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Archives of Applied Science Research, 2011, 3 (4):63-77  
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ISSN 0975-508X  
CODEN (USA) AASRC9

### Impact on physico-chemical characteristics of soil after irrigation with distillery effluent

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#### ABSTRACT

The effect of seven rates viz. 0 (control), 5, 10, 25, 50, 75 and 100 ml/Kg of treated distillery effluent on the physico-chemical properties of soils was studied under natural environment in pot experiment. The characteristics of the soil were determined before and after 12 weeks of effluent irrigation. The results revealed that the 100% concentration of distillery effluent decreased BD (5.63%) and pH (16.67%) and increased moisture content (30.82%), WHC (16.41%), and EC (84.13%), ECEC (160.67%), Cl<sup>-</sup> (292.38%), OC (3811.63%), HCO<sub>3</sub><sup>-</sup> (27.76%), CO<sub>3</sub><sup>-2</sup> (43.58%), Na<sup>+</sup> (273.01%), K<sup>+</sup> (31.59%), Ca<sup>2+</sup> (729.77%), Mg<sup>2+</sup> (740.47%), Fe<sup>2+</sup> (301.90%), TKN (1390.63%), NO<sub>3</sub><sup>2-</sup> (98.02%), PO<sub>4</sub><sup>3-</sup> (337.80%), SO<sub>4</sub><sup>2-</sup> (77.79%), Zn (333.33%), Cd (565.00%), Cu (417.57%), Pb (1487.50%) and Cr (1365.38%) in comparison to control irrigated soil. The distillery effluent concentrations showed significant ( $P < 0.001$ ) effect on EC, pH, Cl<sup>-</sup>, OC, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-2</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, TKN, NO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>, Zn, Cd, Cu, Pb and Cr and insignificant ( $P > 0.05$ ) effect on, moisture content, WHC and bulk density after effluent irrigation when compared to control. The enrichment factor of various micronutrients was in order of Pb > Cr > Cd > Cu > Zn after amended with distillery effluent.

**Keywords:** Distillery effluent, irrigation, soil characteristics, micronutrients, enrichment factor.

#### INTRODUCTION

Wastewater reclamation and reuse is one of the best alternatives for compensating water shortages. In arid and semi-arid regions, wastewater reclamation and reuse has become an important element in water resources planning. In the agriculture, the irrigation water quality is believed to have effects on the soils and agricultural crops [27]. Applications of industrial wastes as fertilizer and soil amendment have become popular in agriculture. Moreover, agricultural irrigation with wastewater effluents became a common practice in arid and semiarid regions,

where it was used as a readily available and inexpensive option to fresh water [7, 52]. Some characteristics of effluents material are favourable for agriculture since the effluent is rich in organic matter, nitrogen (N), phosphorous (P), potassium (K) and magnesium (Mg). 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 [25].

Wastewater generation results of increasing fresh water scarcity, their nutrients enrichment required advanced treatment for other applications including application in the agricultural lands. The use of soil as a medium for the treatment and disposal of industrial wastewater is becoming common practice. The increasing application of wastewater in agricultural fields may serve as a viable method of disposing the wastewater; improve soil fertility and sustaining agriculture production in non-irrigated areas having shortage of fresh water for irrigation. In India there are about 330 distilleries, the total installed capacity is about 3500 million liters of alcohol [1, 32, 50]. Distilleries generate a huge amount of wastewater (spent wash) with enormous quantity of organic and inorganic nutrients, thus having high Na, K, Ca, Mg, TKN, BOD and COD load. Distilleries producing alcohol from molasses are considered among the most polluting agro-based industries [22, 23]. For production of each liter of alcohol, 12–15 liter of effluent is produced. Approximately 40 billion liters of effluent is generated per annum from 330 distilleries in the country [42]. The effluent causes concern of environmental pollution owing to its very high organic content. The effluent contains considerable amount of organic matter and plant nutrients, particularly potassium and sulphur, this can be applied to arable land as irrigation water and as an amendment. It may act as a source of plant nutrients and has been reported to increase the yield of the crops [24, 37].

Thus, application of distillery effluent to arable land as irrigation water and as a source of plant nutrients offers a promising alternative for its safe disposal. However, the distillery effluent contains a significant quantity of salt ( $EC, 25.3 \text{ dS m}^{-1}$ ) its indiscriminate use may affect the physico-chemical properties of soil in the long run. The application of distillery effluent in irrigation increase the saturated hydraulic conductivity and decrease in bulk density of the soil after harvest of wheat [24]. It was observed earlier that an increase in hydraulic conductivity and infiltration rate and improvement in aggregate stability following addition of distillery slops and molasses to the columns of a saline sodic soil [18]. The significant increase was recorded in infiltration rate and decrease in bulk density of an Inceptisol with application of distillery effluent [57]. The author [37] found that application of distillery effluent improved the water retention characteristics of the soil; whereas, non-judicious use of distillery effluent might adversely affect the crop growth and soil properties by increasing soil salinity [21].

The utilization of industrial waste as soil amendment has generated interest in recent times. Wastewater irrigation; reduce the need for chemical fertilizers, resulting in net cost savings to farmers. In recent past various studies have been made on the characteristics of effluent of industries, and their application in agricultural practices [2, 3, 4, 5, 26, 32, 39, 44, 53]. Keeping in view the above facts, a field experiment was conducted to study the effect of graded doses of distillery effluent application on the physical and physico-chemical properties of a loamy sand soil.

## MATERIALS AND METHODS

### 2.1. Experimental design

A field study was conducted in the Experimental Garden of the Department of Zoology and Environmental Sciences, Faculty of Life Sciences, Gurukula Kangri University Haridwar, for studying the irrigation effect of distillery effluent (DE) on soil characteristics. Pots (dia-30cm.) were used for the amendment of soil and were laid under completely randomized designed. The experiment was replicated by six times and was labeled for various treatments viz. 0 (control), 5, 10, 25, 50, 75 and 100%.

### 2.2. Effluent collection and analysis

Doon distillery Dehradun (Uttarakhand) which produces wine as its main product from molasses at the rate of 150 Kiloliter alcohols per day was selected for the collection of effluent samples. The effluents were collected from outlet of the secondary settling tank situated in the campus, installed by the distillery to reduce the BOD and solids using plastic container. The distillery effluent brought to the laboratory and was analyzed for various physico-chemical and microbiological parameters viz. TS, TDS, TSS, EC, turbidity and pH, DO, BOD, COD, Cl<sup>-</sup>, alkalinity, hardness, TKN, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, Fe, Zn, Cd, Cu, Cr, Pb, SPC and MPN following standard methods [8].

### 2.3. Soil preparation, filling of pots, irrigation pattern, sampling and analysis

The soil used was collected at a depth of 0 – 15 cm. Each pot (30x30cm.) was filled with 5 Kg well prepared soil, earlier air-dried and sieved to remove debris. The distillery effluent (DE) was applied weekly with 500 mL with its dilutions of 5, 10, 25, 50, 75 and 100% concentration at the rate of 5, 10, 25, 50, 75 and 100 ml/ Kg soil along with bore well water (control) in each of the forty two of pots. The pot soils were kept moist with effluent concentrations during the 12-week duration (growing period of most of the crops) of the experiment and no drainage were allowed. The soil was analyzed before and after effluent irrigation (12-week duration) as per effluent concentration for various physico-chemical following standard methods [40] for moisture content and EC, [12] for soil texture, [13] for bulk density, and WHC. The soil pH was determined using glass electrode pH meter and Cl<sup>-</sup>, OC, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, TKN, NO<sub>3</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> and heavy metals Zn, Cd, Cu, Cr and Pb were determined by using standard methods [8].

### 2.4. Heavy metals analysis

For heavy metal analysis, 5-10 ml sample of effluent and 0.5-1.0 g sample of air dried soil were taken separately in digestion tube and add 3 mL conc. HNO<sub>3</sub> was digested on electrically heated block for 1 h at 145° C. After that 4 mL of HClO<sub>4</sub> was added and heated to 240° C for an additional hour. The aliquot was cooled, filtered through Whatman # 42 filter paper. The volume was made up to 50 mL and used for analysis following standard methods [8]. The enrichment factor (Ef) for heavy metals accumulated in Paper mill effluent irrigated soil was calculated as follows [31]:

$$\text{Enrichment factor (Ef)} = \frac{\text{Mean metal concentration of sample}}{\text{Metal concentration of reference}}$$

### 2.5. Statistical analysis

Data were analyzed for one way analysis of variance (ANOVA) for determining the difference between soil parameters before and after irrigation with different effluent concentration, standard deviation, linear regression for soil parameters with effluent concentration were also calculated with the help of MS Excel, SPSS12.0 and Sigma plot, 2000.

## RESULTS AND DISCUSSION

### 3.1. Characteristics of effluent

The mean  $\pm$  SD values of physico-chemical and microbiological parameters TS, DS, SS, turbidity, EC, pH, DO, BOD, COD,  $\text{Cl}^-$ , alkalinity, hardness  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , TKN,  $\text{NO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Fe}^{2+}$ , Zn, Cd, Cu, Pb, Cr, SPC and MPN of distillery effluent (spent wash) are presented in Table 1.

The results revealed that the effluent was acidic in nature pH (5.28). Among various parameters, BOD ( $3265.50 \text{ mg L}^{-1}$ ), COD ( $8653.00 \text{ mg L}^{-1}$ ),  $\text{Cl}^-$  ( $1653.75 \text{ mg L}^{-1}$ ), alkalinity ( $764.50 \text{ mg L}^{-1}$ ), hardness ( $2139.00 \text{ mg L}^{-1}$ ),  $\text{Ca}^{2+}$  ( $1855.00 \text{ mg L}^{-1}$ ),  $\text{Fe}^{2+}$  ( $30.50 \text{ mg L}^{-1}$ ), TKN ( $572.50 \text{ mg L}^{-1}$ ),  $\text{NO}_3^{2-}$  ( $1455.25 \text{ mg L}^{-1}$ ),  $\text{SO}_4^{2-}$  ( $1246.00 \text{ mg L}^{-1}$ ), MPN ( $4.58 \times 10^6 \text{ 100 ml}^{-1}$ ), SPC ( $3.64 \times 10^{10} \text{ ml}^{-1}$ ), were not found to be in the prescribed limit of Indian Irrigation Standards (BIS, 1991). The acidic pH (5.5) and higher values of solids ( $3450 \text{ mg L}^{-1}$ ), alkalinity ( $1500 \text{ mg L}^{-1}$ ), BOD ( $1649 \text{ mg L}^{-1}$ ) and COD ( $2036 \text{ mg L}^{-1}$ ) and heavy metals viz. Cd, Cr, Ni and Zn content, low values of DO ( $0.34 \text{ mg L}^{-1}$ ) indicated the higher inorganic and organic load in distillery effluent of Mohan Meakin Distillery, Lucknow (U.P.), India [47].

### 3.2. Characteristics of soil

The mean  $\pm$  SD values of various physico-chemical characteristics and heavy metals moisture content; WHC, BD and pH, EC, ECEC,  $\text{Cl}^-$ , OC,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ , TKN,  $\text{NO}_3^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$  and Zn, Cd, Cu, Pb and Cr of the soil before and after irrigation with different concentrations of distillery effluent (DE) viz. 0% (BWW), 5%, 10%, 25%, 50%, 75% and 100% are given in the Tables.

The recent studies have indicated that the moisture content of the soil is useful and an important factor which affects the pH, availability of nutrient to plant and aeration. The moisture content and overall water content in soil at any moment are governed by the amount of water coming and going out from soil. Presence of large soil particles reduces the soil moisture content [15]. The water holding capacity is the amount of water, which is absorbed and retained by the given amount of the soil. Water holding capacity is related to the number and size distribution of soil pores and consequently increases with soil organic matter level. It is related to soil moisture content, textural class, structure, salt content and organic matter. The increase in case of coarse textured soil is larger than that in the fine textured soil. Bulk density of the soil changes with land use and management practices. Fertilizer use and application of organic manure to soil can substantially modify and lower the bulk density of the soil, which is useful for root development. It is used for determining the amount of pore space and water storage capacity of the soil. Organic matter supplied through the sludge and other kind of wastes also lower the bulk density [43].

Table1. Physico-chemical and microbiological characteristics of control (Bore well water) and Doon distillery effluent.

Parameter	Effluent concentration (%)							BIS for Drinking water	BIS for irrigation water
	0 (BWW)	5	10	25	50	75	100		
TS (mg L <sup>-1</sup> )	215.50±7.00	290.75±5.85	380.50±4.43	438.00±9.09	873.25±10.24	1409.50±14.82	1860.00±10.33	600	2100
TDS (mg L <sup>-1</sup> )	198.50±10.75	255.50±7.55	289.00±4.76	337.50±9.57	681.00±6.22	1003.00±8.41	1330.50±4.43	500	1900
TSS (mg L <sup>-1</sup> )	13.33±2.62	35.75±4.11	91.25±6.08	101.50±5.45	192.00±5.16	406.00±12.75	530.50±5.97	100	200
Turbidity (NTU)	4.46±2.56	12.25±3.22	14.64±4.25	18.84±3.85	32.26±4.32	56.48±4.16	65.75±3.86	4	10
EC(dS m <sup>-1</sup> )	1.34±0.19	3.07±0.21	3.77±1.03	6.87±1.42	12.00±1.83	17.50±1.29	21.46±2.58	-	-
pH	7.50±0.24	7.47±0.25	7.40±0.26	7.02±0.18	6.65±0.33	6.27±0.31	5.28±0.50	6.5-8.5	5.5-9.0
DO (mg L <sup>-1</sup> )	8.24±2.65	6.36±2.74	4.68±2.86	4.87±2.89	2.42±0.23	1.18±0.14	NIL	6-8	-
BOD (mg L <sup>-1</sup> )	3.83±0.59	164.00±7.48	334.25±10.28	850.50±15.00	1635.50±5.97	2462.50±11.82	3265.50±8.54	4.0	100
COD (mg L <sup>-1</sup> )	5.88±1.37	448.00±3.59	897.75±6.05	2231.00±11.94	4352.50±10.25	6495.50±11.82	8653.00±9.87	150-200	250
Cl <sup>-</sup> (mg L <sup>-1</sup> )	15.68±2.50	105.25±3.40	185.50±7.72	460.50±17.31	859.00±14.09	1248.00±10.95	1653.75±8.81	250	500
Alkalinity (mg L <sup>-1</sup> )	153.50±11.00	166.00±5.89	175.00±6.83	224.00±5.89	356.75±7.17	584.50±8.39	764.50±9.57	200	600
Hardness (mg L <sup>-1</sup> )	25.61±3.88	172.50±3.24	259.25±4.66	576.50±4.22	1112.50±3.36	1656±4.88	2139.00±8.99	300	600
HCO <sub>3</sub> <sup>-</sup> (mg L <sup>-1</sup> )	182.00±13.95	185.00±7.75	190.50±3.99	214.50±9.15	232.50±5.97	244.50±8.39	254.50±7.55	-	-
CO <sub>3</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	55.75±5.91	60.50±8.70	78.00±7.83	87.50±9.57	95.50±9.29	115.25±9.57	126.50±9.98	-	-
Na <sup>+</sup> (mg L <sup>-1</sup> )	9.65±1.25	14.00±1.63	27.50±3.42	69.00±8.41	138.00±6.81	217.00±5.29	277.00±9.31	-	-
K <sup>+</sup> (mg L <sup>-1</sup> )	5.54±2.25	35.00±5.29	61.50±3.42	154.50±7.00	278.00±7.12	408.75±7.72	536.50±9.29	-	-
Ca <sup>2+</sup> (mg L <sup>-1</sup> )	23.46±4.16	135.00±6.22	213.25±4.43	480.00±12.11	953.00±11.14	1425.00±10.00	1855.00±6.83	75	200
Mg <sup>2+</sup> (mg L <sup>-1</sup> )	12.15±1.50	37.50±4.43	46.00±5.89	96.50±8.39	159.50±3.42	231.00±5.29	284.00±11.78	-	-
TKN (mg L <sup>-1</sup> )	24.27±5.08	60.59±3.07	75.56±6.49	136.00±8.60	320.50±5.17	456.00±10.77	572.50±8.29		100
NO <sub>3</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	25.17±4.16	117.50±5.00	173.25±7.80	430.50±5.26	760.00±6.73	1139.50±7.72	1455.25±8.14	45	100
PO <sub>4</sub> <sup>3-</sup> (mg L <sup>-1</sup> )	0.04±0.00	32.00±4.32	66.50±5.97	168.00±7.12	323.00±8.08	476.50±9.71	637.50±9.15	-	-
SO <sub>4</sub> <sup>2-</sup> (mg L <sup>-1</sup> )	17.64±2.57	96.50±9.57	155.25±4.99	298.50±18.41	633.00±7.75	954.50±5.97	1246.00±10.58	200	1000
Fe <sup>2+</sup> (mg L <sup>-1</sup> )	0.28±0.04	1.53±0.30	3.05±0.60	7.75±1.71	15.25±2.99	22.75±4.27	30.50±5.97	0.30	1.0
Zn (mg L <sup>-1</sup> )	0.06±0.02	0.31±0.09	0.62±0.07	3.08±0.80	6.16±1.61	9.24±2.41	12.96±3.22	5.00	15
Cd (mg L <sup>-1</sup> )	0.01±0.00	0.13±0.04	0.26±0.02	0.74±0.06	1.67±0.11	2.99±0.17	3.33±0.22	0.01	2.00
Cu (mg L <sup>-1</sup> )	0.04±0.01	0.19±0.03	0.41±0.03	0.86±0.06	1.89±0.13	2.29±0.19	4.98±0.25	0.05	3.00
Pb (mg L <sup>-1</sup> )	0.02±0.01	0.09±0.02	0.18±0.01	0.45±0.03	0.91±0.06	1.36±0.09	1.81±0.12	0.05	1.00
Cr (mg L <sup>-1</sup> )	0.04±0.02	0.15±0.01	0.37±0.01	0.88±0.04	1.36±0.07	1.94±0.11	2.72±0.14	0.05	2.00
MPN(MPN100 ml <sup>-1</sup> )	2.56x10 <sup>2</sup> ±15.25	4.86x10 <sup>3</sup> ±236	6.75x10 <sup>3</sup> ±342	8.36x10 <sup>3</sup> ±423	4.56x10 <sup>4</sup> ±652	6.62x10 <sup>5</sup> ±864	4.58x10 <sup>6</sup> ±1000	50	5000
SPC(SPC ml <sup>-1</sup> )	63±6.20	3.84x10 <sup>4</sup> ±172	5.26x10 <sup>5</sup> ±211	7.42x10 <sup>6</sup> ±245	4.56x10 <sup>7</sup> ±231	2.36x10 <sup>8</sup> ±236	3.64 x10 <sup>10</sup> ±245	-	10000

Mean ± of four values; BWW - Borewell water; BIS- Bureau of Indian standard

Table 2. Physico-chemical characteristics of soil before and after irrigation with distillery effluent

Parameters	Before effluent irrigation	After effluent irrigation							F-calculated	Critical difference
		Effluent concentration (%)								
		0 (BWW)	5	10	25	50	75	100		
Soil moisture (%)	53.16±2.90	52.20±4.38	52.84±3.69 (+1.23)	54.64±6.14 (+4.67)	60.28±4.88 (+15.48)	62.92±2.79 (+20.54)	66.79±4.95 (+27.95)	68.29±6.04 (+30.82)	5.67NS	8.19
Soil texture	Loamy Sand	Loamy Sand	Loamy Sand	Loamy Sand	Loamy Sand	Loamy Sand	Loamy Sand	Loamy Sand	-	-
WHC (%)	49.54±1.77	48.32±3.96	49.28±4.09 (+1.98)	50.09±3.65 (+3.66)	52.46±5.82 (+8.57)	53.90±6.69 (+11.55)	54.70±6.48 (+13.20)	56.25±5.32 (+16.41)	0.96NS	8.96
BD (gm cm <sup>-3</sup> )	1.45±0.06	1.42±0.12	1.41±0.13 (-0.70)	1.38±0.13 (-2.81)	1.37±0.11 (-3.52)	1.36±0.10 (-4.22)	1.35±0.11 (-4.92)	1.34±0.12 (-5.63)	0.53NS	0.20

pH	7.99±18	7.50±0.26	7.47±0.25 (-0.40)	7.40±0.26 (-1.33)	7.02±0.18 (-6.40)	6.65a±0.33 (-11.33)	6.27a±0.31 (-16.40)	6.25a±0.85 (-16.67)	7.39***	0.60
EC (dS m <sup>-1</sup> )	2.21±0.69	2.08±0.08	2.42±0.32 (+16.35)	2.52a±0.14 (+21.15)	2.80a±0.13 (+34.61)	3.13a±0.20 (+50.48)	3.40a±0.13 (+63.46)	3.83a±0.33 (+84.13)	33.68***	0.31
ECEC (cmol kg <sup>-1</sup> )	10.24±1.26	12.00±1.03	12.83a±0.77 (+6.92)	15.64a±1.81 (+30.33)	21.80a±2.11 (+81.67)	24.81a±1.79 (+106.75)	28.43a±0.74 (+136.92)	31.28a±4.26 (+160.67)	52.64***	0.24
Cl <sup>-</sup> (mg Kg <sup>-1</sup> )	94.76±4.85	88.18±1.45	93.14±3.16 (+5.62)	97.14a±6.44 (+10.16)	123.26a±4.24 (+39.78)	173.70a±2.95 (+96.98)	261.52a±4.81 (+196.57)	346.00a±7.83 (+292.38)	1088.7***	8.87
OC(mg Kg <sup>-1</sup> )	0.54±11	0.43±0.10	0.99±0.10 (+130.23)	1.95a±0.19 (+353.48)	5.16a±0.38 (+1100.00)	9.81a±0.63 (+2181.40)	14.79a±1.43 (+3339.53)	16.82a±1.93 (+3811.63)	199.83***	1.40
HCO <sub>3</sub> <sup>-</sup> (mg Kg <sup>-1</sup> )	393.61±3.86	382.39±4.23	395.52a±6.31 (+3.43)	410.16a±8.19 (+7.26)	424.31a±6.55 (+10.96)	437.35a±4.29 (+14.37)	466.63a±5.07 (+22.02)	488.56a±4.15 (+27.76)	177.31***	8.41
CO <sub>3</sub> <sup>-2</sup> (mg Kg <sup>-1</sup> )	237.85±7.35	228.40±4.16	236.52a±5.87 (+3.55)	250.78a±6.33 (+9.80)	263.71a±4.17 (+15.46)	279.14a±2.91 (+22.21)	291.11a±4.17 (+27.46)	327.94a±3.45 (+43.58)	226.09***	6.74
Na <sup>+</sup> (mg Kg <sup>-1</sup> )	23.82±5.31	17.56±2.51	22.81±1.71 (+29.90)	24.22±2.95 (+37.93)	27.10a±4.57 (+54.33)	33.28a±3.48 (+89.52)	49.84a±3.09 (+183.83)	65.50a±3.70 (+273.01)	50.82***	7.11
K <sup>+</sup> (mg Kg <sup>-1</sup> )	171.51±5.30	154.09±2.70	160.63±3.74 (+4.24)	171.84a±5.48 (+11.52)	224.55a±8.21 (+45.73)	219.97a±9.85 (+42.75)	210.06a±4.30 (+36.32)	202.77a±6.03 (+31.59)	77.37***	9.76
Ca <sup>2+</sup> (mg Kg <sup>-1</sup> )	20.23±3.86	14.11±2.69	19.15±3.24 (+35.72)	23.56a±2.42 (+66.97)	132.54a±7.36 (+839.33)	129.92a±4.02 (+820.76)	122.03a±4.59 (+764.85)	117.08a±4.76 (+729.77)	498.99***	7.53
Mg <sup>2+</sup> (mg Kg <sup>-1</sup> )	1.77±0.04	1.68±0.59	3.43±0.77 (+104.17)	4.43±0.65 (+163.69)	21.04a±2.38 (+1152.38)	18.94a±5.62 (+1027.38)	16.75a±4.05 (+897.02)	14.12a±3.04 (+740.47)	28.49***	4.46
TKN(mg Kg <sup>-1</sup> )	35.91±2.18	30.96±4.09	58.63a±3.11 (+89.37)	74.50a±3.85 (+140.63)	144.08a±3.27 (+365.37)	285.18a±3.48 (+821.12)	405.50a±5.97 (+1209.75)	461.50a±5.00 (+1390.63)	3478.5***	8.75
NO <sub>3</sub> <sup>-2</sup> (mg Kg <sup>-1</sup> )	43.08±4.73	38.07±4.34	44.84a±3.64 (+17.78)	49.94a±4.26 (+31.17)	57.66a±4.24 (+51.45)	62.84a±3.73 (+65.06)	73.45a±3.80 (+92.93)	75.39a±5.12 (+98.02)	45.55***	6.16
PO <sub>4</sub> <sup>3-</sup> (mg Kg <sup>-1</sup> )	58.04±3.87	51.75±4.79	57.39±3.65 (+10.90)	66.78a±4.34 (+29.04)	70.56a±3.24 (+36.35)	121.06a±5.23 (+133.93)	173.27a±4.55 (+234.82)	226.56a±6.63 (+337.80)	453.43***	9.32
SO <sub>4</sub> <sup>2-</sup> (mg Kg <sup>-1</sup> )	78.14±2.85	73.12±2.37	79.09±3.33 (+8.16)	89.72a±6.86 (+22.70)	102.39a±8.43 (+40.03)	110.95a±5.19 (+51.73)	121.18a±8.92 (+65.73)	130.00a±9.52 (+77.79)	33.52***	10.84
Fe <sup>2+</sup> (mg Kg <sup>-1</sup> )	3.18±0.38	2.63±0.85	3.14±0.38 (+19.39)	3.63±0.40 (+38.02)	4.76a±0.37 (+80.99)	5.71a±0.44 (+117.11)	8.71a±0.54 (+231.18)	10.57a±2.21 (+301.90)	28.72***	1.64
Zn (mg Kg <sup>-1</sup> )	1.121±0.18	0.765±0.16	1.068±0.12 (+39.61)	1.405a±0.12 (+83.66)	2.481a±0.27 (+224.31)	2.745a±0.29 (+258.82)	3.275a±0.35 (+328.10)	3.315a±0.64 (+333.33)	42.28***	0.48
Cd (mg Kg <sup>-1</sup> )	0.082±0.06	0.040±0.05	0.096a±0.06 (+140.00)	0.101a±0.01 (+152.50)	0.160a±0.02 (+300.00)	0.166a±0.02 (+315.00)	0.213a±0.03 (+432.50)	0.266a±0.03 (+565.00)	17.65***	0.05
Cu (mg Kg <sup>-1</sup> )	2.162±0.32	2.003±0.33	2.199±0.32 (+9.78)	2.305±0.33 (+15.08)	5.049a±0.20 (+152.07)	6.667a±1.07 (+232.85)	9.420a±0.91 (+370.29)	10.367a±0.80 (+417.57)	116.55***	0.96
Pb (mg Kg <sup>-1</sup> )	0.017±0.01	0.016±0.01	0.041±0.00 (+156.25)	0.046±0.01 (+187.50)	0.096a±0.01 (+500.00)	0.155a±0.01 (+868.75)	0.236a±0.02 (+1375.00)	0.254a±0.09 (+1487.50)	27.29***	0.05
Cr (mg Kg <sup>-1</sup> )	0.119±0.05	0.104±0.06	0.248±0.01 (+138.46)	0.269±0.01 (+158.65)	0.572a±0.04 (+450.00)	0.883a±0.09 (+749.04)	1.381a±0.16 (+1227.88)	1.524a±0.38 (+1365.38)	49.37***	0.24

Mean ± of four values; Significant F - \*\*\*P > 0.1% level, r-Coefficient of correlation; % Increase or decrease in comparison to control given in parenthesis; a - significantly different to the control; NS - Not Significant; BWW - Borewell water.

The basic pH of the soil is to reduce 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 by the pH effect on activity of beneficial microorganisms. Most nitrogen fixing legume bacteria is not very active in strongly acidic soils. The acidification results in a gradual leaching of basic cations, e.g. (Ca<sup>2+</sup>, Mg<sup>2+</sup> and K<sup>+</sup>) from the uppermost horizons, leaving Al<sup>3+</sup> as the dominant exchangeable cation. Exchangeable Al<sup>3+</sup> is in equilibrium with soluble Al<sup>3+</sup> in the soil solution that can react with water to produce H<sup>+</sup> and thus acidify the soil. Clays, organic matter oxides of Al and Fe, Ca and Mg carbonates are the components responsible for pH buffering in most soils [41]. In the acidic soil environment the availability of the basic cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>) becomes lower due to leaching.

The soil having pH value 8.5 and above are expected to have more Na in the exchange complex and when unaccompanied by the presence of soluble salts, is classified as an alkaline soil [48]. A number of valuable constituents in the soil help to maintain its pH at certain original level. The EC of water and waste water is due to the presence of total dissolved solids. It 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 (i.e.  $EC > 4 \text{ dS m}^{-1}$ ) 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 ( $EC < 4 \text{ dS m}^{-1}$  and  $SAR > 13$  or  $ESP > 15$ ) high enough to control a soil's chemical attributes, they are known as sodic soils [41]. The ion exchange is one of the most significant functions that occur in soils. Ion exchange is a consequence of mineral charge that is derived from isomorphous substitution, broken edges, and pH dependent charge sites. For organic matter most of the charge is related to the pH dependent characteristics of organic acid functional groups. These charged sites are the result of ionization ( $H^+$  dissociation) or protonation of uncharged sites; ionization results in a negative charged site and protonation a positive charged site. Both of these reactions are dependent on pH and are called pH dependent charge. As the pH increases, the cation exchange capacity of the soil is generally greater due to an increase in the number of pH dependent charged sites. Under acidic soil conditions, some clay minerals, metal oxides and organic matter will have positively charged, anion exchange sites [13].

Organic matter plays an important role in the chemistry of soil. Soil properties associated with soil organic matter include soil structure, macro and micronutrients supply, cation exchange capacity and pH buffering. Soil organic matter can sorbs trace element pollutant, such as Pb, Cd, and Cu and Zn. Organic matter is the source of 90-95% of the nitrogen in unfertilized soil. It can also be the major source both available phosphorus and available sulfur when soil humus is present in appreciable amounts. Organic matter contributes to the cation exchange capacity, often furnishing 30-70 percent of the total amount. The large surfaces of humus have many cation exchange sites that adsorb nutrients for eventual plant use and temporarily adsorb heavy metals pollutants (Pb, Cd, and Cu) which are usually derived from applied waste water. Organic matter commonly increases water content at field capacity, increases available water content in sandy soil, and increases both air and water flow rates through fine textured soil [43].

The higher concentration of bicarbonates and carbonates increases the sodicity while their lower concentration increases the salinity of the soil. Alkaline soil tends to have high pH levels and significant amount of K, Ca, Na and Mg in the soil. Salinity and sodicity can influence the soil's structure, which in turn affects water infiltration and permeability by reducing water entry into the soil and its hydraulic conductivity. The major reason for the detrimental response to salts and Na is due to swelling of clay minerals. The higher concentration of Na in soil after effluent irrigation is associated with presence of higher concentration of carbonate, bicarbonate in the effluent [20].

The higher concentration of Na causes the decrease the bulk density as well as water holding capacity and porosity in clay soil due to deflocculating of clay particles in presence of higher Na content as it affects the cation exchange capacity in the soil and it adversely affects the seed germination and plant growth. Calcium and potassium are also an essential fertilizers element. They are essential for photosynthesis, protein synthesis, starch formation and translocation of sugars. It is important for grain formation and is absolutely necessary for tuber development. Effluent irrigation generally adds significant quantities of salts to the soil environment, such as sulfates, phosphates, bicarbonates, chlorides of the cations sodium, calcium, potassium and

magnesium that stimulate the growth at lower concentration but inhibit at higher concentration [49].

Potassium is the third most commonly added fertilizer nutrient (nitrogen is the most used; phosphorus is the second). Potassium is known to affect cell division, cell permeability formation of carbohydrates, translocation of sugars, various enzyme actions and resistance of some plants to certain diseases. Potassium,  $K^+$  is a very soluble cation in solution, yet it moves only slowly in soils. The K ions, on being adsorbed by the colloids, displace some other ions such as Ca, Mg or Na. Soils ability to absorb and hold K is of great importance as it serves to decrease leaching and provides more continuous supply of available K. The addition of any organic material to the soil that increases the production of carbonic, nitric or sulfuric acid favors the availability of phosphates. Soil usually contains sufficient quantities of iron for normal plant growth. Its availability varies widely with the degree of soil aeration, being higher under anaerobic conditions. The movement and activity of the iron with in plants are reduced in some manner by the presence of excess calcium. The soil cation exchange sites also attract potassium ions from water, reducing the potassium mobility through soil. Potassium because a positive ion, has limited ability to move through the soil. Potassium fertilizers should be placed in the soil where roots have good access to potassium [15].

Nitrate is the most essential and available form of nitrogen to plants because plant roots take up nitrogen in the form of  $NO_3^{2-}$  and  $NH_4^+$ . 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 exceed the soil nitrate immobilization potential, a state of N-saturation is said to exist (10, 19, 28). As nitrate immobilization is believed to be mediated biologically, N-saturation has been related to nitrate input, successional status of the vegetation, season, temperature and availability of other nutrients [28].

It was observed that various concentration (25%, 50%, 75% and 100%) of the Mohan Meak & Breweries Ltd, Ghaziabad, UP, India (MMBL) effluent were rich in ammonia nitrogen, nitrate-nitrogen, phosphorus and potassium, so that its application to the soil increased the values of available nutrients in the soil. The upper soil had high values of N, P, K and organic matter compared with the lower soil in the pots used. The pH of the soil decreased gradually with increasing concentration of the effluent. Depletion was noted in the  $CaCO_3$  content of the soil irrigated with 100% and 75% effluent, while it increased with 50% and 25% effluent. The highest perturbation was observed in the available potassium of the soil, when 100% effluent was used for irrigation followed by 75%, 50% and 25%, and the values of organic matter, ammonia-nitrogen and phosphorus also increased significantly [35]. The long term application of PME proved useful in significantly increasing TOC, TKN, K, P and soil enzymatic activities in the soil but tended to build up harmful concentration of Na that could be chelated by bioamendments. In short terms studies, application of 50% PME along with bioamendments proved to be the most useful in improving the properties of sodic soil [5].

The use of distillery effluent, a waste by-product of distillery industries as irrigation water or as a soil amendment showed significant effect on soil organic carbon of Vertisol [34]. It was observed that variability of soil pH, organic matter (OM), cation exchange capacity (CEC), total



nitrogen (TN), total phosphorus (TP), available phosphorus and available potassium on Cambosols and Anthrosols in Zhangjiagang County, China due to increase the annual application of N fertilizer and P fertilizer rates [2]. Fertilizer input rates are causing nutrient imbalances, contributing to acidification in Anthrosols, and decreasing C/N ratios. The use of paper mill lime sludge as a soil amendment in an acidic soil was significantly increased pH, which was proportional to the application rate of paper mill sludge. The application of 2% sludge (based on soil dry mass) remarkably increased shoot dry matter and P, K, Fe, Mn, K and P uptake [6]. It was observed that the soil was treated with seven rates of abattoir effluent (viz. 0, 25, 50, 100, 125 and 150 ml/kg soil), the effluent application increased pH, available P and micronutrients (Zn, Mn and Fe) significantly in the soil whilst exchangeable cations were reduced significantly when compared to the control [39].

**Table 3. Regression linear equation between Doon distillery effluents and soil characteristics**

Effluent/soil characteristics	Regression equation	R <sup>2</sup>
Distillery effluent versus soil moisture content	$y = 53.376 + 0.1673x$	0.938
Distillery effluent versus soil WHC	$y = 49.303 + 0.075x$	0.928
Distillery effluent versus soil BD	$y = 1.4023 - 0.0007x$	0.813
Distillery effluent versus soil pH	$y = 7.4669 - 0.014x$	0.950
Distillery effluent versus soil EC	$y = 2.2927 + 0.0156x$	0.966
Distillery effluent versus soil ECEC	$y = 13.653 + 0.1933x$	0.937
Distillery effluent versus soil Cl <sup>-</sup>	$y = 72.089 + 2.5597x$	0.974
Distillery effluent versus soil OC	$y = 0.5247 + 0.1746x$	0.987
Distillery effluent versus soil HCO <sub>3</sub> <sup>-</sup>	$y = 392.24 + 0.9782x$	0.972
Distillery effluent versus soil CO <sub>3</sub> <sup>2-</sup>	$y = 234.89 + 0.8806x$	0.962
Distillery effluent versus soil Na <sup>+</sup>	$y = 17.684 + 0.4397x$	0.959
Distillery effluent versus soil K <sup>+</sup>	$y = 173.63 + 0.485x$	0.406
Distillery effluent versus soil Ca <sup>2+</sup>	$y = 37.55 + 1.1153x$	0.560
Distillery effluent versus soil Mg <sup>2+</sup>	$y = 6.5209 + 0.1311x$	0.387
Distillery effluent versus soil TKN	$y = 36.62 + 4.5434x$	0.987
Distillery effluent versus soil NO <sub>3</sub> <sup>2-</sup>	$y = 44.06 + 0.3539x$	0.924
Distillery effluent versus soil PO <sub>4</sub> <sup>3-</sup>	$y = 43.813 + 1.7384x$	0.979
Distillery effluent versus soil SO <sub>4</sub> <sup>2-</sup>	$y = 80.611 + 0.5365x$	0.931
Distillery effluent versus soil Fe <sup>2+</sup>	$y = 2.6618 + 0.0774x$	0.984
Distillery effluent versus soil Zn	$y = 1.1865 + 0.0256x$	0.858
Distillery effluent versus soil Cd	$y = 0.0855 + 0.0018x$	0.918
Distillery effluent versus soil Cu	$y = 2.0124 + 0.0903x$	0.973
Distillery effluent versus soil Pb	$y = 0.0302 + 0.0024x$	0.971
Distillery effluent versus soil Cr	$y = 0.1554 + 0.0147x$	0.983

### 3.2.1. Moisture content, soil texture, WHC and BD

During the present study, the soil moisture content was increased (52.20 to 68.29%) on irrigation with different concentrations of the distillery effluent (DE). The increasing dose of DE appreciably reduced the bulk density (BD) of the surface soil (Table 2). The BD was minimum (1.42 g cm<sup>-3</sup>) in 100% of DE followed by 75%, 50%, 25%, 10% and 5%. The BD was maximum

(1.42 g cm<sup>-3</sup>) in control, which was insignificantly different ( $P > 0.05$ ) with the concentrations of DE. The available water content varied from the control soil 48.32% to 56.25% with 100% concentration of DE (Table 2). The ANOVA analysis on data showed that the soil moisture content, WHC and BD was recorded to be insignificantly ( $P > 0.05$ ) different with different concentration of DE in comparison to control irrigated soil (Table 2). The regression equation and  $R^2$  value, 93%, 92% and 93% of the variation in soil moisture, WHC and BD content was represented for by DE (Table 3). During present study, the soil characteristics have been found to change on irrigation with DE. It was observed that the soil particle size depicted that the experimental soil was of loamy sand type (Table 3).

This reduction in BD was due to higher organic matter content in the treatments where DE was added in higher doses. The reduction in BD with addition of organic matter was also reported earlier [14, 46]. The BD showed an insignificant ( $P > 0.05$ ) and negative linear relationship with the soil organic carbon. The negative linear relationship was found between soil organic matter content and BD on a soil amended with increasing rates of poultry manure application [55]. It was reported that the increase in retention of soil water with an increase in waste application rate [54, 55]. An increased WHC at low tensions such as FC was primarily due to increased number of small pores caused by the improvement in aggregation in the soil [46]. Treatment differences had not shown any significant effect on the WHC. The moisture content of soil is useful and an important factor which affects the pH, availability of nutrient to plant and aeration. The moisture content and overall water content in soil at any moment are governed by the amount of water coming and going out from soil. Presence of large soil particles reduces the soil moisture content [15, 45]. Water holding capacity is related to the number and size distribution of soil pores and consequently increases with soil organic matter level. It is related to soil moisture content, textural class, structure, salt content and organic matter [29]. It was found that water content of soils did not change with the rate and type of organic matter [9]. Organic matter supplied through the sludge and other kind of wastes also lower the bulk density as stated by [43]. The decrease in moisture content from control irrigated soil (45.33%) to (38.67%) in 100% concentration of paper mill effluent irrigated soil was also reported earlier [53]. The higher concentration of Na in soil after effluent irrigation is associated with presence of higher concentration of carbonate, bicarbonate in the effluent [20]. Higher concentration of Na causes the decrease the bulk density as well as WHC by decreasing the porosity in clay soil due to deflocculating of clay particles in presence of high Na content as it affects the cation exchange capacity in the soil.

### **3.2.2. pH and EC**

The soil pH was recorded slightly alkaline (7.50) at initial (control) level and it was turned to acidic (6.25) with 100% concentration of DE. The effluent concentration 50%, 75% and 100% of DE showed significant ( $P < 0.001$ ) effect on soil pH in comparison to control soil (Table 2). The regression equation and  $R^2$  value, 95% of the variation in soil pH was recorded for by DE (Table 3). Soil pH change to acidic with application of DE significantly. High buffering capacity of the clay soil and nominal presence of any weak salts namely carbonates or bicarbonates, which on dissolution release free cations, might be the possible causes for the stability of the soil reaction. This is the pH range of maximum nutrient availability in the soils [36]. The pH levels that resulted from the different levels of pollution appeared favourable to both biological and chemical reactions in the soils [36].

The increase in the rate of application of effluent significantly ( $P < 0.001$ ) increased the EC of the soil (Table 2). It was recorded to be significantly different with 10% to 100% concentration of DE in comparison to control soil. The effluent treated plots registered significantly higher EC ( $3.83 \text{ dS m}^{-1}$ ) than control ( $2.08 \text{ dS m}^{-1}$ ) this was due to very high salt load ( $21.46 \text{ dS m}^{-1}$ , EC) of the DE. The regression equation and  $R^2$  value, 96% of the variation in soil EC was recorded for by DE (Table 3). Similar findings were also reported by [33, 42]. The increase in EC from control irrigated soil ( $1.03 \text{ dS m}^{-1}$ ) to ( $2.26 \text{ dS m}^{-1}$ ) in 100% concentration of paper mill effluent irrigated soil was also reported earlier [53].

The build-up of salt concentration with DE application, particularly at higher rate of application, is a cause of concern for its application. In the long run indiscriminate application of DE may create problem of soil salinity. The acidification results in a gradual leaching of basic cations, e.g. calcium ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$ ) from the uppermost horizons, leaving  $\text{Al}^{3+}$  as the dominant exchangeable cation. Exchangeable  $\text{Al}^{3+}$  is in equilibrium with soluble  $\text{Al}^{3+}$  in the soil solution that can react with water to produce  $\text{H}^+$  and thus acidify the soil [20].

### 3.2.3. Effective cation exchange capacity

The ECEC was increased in the DE irrigated soil were increased significantly from initial level 12.00-31.28  $\text{cmol Kg}^{-1}$  in 100% of DE. The ECEC of the DE irrigated soil was found to be significantly ( $P < 0.001$ ) different with 5% to 100% concentrations of DE (Table 2). The regression equation and  $R^2$  value, 93% of the variation in soil ECEC was recorded for by DE (Table 3).

### 3.2.4. Chlorides

The chlorides in the DE irrigated soil were increased with the effluent concentration increased. The DE concentrations 10, 25, 50, 75 and 100% showed significant ( $P < 0.001$ ) effect on chlorides of the soil in comparison to control soil (Table 2). The regression equation and  $R^2$  value, 97% of the variation in soil chlorides was recorded for by DE (Table 3). Chlorides in the DE irrigated soil were increased significantly from initial level 88.18-346.00  $\text{mg Kg}^{-1}$  in 100% of DE. The increase in chlorides from control irrigated soil ( $32.32 \text{ mg Kg}^{-1}$ ) to ( $50.87 \text{ mg Kg}^{-1}$ ) in 100% concentration of paper mill effluent irrigated soil was also reported earlier [53].

### 3.2.5. Organic carbon

The organic carbon content of the soil increased considerably with the application of DE. It increased from an initial level of 0.43–16.82  $\text{mg Kg}^{-1}$  in 100% of DE. The soil organic carbon was found to be significantly ( $P < 0.001$ ) different with 10% to 100% concentrations of DE (Table 2). The regression equation and  $R^2$  value, 98% of the variation in soil organic carbon was recorded for by DE (Table 3). Addition of organic matter through effluent and better crop growth with concomitant increase in root biomass could be the probable reasons for the improvement in organic carbon content particularly in high DE treated plots. The results of the authors support these findings [24, 37].

### 3.2.6. Bicarbonates and carbonates

The bicarbonates and carbonates content of the soil increased significantly with the appliance of DE. It increased from an initial level of 382.39–488.56  $\text{mg Kg}^{-1}$  and 228.40–327.94  $\text{mg Kg}^{-1}$  in 100% of DE respectively. The effluent concentration 5% to 100% of DE showed significant ( $P < 0.001$ ) affect on bicarbonates and carbonates in the DE effluent irrigated soil (Table 2). The

regression equation and  $R^2$  value, 97% and 96% of the variation in soil bicarbonates and carbonates were recorded for by DE (Table 3). Clays, organic matter oxides of Al and Fe, Ca and Mg carbonates are the components responsible for pH buffering in most soils. The soil pH can also influence plant growth by the pH effect on activity of beneficial microorganisms. Most nitrogen fixing legume bacterial is not very active in strongly acidic soils. Bacteria that decompose organic matter and thus release nitrogen and other nutrients for plant use are also hindered by strong acidity.

### **3.2.7. Exchangeable sodium, potassium, calcium and magnesium**

On irrigation of the soil with of DE the exchangeable sodium, potassium, calcium and magnesium were found to be changed with different concentrations of the effluent. The effluent concentrations 25%, 50%, 75% and 100% of DE showed significant ( $P<0.001$ ) change in the content on Na, K, Ca and Mg in comparison to control soil. It was quite interesting to note that the content of K, Ca and Mg were also recorded to be significantly ( $P<0.001$ ) different with 10% concentration of DE (Table 2). The regression equation and  $R^2$  value, 95%, 40%, 56% and 38% of the variation in soil Na, K Ca and Mg were found for by DE (Table 3). The content of exchangeable sodium, potassium, calcium and magnesium were increased significantly from an initial (control) level of 17.56-65.50 mg Kg<sup>-1</sup>, 154.09-202.77 mg Kg<sup>-1</sup>, 14.11-117.08 mg Kg<sup>-1</sup> and 1.68-14.12 mg Kg<sup>-1</sup> in 100% of DE respectively. The increase in Na, K and Ca from control irrigated soil (42.86 mg Kg<sup>-1</sup>, 129.29 mg Kg<sup>-1</sup>, and 51.05 mg Kg<sup>-1</sup>) to (59.49 mg Kg<sup>-1</sup>, 146.83 mg Kg<sup>-1</sup> and 60.59 mg Kg<sup>-1</sup>) respectively in 100% concentration of paper mill effluent irrigated soil was also reported earlier [53].

### **3.2.8. Total nitrogen, nitrate, phosphate and sulphates**

The content of total nitrogen, nitrate, phosphate and sulphates were increased significantly from an initial (control) level of 35.91-461.50 mg Kg<sup>-1</sup>, 38.07-75.39 mg Kg<sup>-1</sup>, 51.75-226.56 mg Kg<sup>-1</sup> and 73.12-130.00 mg Kg<sup>-1</sup> in 100% of DE respectively. The effluent concentrations 10%, 25%, 50%, 75% and 100% of DE showed significant ( $P<0.001$ ) change in the content of total nitrogen, nitrate, phosphate and sulphate in comparison to control soil. It was quite interesting to note that the content of total nitrogen, nitrate and sulphate were also recorded to be significantly ( $P<0.001$ ) different with 5% concentration of DE (Table 2). The regression equation and  $R^2$  value 98%, 92%, 97% and 93% of the variation in soil total nitrogen, nitrate, phosphate and sulphate were found for by DE (Table 3). The increase in nitrate, phosphate and sulphate from control irrigated soil (31.01 mg Kg<sup>-1</sup>, 11.96 mg Kg<sup>-1</sup> and 41.41 mg Kg<sup>-1</sup>) to (42.31 mg Kg<sup>-1</sup>, 19.53 mg Kg<sup>-1</sup> and 52.02 mg Kg<sup>-1</sup>) respectively in 100% concentration of paper mill effluent irrigated soil was also reported earlier [53].

**Table 4. Enrichment factor of various micronutrients in soil after irrigation with Doon distillery effluent**

Heavy metals	Enrichment factor (Ef) in soil
Zn	4.33
Cd	6.65
Cu	5.17
Pb	15.87
Cr	14.65

### 3.2.9. Micronutrients

The concentration of micronutrients viz. Fe, Zn, Cd, Cu, Pb, and Cr were recorded to be significantly ( $P < 0.001$ ) affected with 25% to 100% concentration of DE. The content of Zn and Cd were also found significantly ( $P < 0.001$ ) affected with 10% concentration of DE. It was quite interesting to note that the concentration of Cd in effluent irrigated soil was also found to be significantly ( $P < 0.001$ ) different with 5% concentration of DE (Table 2). The regression equation and  $R^2$  value, 98%, 85%, 91%, 97%, 97% and 98% of the variation in soil Fe, Zn, Cd, Cu, Pb, and Cr were recorded for by DE (Table 3). Among the micronutrients the maximum enrichment factor (Ef) was shown by Pb (15.87) while the minimum by Zn (4.33) and it was in order of Pb>Cr>Cd>Cu>Zn after irrigation with DE (Table 4). 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 [41]. The content of Fe, Zn, Cd, Cu, Pb and CR were increased significantly with the application of DE. It increased from an initial (control) level of 2.63–10.57 mg Kg<sup>-1</sup>, 0.765–3.315 mg Kg<sup>-1</sup>, 0.040–0.266 mg Kg<sup>-1</sup>, 2.003–10.367 mg Kg<sup>-1</sup>, 0.016–0.254 mg Kg<sup>-1</sup> and 0.104–1.524 mg Kg<sup>-1</sup> in 100% of DE respectively. This is in agreement with which was reported by other workers that organic wastes contain high amounts of macro and micronutrients [16, 17].

## CONCLUSION

The present study concluded that the effluent of the Doon distillery Dehradun (Uttarakhand) decreased the pH and moisture content and increased it, WHC, bulk density EC, Cl<sup>-</sup>, OC, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-2</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup>, TKN, NO<sub>3</sub><sup>-2</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> and Zn, Cd, Cu, Pb and Cr of the soil. The micronutrients such as Fe, Zn, Cd, Cu, Pb and Cr was also recorded higher in the soil irrigated with distillery effluent (DE) which leads to toxicity of soil at higher concentration in comparison to control. The results indicate that nutrients and trace elements of DE irrigation contributed some significant changes to the soil quality and affected the natural composition of the soil. Such alterations improved the fertility and enhanced the nutrients status of soil at lower concentration of effluent irrigation. Thus, effluent irrigation improved the soil nutrient status. All effluent concentrations were better than the control in nutrient accumulation. The enrichment factor (Ef) indicated the order of accumulation of various heavy metals in the soil after DE irrigation. Among various micronutrients the maximum enrichment factor (Ef) was shown by Pb and minimum by Zn and it was in order of Pb>Cr>Cd>Cu>Zn after irrigation with DE. Thus application of DE to the agricultural field, as an amendment, might be a viable option for the safe disposal of this industrial waste with improvement in physico-chemical properties of the soil. However, the level of application should be within the prescribed limit to avoid development of soil salinity in the long run.

### Acknowledgements

The University Grants Commission, New Delhi, India is acknowledged for providing the financial support in the form of UGC research fellowship (F.7-70/2007-09 BSR) to Dr. Vinod Kumar.

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