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# Effects of pulp and paper mill effluent disposal on soil characteristics in the vicinity of Uttaranchal Pulp and Paper Mill, Haridwar (Uttarakhand), India

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The present investigation was conducted to study the effects of pulp and paper mill effluent disposal on soil characteristics in the vicinity of Uttaranchal Pulp and Paper mill, Haridwar (Uttarakhand), India. The results showed that the values of TS ( $1372.75 \text{ mg L}^{-1}$ ), TDS ( $1008.50 \text{ mg L}^{-1}$ ), TSS ( $364.25 \text{ mg L}^{-1}$ ), BOD ( $1226.50 \text{ mg L}^{-1}$ ), COD ( $2832.50 \text{ mg L}^{-1}$ ),  $\text{SO}_4^{2-}$  ( $678.00 \text{ mg L}^{-1}$ ), Cu ( $1.37 \text{ mg L}^{-1}$ ), Cd ( $0.221 \text{ mg L}^{-1}$ ), Pb ( $0.06 \text{ mg L}^{-1}$ ) and Zn ( $0.38 \text{ mg L}^{-1}$ ) were found beyond the prescribed limit of BIS standards for drinking water. Moreover the values of TSS, BOD, COD, Cd, Cr and Cu were noted above the prescribed limit of BIS standards for irrigation water. The disposal of paper mill effluent showed significant ( $P < 0.05$ ) changes in soil characteristics. The soil parameters namely: moisture content (10.19%) and WHC (11.48%) were decreased, while pH (2.75%), EC (126.08%),  $\text{Cl}^-$  (46.35%), OC (38.70%),  $\text{Na}^+$  (66.44%),  $\text{K}^+$  (24.03%),  $\text{Ca}^{2+}$  (72.16%),  $\text{Mg}^{2+}$  (144.97%), TKN (66.73%),  $\text{PO}_4^{3-}$  (238.83%),  $\text{SO}_4^{2-}$  (23.78%), Cd (1451.47%), Cr (2082.85%), Cu (115.47%), Fe (107.81%), Pb (496.51%) and Zn (138.68%) of the soil were increased after disposal of paper mill effluent in comparison to control soil. The contents of heavy metals in the paper mill effluent contaminated soil were found to be below the maximum levels permitted for Cd ( $6.0 \text{ mg Kg}^{-1}$ ), Cr ( $10.0 \text{ mg Kg}^{-1}$ ), Cu ( $270 \text{ mg Kg}^{-1}$ ), Fe ( $1000 \text{ mg Kg}^{-1}$ ), Pb ( $250 \text{ mg Kg}^{-1}$ ) and Zn ( $600 \text{ mg Kg}^{-1}$ ) for soil in India. Among different heavy metals, Cr (21.82) showed maximum contamination, whereas Fe (2.08) showed minimum contamination. The contamination factor of heavy metals in the soil was recorded in the order of  $\text{Cr} > \text{Cd} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Fe}$  after disposal of paper mill effluent. Thus, paper mill effluent significantly affected the soil characteristics in the vicinity of effluent disposal.

**Key words:** Enrichment factor (Ef), heavy metals, pulp and paper mill effluent, soil characteristics.

## INTRODUCTION

The pulp and paper industry uses large quantity of freshwater and lignocellulosic materials in the process of production of paper and it generates large quantity of effluent (Kumar and Chopra, 2011, 2013a, b, 2015). The generated effluent is characterized by dark color, foul odour, high organic content and extreme quantities of chemical oxygen demand (COD), biochemical oxygen demand (BOD) and pH (Deilek and Bese, 2001; El-Bestawy et al., 2008; Kumar and Chopra, 2014a, b, c, d).

The dark color in paper mill effluent is caused by the organic ligands such as wood extractives, resins, synthetic dyes, tannins, lignin and its degradation products. The dark color in untreated effluent is a major environmental concern as its discharge to water bodies

inhibits the photosynthetic activity of aquatic biota by reducing sunlight, besides exhibiting the toxic effects on biota (Kumar and Chopra, 2012b, 2013a, 2014e). The chlorinated phenols generated during pulp bleaching stages of paper production are a class of harmful pollutants found in paper mill effluents. These phenols contribute considerably towards the toxicity of effluent that severely affects the fish community (Kumar, 2014a, b; Kumar et al., 2014). The harmful environmental effects of effluents and the stricter environmental norms compel

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the mills to reduce color, toxic phenols and other pollutants to safe disposal levels prior to effluent discharge (Kannan and Oblisami, 1990; Raina et al., 2003; Patterson et al., 2008). The use of saline water may result in the reduction of crop yield, whereas sodic water may deteriorate the physicochemical properties of the soil with consequent reductions in the crop yields (Malla and Mohanty, 2005; Müller et al., 2007; Merilainen and Oikari, 2008).

Industrialization plays an important role in development, but wastewater disposal has become a global dilemma for industries because of the generation of high volumes of effluents, limited space for land-based treatment and disposal, and high cost of treatment technologies (Kannan and Oblisami, 1990; Thompson et al., 2001; Kumar and Chopra, 2013c). Discharge of industrial effluent without adequate treatment causes severe degradation in the pedosphere, hydrosphere, and atmosphere (Howe et al., 1996; Fazeli et al., 1998; Barzegar et al., 2002). Effluents from industries contain appreciable amounts of nitrogen (N), phosphorous (P), sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg) along with zinc (Zn), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), nickel (Ni), and cadmium (Cd), which cause eutrophication in aquatic ecosystems (Abdel, 2003; Kumar, 2014b; Kumar and Chopra, 2015). In agriculture, irrigation water quality is believed to have effects on the soils and agricultural crops (Thompson et al., 2001; Ugurlu et al., 2008; Kumar and Chopra, 2012c).

The disposal of wastewater is a major problem faced by industries, due to generation of high volume of effluent and with limited space for land based treatment and disposal. On the other hand, wastewater is also a resource that can be applied for productive uses since wastewater contains nutrients that have the potential for use in agriculture, aquaculture, and other activities (Andaleeb et al., 2008; Kiziloglu et al., 2008; Kumar 2014a).

The various elements introduced via pulp mill wastewater irrigation affect not only the crop growth and soil properties but also their relative mobility in the soil profile (Gomathi and Oblisami, 1992; Hanafi et al., 2010). For example, cations tend to accumulate in upper horizons on the cation exchange sites in the soil (Kim, 1996; Kretschmer et al., 2000; Kiziloglu et al., 2008). Because of the high chemical diversity of the organic pollutants in pulp and paper mill water, a high variety of toxic effects on aquatic communities in recipient watercourses have been observed (Kim, 1996; Patterson et al., 2008; Palese et al., 2009). On the other hand, wastewater is also a resource that can be applied for productive uses because wastewater contains nutrients that have potential for use in agriculture, aquaculture and other activities (Raina et al., 2003; Ramchandra et al., 2009; Kumar, 2014b).

Globally, pulp and paper industry is considered as one of the most polluting industry contributing 100 million kg

of toxic pollutants that are being released every year in the environment (Reddy and Borse, 2001; Siddiqui et al., 2011). In India, the paper industry has been one of the major sources of aquatic pollution (Reddy and Borse, 2001; CPPRI, 2005; Siddiqui et al., 2011). Pollutants from the industry include suspended solids, compounds coloured by lignin, Na, dissolved inorganic salts, toxic compounds like chlorinated lignins, and phenolic derivatives (Lacorte et al., 2003; Kumar, 2014a). Discharge of untreated effluent will therefore, create serious water pollution problems, resulting in the deterioration of water quality and toxicity to aquatic life. However, the application of pollutants from the pulp and paper industry leads to the deterioration of soil physical, chemical, and biological properties (Deilek and Bese, 2001; Ansari, 2004; Pokhrel and Viraraghavan, 2004).

Pulp and paper mills in India are one of the most polluting industries; in addition, they are high consumer of fresh water and they discharge huge quantity of effluent. The pulp and paper industries is one of the core industrial sectors in India which ranks 15th among the paper producing countries in the world, generating more than 0.3 million direct employments and around 1 million indirect employments through agricultural activities. At present, there are 666 pulp and paper mills in India, of which 632 units are agro residue and recycled fiber based units with manufacturing capacity of 7.6 million tons. The Indian pulp and paper industry is highly water intensive, consuming 100-250 m<sup>3</sup> freshwater/ton paper and also generating the corresponding waste water of 75-225 m<sup>3</sup> waste water/ton paper (Thompson et al., 2001; Kumar and Chopra, 2012b, 2015). The various elements introduced via pulp mill wastewater irrigation not only affect the crop growth and soil properties but also their relative mobility in the soil profile (Thompson et al., 2001; Patterson et al., 2008; Kumar and Chopra, 2015). Keeping in view, the present investigation was conducted to study the pollution load of Uttaranchal Pulp and Paper Mill effluent and its effect on soil characteristics in the vicinity of effluent disposal.

## MATERIALS AND METHODS

### Study area

Uttaranchal Pulp and Paper Mills (P) Ltd. Mundate, Haridwar (29°46'4"N 77°50'47"E) was selected for the collection of paper mill effluent samples. The pulp and paper mill is located about 40 Km away from Haridwar at Haridwar Deoband Highway. The Uttaranchal Pulp and Paper Mills mill is a leading manufacturer and suppliers of brown, white and coloured Kraft paper, packaging paper and newspaper.

### Collection of paper mill effluent samples and analysis

The paper mill effluent samples were collected from the

effluent disposal channel. The bore well (control) were collected from bore well located adjacent to the agricultural fields. The samples were collected in thoroughly cleaned plastic container of 5 L capacity with provision of a double cap device. Some of the parameters like pH were carried out on the spot and DO was also fixed on the spot because time consumed during transportation could alter the results. The remaining parameters could be carried out on composite sample. The collected samples were brought to the laboratory and analyzed for various physico-chemical parameters and heavy metals following parameters namely: total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), electrical conductivity (EC), pH, dissolved oxygen demand (DOD), biochemical oxygen demand (BOD), chemical oxygen demand (COD), chloride ( $\text{Cl}^-$ ), sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), total Kjeldahl nitrogen (TKN), phosphate ( $\text{PO}_4^{3-}$ ), sulphate ( $\text{SO}_4^{2-}$ ), cadmium (Cd), iron (Fe), chromium (Cr), lead (Pb), copper (Cu), and zinc (Zn) using standard methods (APHA, 2005; Chaturvedi and Sankar, 2006).

### Collection of soil samples and analysis

The composite soil samples from the surface (0-20 cm) were collected in the vicinity of effluent disposal channel emerging from Uttaranchal Pulp and Paper Mill. The bore well water irrigated soil was taken as control. The samples were brought to the laboratory and dried in clean plastic trays for 7 days at room temperature and then sieved through a 2-mm or 5-mm sieve. The samples were analyzed for various physico-chemical parameters namely: soil moisture, bulk density (BD), water holding capacity (WHC), pH, EC,  $\text{Cl}^-$ , OC,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , TKN,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  and heavy metals like Cd, Cr, Cu, Fe, Pb and Zn following standard methods (Chaturvedi and Sankar, 2006).

### Heavy metal analysis

For heavy metal analysis, 10 ml sample of paper mill effluent, 100 ml sample of bore well water and 0.5 g sample of soil was digested with a mixture of concentrated  $\text{HNO}_3$  and  $\text{HClO}_4$  (10 ml + 2 ml) separately. The digested samples were filtered through Whatman filter No. 42 and finally the volume was made with 50 ml of 0.1 N  $\text{HNO}_3$  and analyzed for heavy metals using AAS (Model ECIL-4129). The contamination of heavy metals in the soil was determined by the following standard method (Håkanson, 1980):

$$\text{Contamination factor (Cf)} = \frac{\text{Mean content of metal in the sample}}{\text{Background metal content of the substance}}$$

### Data interpretation and statistical analysis

Data were analyzed for student t-test for determining the

difference between soil parameters before and after paper mill effluent disposal using SPSS 12.0. Mean and standard deviation were also calculated with the help of MS Excel 2003. Graphs were plotted with the help of Sigma plot, 2000.

## RESULTS AND DISCUSSION

### Characteristics of Uttaranchal pulp and paper mill effluent

The mean $\pm$ SD of various physico-chemicals and heavy metals characteristics of Uttaranchal pulp and paper mill effluent are given in Table 1.

During the present study, the values of TSS ( $364.25 \text{ mgL}^{-1}$ ) of paper mill effluent were recorded beyond the prescribed limit of Indian Standards for irrigation water (BIS, 1991). The higher values of TS, TDS and TSS in the paper mill effluent were recorded as compared to the control (Bore well water) and this is likely due to the utilization of agro-residues in the manufacturing of paper by the paper mill (Table 1). Kumar and Chopra (2012b) also recorded slightly lower values of TS ( $860\pm 5.50 \text{ mgL}^{-1}$ ) in the paper mill effluent. Baruah and Das (1998) also reported higher values of TDS ( $1945.44\pm 8.62 \text{ mgL}^{-1}$ ) and TSS ( $245.50\pm 3.20 \text{ mgL}^{-1}$ ) in the paper mill effluent. The pH of paper mill effluent was alkaline (7.91) in nature and it might be due to the use of alkalis in the production of pulp from the raw material. The value of EC in the paper mill effluent was also noted to be higher and it is likely due to the presence of more ionic species in the paper mill effluent (Table 1). Higher values of EC ( $6.84\pm 0.40 \text{ dS m}^{-1}$ ) were also reported by Kumar and Chopra (2012b, 2015) in the untreated paper mill effluent.

The results showed that the values of BOD ( $1226.50 \text{ mgL}^{-1}$ ), COD ( $2832.50 \text{ mgL}^{-1}$ ) in the paper mill effluent were found beyond the irrigation standard (Table 1). The higher values of BOD and COD in the paper mill effluent are likely due to the presence of more degradable or oxidizable organic matter, inorganic chemical species or dissolved solids in the paper mill effluent as earlier reported by Kumar and Chopra (2012b). Ghaly et al. (2011) reported higher BOD ( $1874.20 \text{ mgL}^{-1}$ ) and COD ( $2450.60 \text{ mgL}^{-1}$ ) in the paper mill effluent.

During the present investigation, the values of  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , TKN,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  in the paper mill effluent were also found higher compared to the control (Table 1). The findings were in accordance with those of Patterson et al. (2008) who reported higher values of  $\text{Na}^+$  ( $70.90 \text{ mgL}^{-1}$ ),  $\text{Mg}^{2+}$  ( $34.90 \text{ mgL}^{-1}$ ) and  $\text{PO}_4^{3-}$  ( $14.98 \text{ mgL}^{-1}$ ) in the paper mill effluent. Kumar and Chopra (2012a) also reported higher values of  $\text{Cl}^-$  ( $345.80 \text{ mgL}^{-1}$ ),  $\text{K}^+$  ( $56.70 \text{ mgL}^{-1}$ ),  $\text{Ca}^{2+}$  ( $287.70 \text{ mgL}^{-1}$ ), TKN ( $38.60 \text{ mgL}^{-1}$ ), and  $\text{SO}_4^{2-}$  ( $468.70 \text{ mgL}^{-1}$ ) in the distillery effluent. The results revealed that the values of Cd ( $1.75 \text{ mgL}^{-1}$ ), Cr ( $2.53 \text{ mgL}^{-1}$ ) and Cu ( $1.37 \text{ mgL}^{-1}$ ) in the paper mill effluent were found above the prescribed limit of BIS standards

**Table 1.** Physico-chemical characteristics of control (bore well water) and Uttaranchal pulp and paper mill effluent.

Parameter	Bore well water	Effluent	BIS for drinking water	BIS for irrigation water
TS (mg L <sup>-1</sup> )	154.75±5.38	1372.75±6.55	600	2100
TDS (mg L <sup>-1</sup> )	134.75±8.62	1008.50±4.65	500	1900
TSS (mg L <sup>-1</sup> )	20.00±3.65	364.25±6.95	100	200
EC (dS m <sup>-1</sup> )	0.18±0.04	1.34±0.19	-	-
pH	7.55±0.25	7.91±0.33	6.5-8.5	5.5-9.0
DO (mg L <sup>-1</sup> )	8.24±2.65	NIL	6-8	-
BOD (mg L <sup>-1</sup> )	4.78±0.32	1226.50±9.15	4.0	100
COD (mg L <sup>-1</sup> )	5.88±1.37	2832.50±7.37	150-200	250
Cl <sup>-</sup> (mg L <sup>-1</sup> )	154.88 ±13.89	340.75±1.21	250	500
Na <sup>+</sup> (mg L <sup>-1</sup> )	10.73±1.49	34.87±5.19	-	-
K <sup>+</sup> (mg L <sup>-1</sup> )	15.44±2.36	77.99±2.90	-	-
Ca <sup>2+</sup> (mg L <sup>-1</sup> )	33.02±3.02	140.70±3.79	75	200
Mg <sup>2+</sup> (mg L <sup>-1</sup> )	16.45±3.01	22.08±2.80	-	-
TKN (mg L <sup>-1</sup> )	1.71±0.53	24.27±5.87	-	100
PO <sub>4</sub> <sup>3-</sup> (mg L <sup>-1</sup> )	0.42±0.19	8.75±0.80	-	-
SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	323.14±4.88	678.00±13.73	200	1000
Cd (mg L <sup>-1</sup> )	ND	1.75±0.02	0.05	1.5
Cr (mg L <sup>-1</sup> )	ND	2.53±0.41	0.05	2.0
Cu (mg L <sup>-1</sup> )	0.51±0.10	1.37±0.06	0.30	1.0
Fe (mg L <sup>-1</sup> )	1.30±0.31	1.90±0.15	5.00	15
Pb (mg L <sup>-1</sup> )	0.01±0.01	0.06±0.01	0.05	3.00
Zn (mg L <sup>-1</sup> )	0.12±0.03	0.38±0.00	0.05	1.00

Mean ± SD of six values; BWW – bore well water; BIS - Bureau of Indian Standard; ND - Not detected.

for irrigation water (Table 1). The studies showed that the heavy metals are toxic to the environment, and affects the plants, human and animals health. The findings were in agreement with those of Patterson et al. (2008) who reported higher values of heavy metals in the paper mill effluent. Thus, the paper mill effluent was rich in various nutrients and heavy metals.

#### Effects of paper mill effluent disposal on soil characteristics

##### Moisture content, BD and WHC

In the present study, the soil moisture content (10.19%) and WHC (11.48%) of the soil were decreased insignificantly ( $P>0.05$ ) after paper mill effluent disposal compared to the control soil (Table 2). Miller and Turk (2002) also reported the decrease in the moisture content and WHC of the soil irrigated with wastewater. The moisture content of the soil is useful and an important factor which affects the pH, availability of nutrients to plant and aeration. Moreover, presence of larger particles in the soil also reduces the soil moisture content. The results showed that no significant ( $P>0.05$ ) change was recorded in the BD of the soil after paper mill effluent disposal. The results of the present investigation were contradictory to the findings of Haynes and Naidu (1998) and Celik (2005) who reported slight reduction in the BD of the soil after long term effluent irrigation due to the

addition of organic matter.

##### EC and pH

The value of EC (2.08 dS m<sup>-1</sup>) in the paper mill effluent contaminated soil was increased compared to the EC (0.92 dS m<sup>-1</sup>) of bore well water irrigated soil. The EC (126.08%) of the paper mill effluent contaminated soil was increased significantly ( $P<0.05$ ) compared to the control soil (Table 2). The increase in the EC of the effluent irrigated soil is likely due to the presence of more salts or ionic species in the paper mill effluent. Mohan et al. (2007) reported that the higher EC (4.52 dS m<sup>-1</sup>) of wastewater is due to the presence of total dissolved solids. Thus, EC is an important criterion to determine the suitability of water and waste water for irrigation. Soils have alkaline pH levels that are greater than 7. If these soils have excessive amount of salts (that is, EC >4 dS m<sup>-1</sup>) they are classified as saline soils. However, if they also contain appreciable exchangeable sodium (sodium absorption ratio SAR >13) or exchangeable sodium percentage (ESP) >15, they are classified as saline-sodic. Finally, if salt concentration are low (EC <4 dS m<sup>-1</sup> and SAR >13 or ESP >15) or high enough to control a soil's chemical attributes, they are known as sodic soils.

The pH of the paper mill effluent contaminated soil was recorded to be more alkaline (8.20) compared to the pH of control soil (7.98). The pH (2.75%) of the paper mill effluent contaminated soil was increased insignificantly

**Table 2.** Physico-chemical characteristics of soil before and after disposal of Uttaranchal pulp and paper mill effluent.

Parameter	Bore well water	Effluent	t-statistics	t-critical
Soil moisture (%)	42.68±2.05	38.33±4.48 (-10.19)	2.169827 <sup>NS</sup>	3.182446
WHC (%)	46.60±3.20	41.25±3.86 (-11.48)	1.824787 <sup>NS</sup>	3.182446
BD (gm cm <sup>-3</sup> )	1.41±0.08	1.41±0.03 (0.00)	0.071489 <sup>NS</sup>	3.182446
pH	7.98±0.18	8.20±0.11 (+2.75)	1.87559 <sup>NS</sup>	3.182446
EC (dS m <sup>-1</sup> )	0.92±0.12	2.08a±0.07 (+126.08)	15.8901*	3.182446
Cl <sup>-</sup> (mg Kg <sup>-1</sup> )	92.26±4.81	135.03a±6.07 (+46.35)	11.6037*	3.182446
OC (mg Kg <sup>-1</sup> )	0.31±0.07	0.43±0.10 (+38.70)	1.59861 <sup>NS</sup>	3.182446
Na <sup>+</sup> (mg Kg <sup>-1</sup> )	10.55±1.75	17.56±2.51 (+66.44)	8.65579*	3.182446
K <sup>+</sup> (mg Kg <sup>-1</sup> )	124.23±2.97	154.09a±5.80 (+24.03)	10.1243*	3.182446
Ca <sup>2+</sup> (mg Kg <sup>-1</sup> )	21.20±2.07	36.50a±6.22 (+72.16)	3.88425*	3.182446
Mg <sup>2+</sup> (mg Kg <sup>-1</sup> )	15.41±1.93	37.75a±4.71 (+144.97)	8.68557*	3.182446
TKN (mg Kg <sup>-1</sup> )	31.38±2.38	52.32a±5.54 (+66.73)	5.52616*	3.182446
PO <sub>4</sub> <sup>3-</sup> (mg Kg <sup>-1</sup> )	2.06±0.78	6.98a±1.21 (+238.83)	7.23819*	3.182446
SO <sub>4</sub> <sup>2-</sup> (mg Kg <sup>-1</sup> )	142.23±7.37	176.06a±10.65 (+23.78)	9.75022*	3.182446
Cd (mg Kg <sup>-1</sup> )	0.068±0.10	1.055a±0.26 (+1451.47)	9.91745*	3.182446
Cr (mg Kg <sup>-1</sup> )	0.035±0.05	0.764a±0.13 (+2082.85)	12.5808*	3.182446
Cu (mg Kg <sup>-1</sup> )	1.053±0.03	2.269a±0.46 (+115.47)	6.32178*	3.182446
Fe (mg Kg <sup>-1</sup> )	1.28±0.31	2.66±0.59 (+107.81)	2.88113 <sup>NS</sup>	3.182446
Pb (mg Kg <sup>-1</sup> )	0.172±0.1	1.026a±0.00 (+496.51)	38.8698*	3.182446
Zn (mg Kg <sup>-1</sup> )	1.259±0.12	3.005a±0.57 (+138.68)	5.0961*	3.182446

Mean ± SD of six values; Significant \*t> 5% level; % increase or decrease in comparison to the control given in parenthesis; a - significantly different to the control; NS - Not significant.

( $P > 0.05$ ) in comparison to control soil (Table 2). Charman and Murphy (1991) also reported that the basic pH (8.68-9.86) of the soil reduces the solubility of all micronutrients (except chlorine, boron and molybdenum), especially those of iron, zinc, copper and manganese. The soil pH can also influence plant growth as it affects the activity of beneficial microorganisms. Most nitrogen fixing legume bacteria are not very active in strongly acidic soils. In the acidic soil environment, the availability of the basic cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) becomes lower due to leaching. Mohan et al. (2007) found that soil having pH value of 8.5 and above is expected to have more Na in the exchange complex and when unaccompanied by the presence of soluble salts, it is classified as an alkaline soil.

### Chlorides (Cl)

The content of  $\text{Cl}^-$  (46.35%) was increased significantly ( $P < 0.05$ ) in the paper mill effluent contaminated soil in comparison to control soil (Table 2). Chloride is generally considered to be a hydrologically and chemically inert substance. Past research suggested that  $\text{Cl}^-$  participates in a complex biogeochemical cycle involving the formation of organically bound chlorine. Generally, cation  $\text{K}^+$  is usually considered as one of the major plant

nutrients; the accompanying anion  $\text{Cl}^-$  has been generally referred to as undesirable but unavoidable. However,  $\text{Cl}^-$  is now considered as an essential micronutrient for optimal growth. Both  $\text{K}^+$  and  $\text{Cl}^-$  are the main ions involved in the neutralization of charges, and as the most important inorganic osmotic active substances in plant cells and tissues. The association of  $\text{K}^+$  and  $\text{Cl}^-$  is related to the opening and closing of stomata (Öberg and Sandén, 2005).

### $\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$

The values of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were increased significantly ( $P < 0.05$ ) in the paper mill effluent contaminated soil compared to the bore well water irrigated soil. The contents of  $\text{Na}^+$  (66.44%),  $\text{K}^+$  (24.03%),  $\text{Ca}^{2+}$  (72.16%) and  $\text{Mg}^{2+}$  (144.97%) in the soil were increased from their respective control soils (Table 2). The increase in the concentration of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  is likely due to the presence of more  $\text{Na}^+$  (34.87 mg L<sup>-1</sup>),  $\text{K}^+$  (77.99 mg L<sup>-1</sup>),  $\text{Ca}^{2+}$  (140.70 mg L<sup>-1</sup>) and  $\text{Mg}^{2+}$  (22.08 mg L<sup>-1</sup>) in the paper mill effluent. Patterson et al. (2008) reported the higher concentration of  $\text{Na}^+$  (128.95 mg Kg<sup>-1</sup>) in the paper mill effluent irrigated soil. Miller and Turk (2002) reported the values of  $\text{K}^+$  (86.45 mg Kg<sup>-1</sup>) in the wastewater irrigated soil and stated that  $\text{K}^+$  is the third

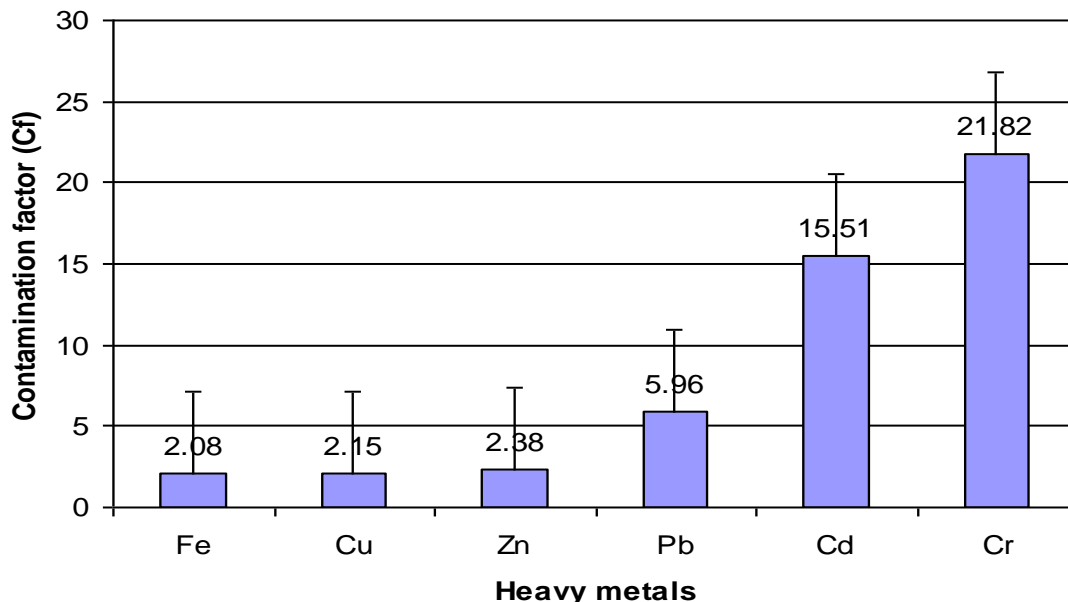


Figure 1. Contamination of heavy metals in the soil after disposal of paper mill effluent.

most commonly added fertilizer nutrient (nitrogen is the most used, while phosphorus is the second most used). El-Bestawy et al. (2008) reported the higher values of  $\text{Ca}^{2+}$  ( $248.50 \text{ mg Kg}^{-1}$ ) of agro-residue based paper mill effluent irrigated soil.

#### TKN and organic carbon (OC)

The values of TKN ( $52.32 \text{ mg Kg}^{-1}$ ) and OC ( $0.43 \text{ mg Kg}^{-1}$ ) were recorded in the paper mill effluent contaminated soil. The value of TKN (66.73%) was increased significantly ( $P < 0.05$ ) in the paper mill effluent contaminated soil in comparison to control soil (Table 2). Insignificant change was recorded in the value of OC (38.70%) after paper mill effluent disposal. The increase in the concentration TKN is likely due to the presence of more nitrogen in the paper mill effluent. Nitrate is the most essential and available form of nitrogen to plants because plant roots take up nitrogen in the form of  $\text{NO}_3^{2-}$  and  $\text{NH}_4^+$ . Plants respond quickly to application of nitrogen that encourages the vegetative growth and gives a deep green colour to the leaves. The overall increase in nitrogen is due to the use of wastewater, which contains higher amount of nitrogen. When nitrate input exceeds the soil nitrate immobilization potential, a state of N-saturation is said to exist (Al-Harbi, 2008).

#### $\text{PO}_4^{3-}$ and $\text{SO}_4^{2-}$

The values of  $\text{PO}_4^{3-}$  ( $6.98 \text{ mg Kg}^{-1}$ ) and  $\text{SO}_4^{2-}$  ( $176.06 \text{ mg Kg}^{-1}$ ) were recorded higher in the paper mill effluent contaminated soil compared to control soil. The contents

of  $\text{PO}_4^{3-}$  (238.83%) and  $\text{SO}_4^{2-}$  (23.78%) were increased significantly ( $P < 0.05$ ) in the paper mill effluent contaminated soil, respectively (Table 2). The increase in the concentration of  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  are likely due to the presence of more  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  in the paper mill effluent. Biswas et al. (2009) reported that the use of distillery effluent, as irrigation water or as a soil amendment, showed significant effect on  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$ .

#### Heavy metals

During the present study, the higher values of Cd ( $1.55 \text{ mg Kg}^{-1}$ ), Cr ( $0.764 \text{ mg Kg}^{-1}$ ), Cu ( $2.269 \text{ mg Kg}^{-1}$ ), Fe ( $2.66 \text{ mg Kg}^{-1}$ ), Pb ( $1.026 \text{ mg Kg}^{-1}$ ) and Zn ( $3.005 \text{ mg Kg}^{-1}$ ) were observed in the paper mill effluent contaminated soil in comparison to the control soil (Table 2). The contents of Cd, Cr, Cu, Pb and Zn were increased significantly ( $P < 0.05$ ) in the soil after paper mill effluent disposal. The content of Fe in the paper mill effluent contaminated soil was found to be insignificantly ( $P > 0.05$ ) different to the control soil. The contamination factor (Cf) showed the contamination of heavy metals in the soil after disposal of paper mill effluent. Among different heavy metals, Cr (21.82) showed maximum contamination, whereas Fe (2.08) showed minimum contamination. The contamination factor of heavy metals in the soil was recorded in the order of  $\text{Cr} > \text{Cd} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Fe}$  after disposal of paper mill effluent (Figure 1). Mohammadi et al. (2010) concluded that the use of paper mill lime sludge as a soil amendment in an acidic soil significantly increased pH,

which was proportional to the application rate of paper mill sludge. Under acidic conditions, elements such as iron, aluminium, manganese and the heavy metals (zinc, copper, and chromium) become highly soluble and may create problems for vegetation (Charman and Murphy, 1991; Kumar et al., 2014). The content of Cd, Cr, Cu, Fe, Zn and Pb were increased significantly due to disposal of paper mill effluent. Kumar and Chopra (2015) also reported the higher concentrations of heavy metals like Fe, Zn, Cd, Cu and Pb in the paper mill effluent irrigated soil.

## Conclusion

The present investigation was conducted in such a way that the values of TS, TDS, TSS, BOD, COD,  $\text{SO}_4^{2-}$ , Cu, Cd, Pb and Zn were found beyond the prescribed limit of BIS standards for drinking water. Moreover, the values of TSS, BOD and COD, Cd, Cr and Cu were noted above the prescribed limit of BIS standards for irrigation water. The disposal of paper mill effluent showed significant ( $P < 0.05$ ) changes in soil characteristics, namely: EC,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , TKN,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ , Cd, Cr, Cu, Pb and Zn. The contents of heavy metals in the paper mill effluent contaminated soil were found to be below the maximum levels permitted for Cd ( $6.0 \text{ mg Kg}^{-1}$ ), Cr ( $10.0 \text{ mg Kg}^{-1}$ ), Cu ( $270 \text{ mg Kg}^{-1}$ ), Fe ( $1000 \text{ mg Kg}^{-1}$ ), Pb ( $250 \text{ mg Kg}^{-1}$ ) and Zn ( $600 \text{ mg Kg}^{-1}$ ) for soil in India (BIS, 1991). The contamination factor of heavy metals in the soil was recorded in the order of  $\text{Cr} > \text{Cd} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Fe}$  after disposal of paper mill effluent. Therefore, paper mill effluent disposal significantly increased the nutrients/toxicants in the soil environment. Although, the concentrations of heavy metals in the soil were noted below the permissible limits of Indian standards, however, if the effluent disposal is performed for a prolonged time, the metal contamination may exceed the permissible limits in soil which can be hazardous for the fertility of the soil. Hence, monitoring is needed from time to time where the soil is being disposed with paper mill effluent. It is therefore recommended that the wastewater from pulp and paper mill should be properly treated before being disposed into open land or in canals. Further investigation is required on the characteristics of paper mill effluent and its effects on soil characteristics.

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