts the cost of cultivation thus increasing profit to farmers. Negative side includes high level of organic and inorganic chemicals and heavy amount of heavy metals accumulation in soil which hampers the plant and ultimately leads to human health hazards because heavy metals undergo biomagnification and thus increasing accumulation is we go up in food chains creating a number of abnormalities.

Tannery industry is one of the most polluting industries of India. In the process of turning animal hides into leather, almost every tannery sector utilises a substantial quantity of chemicals (Dargo and Ayalew 2014) [9]. The chrome tanning method is used by roughly 90% of tannery companies because it is simple to use and gives the leather of great qualities. The tanning process is nearly entirely a wet process that uses a lot of water and produces around 90% of it as effluent (Chowdhury *et al*. 2013) [7]. Tannery effluents contain high levels of pollutants due to the presence of highly colored compounds, sodium chloride and sulphate, various inorganic and organic substances, biologically oxidizable tanning materials, toxic metallic compounds, and large amounts of putrefying suspended matter (Akan *et al*. 2007; Khan *et al*. 1999) [1, 14]. The tannery effluent has a negative impact on the health of receiving water bodies and soil surfaces (Cooman *et al*., 2003) [8].

Materials and Methods

These research activities were carried out for assessment of the impact of tannery industry on the soil characteristics of the study area situated at Bela, Muzaffarpur. Surface soil (0-15 cm) were collected and kept for detailed study. Location of Muzaffarpur district is in northern Bihar, which has a geographical area of about 3132 sq. Km. Muzaffarpur lies on the co-ordinates of North latitude between $25^0$54’00” to $26^0$23’00” and East longitude between $84^0$53’00” to $85^0$23’00”. This area receives an average precipitation of 1280 mm in a year. Almost 85% rainfall occurs in monsoon period. Climatic condition of this area severe winter which is followed by a very hot summer and heavy rainfall during the monsoon season. The soil type is alluvium and kankar nodules are found in this region, in general type of soil is calcareous. Fifteen soil samples up to 15cm depth has been collected from different location with a definite interval of 100m which is up to the distance of 1.5 Km and it was started from the point of disposal of Industrial effluent. After removing the surface plants using a spade, soil samples were taken from the location. At first, 1” of surface soil was removed. Then khurpi was used to make a V-shaped furrow. The samples were collected in plastic bags and marked as S1, S2, S3, and so on. After that it was air dried for 10-15 days and the all samples were grinded by wooden mortar and pestle so that it can pass through 2mm sieve. For estimation of organic carbon and free calcium carbonate, grind samples were passed through 0.5 mm sieve and then stored in polythene bags for further laboratory estimation.



Showing pattern of sampling having Tannery industry as reference point.

Results and Discussion

Result and Discussion chapter deals with all the observations, analysis of data, results obtained and its interpretation to achieve the objectives of investigations. Due to rapid urbanisation and industrialisation now a days causing various changes in soil characteristics. This research was done with an aim to study the changes in characteristics of soil of industrial vicinity area of tannery industry of Muzaffarpur district of Bihar. All the results have been discussed in light of the experimental data and its statistical analysis

pH

The data illustrated in Table 3 showed that the pH of soil varied from 6.70 to 8.30 with the mean value of 7.9 (table 4) indicated that soils fall under slightly acidic to alkaline category which increases as going away from the point of disposal as represented in Figure 3. The slightly acidic pH was observed in the soil collected from disposal point and the sample which is in closest vicinity of it. It might be due of the presence of acids which are used in the tannery industry while treating the raw skin of animals (Chowdhary *et al,* 2015) [6]. Similar values of pH ranging from 7.4 to 8.6 was found when worked on sewage water in Ahmadnagar of Maharastra which was safe (Kharche *et al,* 2011*)* [13]. Mohan and Jaya (2015) [16] also studied the impact of effluent on soil chemical characteristics in Tiruvananthpuram, Kerala and found that the pH of soil increases as increasing distance from disposal site. Awomeso (2009) [2] conducted experiment on Impact of Industrial Effluent on soil in Alakia industrial area of Ibadan, South west Nigeria and reported that the average pH of soil sample was 5.0.

Table 3: Different chemical parameters of soil samples

Soil samples	pH	EC (dS/m)	N(Kg/ha)	P(Kg/ha)	K(Kg/ha)	O.C (%)	Free CaCO3 (%)
S1	6.70	1.60	339	100	248	1.32	19.3
S2	6.95	1.59	300	105	244	1.11	19.1
S3	7.20	1.52	304	105	206	1.05	22.0
S4	7.60	1.50	290	86	182	1.05	23.6
S5	8.00	1.49	276	86	176	0.96	24.1
S6	8.10	1.48	256	78	162	0.93	24.5
S7	8.20	1.42	190	73	161	0.70	24.8
S8	8.00	1.15	186	66	148	0.59	25.0

S9	8.20	1.05	150	61	135	0.52	24.9
S10	8.25	1.02	289	60	132	0.82	20.1
S11	8.30	0.98	148	56	131	0.47	25.3
S12	8.20	0.84	144	55	129	0.45	25.9
S13	8.15	0.74	144	50	132	0.45	26.4
S14	8.30	0.65	138	44	125	0.42	24.8
S15	8.30	0.55	120	43	117	0.41	25.7

Table 4: Statistical analysis of Soil chemical properties

Descriptive analysis	**pH**	**EC (dS/m)**	**N(kg/ha)**	**P(Kg/ha)**	**K(Kg/ha)**	**O.C (%)**	**Free CaCO3 (%)**
Mean	7.90	1.17	218.27	71.20	161.87	0.75	23.70
Standard Error	0.14	0.09	19.77	5.49	10.87	0.08	0.62
Median	8.15	1.15	190.00	66.00	148.00	0.71	24.80
Mode	8.20	#N/A	144.00	105.00	132.00	1.05	24.80
Standard Deviation	0.53	0.37	76.57	21.27	42.11	0.30	2.41
Kurtosis	0.76	-1.40	-1.79	-1.13	0.24	-1.24	-0.17
Skewness	-1.43	-0.35	0.16	0.39	1.11	0.39	-1.08
Range	1.60	1.05	219.00	62.00	131.00	0.91	7.30
Minimum	6.70	0.55	120.00	43.00	117.00	0.42	19.10
Maximum	8.30	1.60	339.00	105.00	248.00	1.32	26.40

Electrical Conductivity (EC)

It is the measure of salt content present in soil solution which varied in the range of 0.55 to 1.6 dSm^{-1} as presented in Table 3, with the mean value of 1.17 dsm^{-1} (table 4). The electrical conductivity value was recorded highest in the soil collected from the point of effluent disposal site and it decreased as going away from the discharge point (Figure 3). High electrical conductivity at disposal site might be due to the use of various types of salts in heavy amount and because of that effluent contained high salt concentration which affect the soil in the area where effluent water is drained or used indicting high accumulation of salt. The present study also supported by the work done by Akan *et al.*, 2007 [1]; Khan *et al.,* 1999 [14]. Dash *et al.,* (2009) [10] in the region of where waste water from various sources was used for irrigation and found high salt concentration in the vicinity area of industrial disposal points.

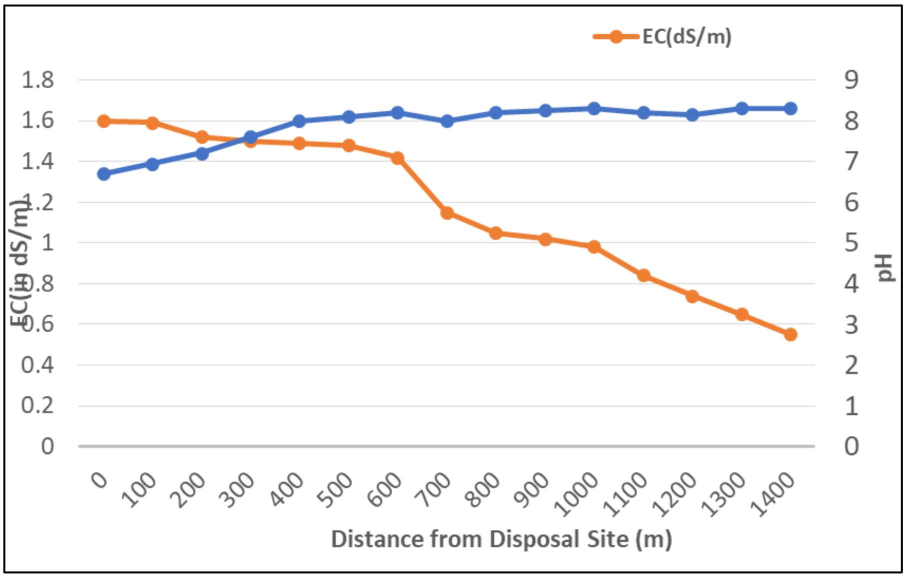


Fig 3: Spatial variation in pH and EC in Soil samples

Organic Carbon (O.C)

The data shown in table 3 showed that the content of organic carbon varied from 0.41% to 1.32% with the mean value of 0.75 % (Table 4). High organic carbon content observed was in soil at the site of disposal point and it decreases as increasing distance from the disposal point also represented in Figure 4. The results in table indicated that disposal of effluents water increase the load of organic carbon content in soil. It was observed that at 900 m distance organic carbon content is high and the reason behind is that sample collected from litchi orchard and so due to litter fall, organic carbon content addition is more as compare to normal soil. The reason behind the presence of high organic carbon in soil collected from the industrial effluent disposal site might be due to use of organic chemicals in tanning industry as well as various chemicals in raw skin treatment is done for leather make which also contains high organic matter content. The findings of Bustamante *et al.,* (2005) [4] and Yadav *et al.,*2002 was similar to the results obtained in this research findings.

Available N

The value of available Nitrogen follows the similar pattern as the organic carbon, as Nitrogen is mainly present in organic form (95-98%). Available N ranged from 120kg/ha to 339kg/ha with their average value of 218.27 Kg/ha (Table 4). A perusal of the data indicated that high build-up of nitrogen content was observed at the site of disposal and the value was decreased with distance from the effluent disposal site represented in Figure 4. The soil sample at 900 m away from disposal point showed higher value of nitrogen because of the sample collected from litchi orchard. This finding is also supported by Subramani *et al., 2014* [19] who also worked on change in soil characteristics due to long term application of waste water. Subramani *et al.*, 2014 [19] and Chhonkar, 2000 [5] also found similar result when they worked on the soil irrigated with wastewater.

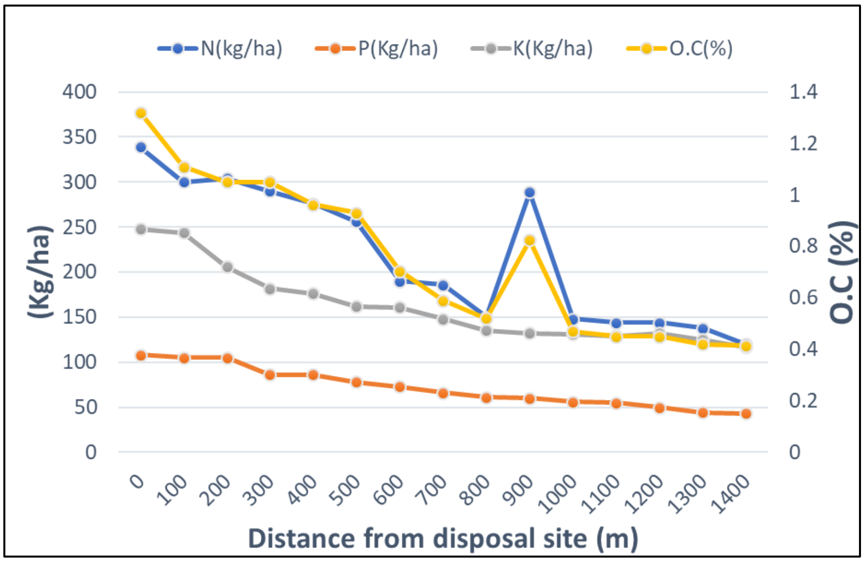


Fig 4: Spatial variation of organic carbon, available nitrogen, phosphorus and potassium in different soil samples.

Available Phosphorus

The data of table 3 and Figure 4 depicted that the concentration of available phosphorus ranged from 43.0 kg/ha to 105.0 kg/ha and the average value of all the fifteen samples were 71.2 kg/ha (Table 4). The content of phosphorus was relatively more at the disposal site than that of other sites. As increasing distance from the point of disposal the availability of phosphorus decreases. This might be due to the presence of phosphatic substance in effluent water which helps in increasing the load of phosphorus in soil of industrial vicinity area. This research finding is in support of the results, also found out by Subramani *et al.*, 2014 [19] and Chhonkar *et al.*, 2000 [5] and reported that there was accumulation of phosphorus in soil irrigated with effluent water.

Available Potassium

The scrutiny of the data in Table 3 revealed that the value of potassium was found 117.0 kg/ha at farthest pint i.e., 1400 m distance from the disposal site to 248.0 kg/ha at nearby effluent disposal site, with an average value of 161.0 kg/ha (Table 4). Figure 2 showed variation in K content from disposal point. It clearly showed the effluent water contained potassium which led to increased amount in soil. The work done by Sweetney & Greatz, 1991 [20], Chhonkar *et al.*, 2000 [5] and Kumar *et al.*, 1998 [15] studied on the soil influenced by the effluent water that showed increased level of potassium concentration in that area supported by present investigations.

Free Calcium Carbonate

Table 3 showed that the value of free $CaCO_3$ ranged from 19.1% to 25.7 %. The minimum value observed at the site of effluent disposal site and maximum value was found at the distant point from disposal site i.e., at 1400 m distance. The minimum value might be due to presence of high organic compound by forming complex compound with $CaCO_3$ that reduces the value of free calcium carbonate and pH may also affect the free $CaCO_3$ substantially. The mean value was observed 23.6% (Table 4). The general reason behind this much high content of free $CaCO_3$ is the calcareous nature of soil of Muzaffarpur district region. Figure 5 shown revealed that the $CaCO_3$ content in soil increased with increasing distance from the disposal point of the effluent.

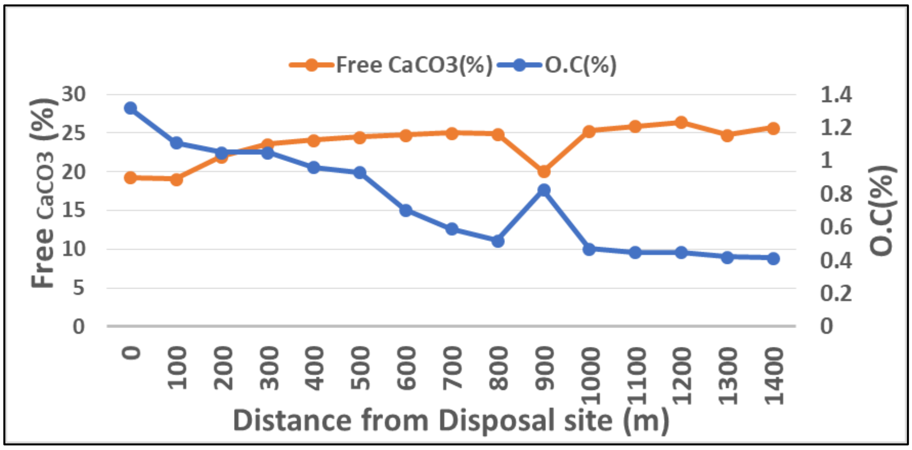


Fig 5: Showing spatial variation of free $CaCO_3$ and also its relation with organic carbon content in soil.

Micronutrients

The concentration of Zn, Cu, Fe, Mn, Cr and Cd at different locations and its descriptive analysis depicted in Table 5 and Table 6 respectively and it revealed that value of Zn varied from 1.03 mg/kg at (S15) site which is farthest point from the disposal site to 2.79 mg/kg at (S1) nearest site of disposal point of tannery industry effluent with an average of 1.916 mg/kg. In case of Cu, it ranged from 1.01mg/kg at farthest point to 2.82 mg/kg in the soil collected from the disposal site and their average value was 1.62 mg/kg. The value of Fe ranged between 15.73 mg/kg to 26.80 mg/kg in soil samples collected from nearby site to farthest point of disposal site with their mean value was 18.60 mg/kg. The minimum value of Mn was observed 10.20 mg/kg in soil sample taken from 1400 m away from disposal point and 14.90 mg/Kg at the industrial disposal point.

Figure 6 revealed that all the four micronutrients taken under observation was accumulated in maximum amount in soil sampled from disposal site and it declined continuously with increasing distance from discharge point. This might be due to the use of very heavy amounts of different coloring agents and dyes with different constituents which increases the content of these micronutrients in effluent water causing the maximum accumulation of micronutrients in vicinity of industry. The order of presence of micronutrients in different soil sample was Fe> Mn> Cu> Zn. The experiment conducted by Subramani *et al.*, 2014 [19] and Awomeso *et al.*, 2009 [2], also support the present study having similar results in case of accumulation of micronutrients in soil when it was irrigated by effluent water or waste water. Rattan *et al.*, (2005) studied on the soil which was irrigated with sewage water for continuous 20 years which showed a high build-up of DTPA extractable micronutrients like Fe, Cu and Zn than in soil which was irrigated with well water.

Table 5: Micronutrients and heavy metals in different soil sample

Soil Samples	Zn(mg/Kg)	Cu(mg/Kg)	Fe(mg/Kg)	Mn(mg/Kg)	Cr(mg/Kg)	Cd(mg/Kg)
S1	2.79	2.82	26.80	14.9	0.903	0.082
S2	2.77	2.13	22.70	12.8	0.899	0.029
S3	2.69	1.87	21.90	12.8	0.637	0.026
S4	2.60	1.77	19.80	12.6	0.622	0.014
S5	2.58	1.87	19.80	12.4	0.512	0.012
S6	2.13	1.73	19.70	11.2	0.513	0.012
S7	1.71	1.53	17.60	11.8	0.482	0.009
S8	1.67	1.54	16.95	12.6	0.410	0.009
S9	1.62	1.37	16.60	11.7	0.382	0.005
S10	1.58	1.31	16.53	11.3	0.361	0.004
S11	1.53	1.27	16.36	11.1	0.352	Tr
S12	1.41	1.70	16.00	11.9	0.350	Tr
S13	1.37	1.26	15.99	10.6	0.391	Tr
S14	1.26	1.05	15.87	10.2	0.292	Tr
S15	1.03	1.01	15.73	10.2	0.216	Tr

Table 6: Descriptive statistical analysis of soil chemical parameters.

Statistical parameters	Zn(mg/kg)	Cu(mg/kg)	Fe(mg/kg)	Mn(mg/kg)	Cr(mg/kg)	Cd(mg/kg)
Mean	1.92	1.62	18.56	11.87	0.49	0.01
Standard Error	0.16	0.12	0.83	0.32	0.05	0.01
Median	1.67	1.54	16.95	11.80	0.41	0.01
Mode	#N/A	1.87	19.80	12.80	#N/A	0.00
Standard Deviation	0.61	0.46	3.22	1.22	0.20	0.02
Kurtosis	-1.52	2.18	1.65	1.43	0.60	8.71
Skewness	0.35	1.16	1.40	0.81	1.08	2.77
Range	1.76	1.81	11.07	4.70	0.69	0.08
Minimum	1.03	1.01	15.73	10.20	0.22	0.00
Maximum	2.80	2.82	26.80	14.90	0.90	0.08

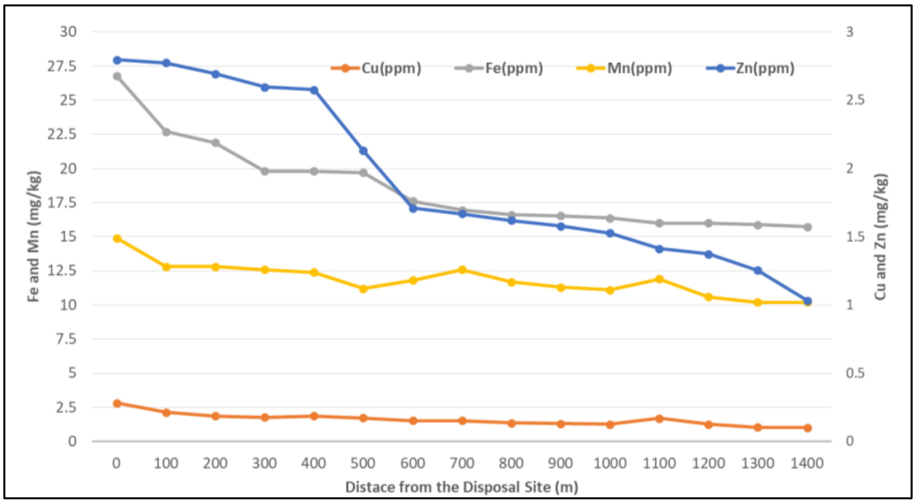


Fig 6: Spatial variation in micronutrients in soil samples

Heavy Metals

A perusal of data manifested that the content of heavy metals like Cr varied from 0.216 mg/Kg to 0.903 mg/Kg. The maximum value 0.903 ppm was at the point of tannery industry effluent disposal point (Table 5). According to WHO recommendation the maximum permissible limit of Cr in soil is 0.78 ppm and the first sample nearby discharge point showed higher value than this which is not in safe limits. It is aware that leather industry is in general Chrome-based tanning industry that used a heavy amount of Chromium salt for the tanning process. This might be the reason of high chromium concentration in soil where effluent was directly disposed off. In case of Cd, the highest concentration was 0.082 mg/Kg which was the highest value, observed in the sample collected from the disposal point and the Cd was detectable up to 900 m (S10 sample) and after that it was found in trace amount which is not detected by machine, however indicated that trace amount of Cd after 900 m away from discharge point might be due to its more volatility than Cr and also, the specific gravity of Cd is more than Cr, which make Cd to leach down more easily. Figure 7 exhibited that the concentration of heavy metals viz., Cr and Cd was highest at the site of disposal point and it decline as we go away from the point of tannery industrial effluent disposal point. The above findings were in strict accordance with the finding made by Behbahaninia *et al.*, 2009 [3], Awomeso, 2009 [2] and Yadav *et al.*, 2002. They found that higher concentration of Cr and Cd was obtained in soil treated with effluent water.

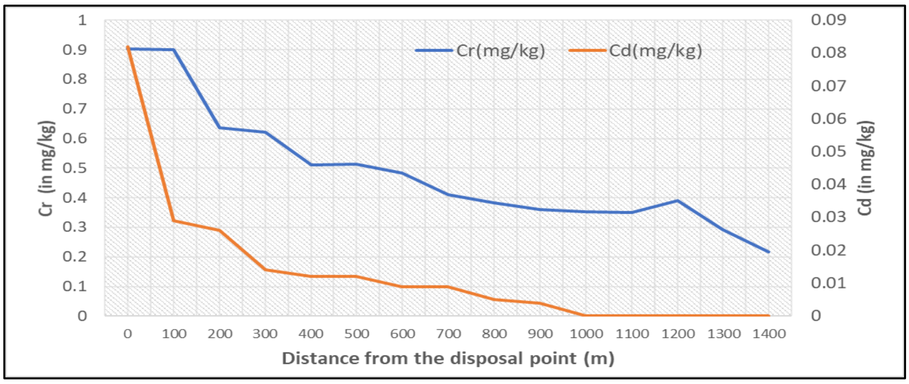


Fig 7: Spatial variation of Cr and Cd in soil samples

Conclusion

According to the experiment conducted it is shown that at discharge point of Effluents, pH was slightly acidic in soil samples, 230% increase in organic carbon, 183% increase in Nitrogen content, 121% increase in Phosphorus, 72% increase in Iron and 318% increase in chromium concentration in soils were found as compared to the soils collected to the soils collected from the farthest point (1400m) away from the discharge site. Free $CaCO_3$ increases as going away from the discharge point of industrial effluents while other nutrients namely N, P and K, organic carbon, micronutrients (Fe, Cu, Zn, Mn) and heavy metals (Cr and Cd) increases as increasing distance from the point of disposal of Tannery industry.

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