Alterations in physico-chemical characteristics of soil after irrigation with Paper mill effluent

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ABSTRACT
The effect of paper mill effluent on the physico-chemical properties of soils was studied under natural environment in pots experiment. The soil was treated to six rates of effluent viz. 5, 10, 25, 50, 75 and 100 ml/Kg soil. The physico-chemical properties of the soil were determined before and at the end of the experiment, 12 weeks after irrigation with the effluent. Results revealed that among various concentrations of paper mill effluent, irrigation with 100% effluent concentration decreased moisture content (18.84%), WHC (13.26%), BD (5.63%) and increased pH (6.48%), EC (50.96%), ECEC (111.75%), Cl⁻ (101.53%), OC (2213.95%), HCO₃⁻ (15.64%), CO₃²⁻ (24.64%), Na⁺ (113.04%), K⁺ (48.27%), Ca²⁺ (977.20%), Mg²⁺ (1236.31%), Fe²⁺ (127.76%), TKN (826.87%), NO₃⁻ (74.96%), PO₄³⁻ (141.72%), SO₄²⁻ (56.98%), Zn (264.71%), Cu (230.94%), Cd (340.00%), Pb (968.75%) and Cr (797.11%) in the soil. Different effluent concentrations showed significant (P<0.001) effect on EC, pH, Cl⁻, OC, HCO₃⁻, CO₃²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺, TKN, NO₃⁻, PO₄³⁻ and SO₄²⁻, Zn, Cu, Cd, Cr and Pb and insignificant (P>0.05) effect on, moisture content, WHC and bulk density after irrigation when compared to the control. The enrichment factor (Ef) of various micronutrients was in the order Pb>Cr>Cd>Zn>Cu.

Keywords: Paper mill effluent, irrigation, soil characteristics, micronutrients, enrichment factor.

INTRODUCTION
In the agriculture, irrigation water quality is believed to have effects on the soil and agricultural crops. [61; 64; 65]. The use of saline water may result in the reduction of crop yield, while the sodic water may deteriorate the physical properties of the soil with consequent reduction in the crop yield [35; 65; 66]. However, wastewater irrigation transports a wide variety of elements into
the soil environment [9; 15; 17]. Some of these elements, such as nitrogen, phosphorous, and potassium are important plant nutrients and may contribute to higher crop yields if these elements are deficient at the application site. Effluents from industries contain appreciable amount of metallic cations like zinc, copper, iron, manganese, lead, nickel and cadmium [3; 43]. Long term irrigation with such effluents increases organic carbon content, heavy metal accumulation in soil and the chances of their entrance in food chain and that may ultimately cause significant bioaccumulation [63].

The nature of the soil is one of the most important factors in determining the heavy metal content of food plants [21; 65; 66]. However, the heavy metal content in plants can also be affected by other factors such as the application of fertilizers, sewage sludge or irrigation with wastewater [11; 27]. Thus the effect of water on soil and crops are of major concern to people when the irrigant is wastewater which may contain agents capable of inducing adverse effects on the soil media and the agricultural products.

The various elements introduced through pulp mill wastewater irrigation not only affect the crop growth and soil properties but also their relative mobility in the soil profile [26; 67]. 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. Due to the high chemical diversity of the organic pollutants in pulp and paper mill process water, a high variety of toxic effects on aquatic communities in recipient water courses have been observed [34; 44; 45]. 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 [29].

Pulp and paper mill is a major industrial sector utilizing a huge amount of lignocellulologic materials and water during the manufacturing process, and release chlorinated lignosulphonic acids, chlorinated resin acids, chlorinated phenols and chlorinated hydrocarbon in the effluent [56]. The highly toxic and recalcitrant compounds, dibenzo-p-dioxin and dibenzofuran, are formed unintentionally in the effluent of pulp and paper mill [47]. At present, there are 666 pulp and paper mills in India, of which 632 units are agro-residue and recycled fiber based units [14]. They generate a large amount of wastewater (black liquor) having high COD and BOD values. Effluent of Kraft mill is highly polluted, and characterized by parameters unique to this waste such as color, absorbable organic halides and related organic compound [18; 53]. The high chlorine contents of bleached plant react with lignin and its derivatives and form highly toxic and recalcitrant compounds that are responsible for higher biological and chemical oxygen demand. Trichlorophenol, trichloroguicol, dichlorophenol, dichloroguicol and pentachlorophenol are major contaminants formed in the effluent of pulp and paper mill [16; 57].

The utilization of industrial waste as soil amendment has generated interest in recent times. Besides this most crops give higher potential yields with 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 effect on agronomical practices [1; 3; 6; 16; 30; 33; 36; 59; 64; 65; 66].
EXPERIMENTAL SECTION

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

2.2. Effluent collection and analysis
Star paper mill, Saharanpur (Uttar Pradesh) which produces paper as its main product from agro based residues 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 Paper mill to reduce the BOD and solids using plastic container. The paper mill effluent was brought to the laboratory and analyzed for various physico-chemical and microbiological parameters viz. Total dissolved solids (TDS), EC, pH, DO, BOD, COD, Cl\(^-\), Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), TKN, NO\(_3\)^2-, PO\(_4\)^3-, SO\(_4\)^2-, HCO\(_3\)^-, CO\(_3\)^2-, Fe, Zn, Cd, Cu, Cr Pb, Standard plate count (SPC) and Most probable numbers (MPN) following standard methods [5].

2.3. Soil preparation, filling of pots, 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 Paper mill effluent (PME) was applied weekly with 500 mL with its dilutions of 5, 10, 25, 75 and 100% concentration at the rate of 5, 10, 25, 50, 75 and 100 ml/ Kg soil. Borewell water (BWW) was used for the dilution of paper mill effluent. The pot soils were kept moist with effluent concentrations during the 12-week duration (growing period of most of the crops) and no drainage was allowed. The soil was analyzed before and after effluent irrigation as per effluent concentration for various physico-chemical parameters following standard methods, Buurman et al., [48] for moisture content and EC, Bouyoucos [23] for soil texture, Carter [68] for bulk density, and WHC. The soil pH was determined using glass electrode pH meter and effective cation exchange capacity (ECEC), Cl\(^-\), OC, HCO\(_3\)^-, CO\(_3\)^2-, Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Fe\(^{2+}\), TKN, NO\(_3\)^2-, PO\(_4\)^3- and SO\(_4\)^2- and heavy metals Zn, Cd, Cu, Cr and Pb were determined using standard methods [52].

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\(_3\) was digested on electrically heated block for 1 h at 145 °C. After that 4 mL of HClO\(_4\) 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 [52]. The enrichment factor (Ef) for heavy metals accumulated in paper mill effluent irrigated soil was calculated [34] as follows:

Keeping in view of the above facts, a field experiment was conducted to study the effect of graded doses of paper mill effluent application on the physical and physico-chemical properties of a loamy sand soil.
2.5. Statistical analysis

Data was analyzed for one way analysis of variance (ANOVA) for determining the difference between soil parameters before and after irrigation with different effluent concentrations. The mean and standard deviation for different parameters of the effluent and soil 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 ± SD values of physico-chemical and microbiological parameters TDS, EC, pH, DO, BOD, COD, Cl⁻, HCO₃⁻, CO₃²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, TKN, NO₃⁻, PO₄³⁻, SO₄²⁻, Fe²⁺, Zn, Cd, Cu, Pb, Cr, SPC and MPN of Paper mill effluent (black liquor), Saharanpur and borewell water (BWW) are given in Table 1.

The results revealed that the effluent was alkaline in nature (pH, 8.48). Among various parameters of effluent (100%), TDS (3097.68 mg L⁻¹), BOD, (1226.50 mg L⁻¹), COD (2832.50 mg L⁻¹), Cl⁻ (839.50 mg L⁻¹), Ca²⁺ (439.50 mg L⁻¹), Fe²⁺ (15.25 mg L⁻¹), NO₃⁻ (378.50 mg L⁻¹), MPN (5.69x10⁶ MPN100 ml⁻¹), SPC (9.89x10⁷ SPC ml⁻¹) were not found in the prescribed limit of Indian irrigation standards [10]. The higher values of BOD (1226.50) and COD (2832.50) indicated the higher inorganic and organic load in Paper mill effluent.

3.2. Characteristics of soil

The mean ± SD values of various physico-chemical characteristics and heavy metals moisture content; WHC, BD and pH, EC, ECEC, Cl⁻, OC, HCO₃⁻, CO₃²⁻, Na⁺, K⁺, Ca²⁺, Mg²⁺, Fe²⁺, TKN, NO₃⁻, PO₄³⁻, SO₄²⁻ and Zn, Cd, Cu, Pb and Cr of the soil before and after irrigation with different concentrations of paper mill effluent (PME), Saharanpur viz. 5%, 10%, 25%, 50%, 75% and 100% are given in the Table 2.

3.2.1. Moisture content, Soil texture, WHC and BD

Haynes and Naidu [54] and Celik [28] reported a reduction in BD with addition of organic matter. Weil and Kroontje [55] observed a negative correlation between soil organic matter and BD on a soil amended with increasing rates of poultry manure application. Webber [38], Weil and Kroontje [55] have reported increased retention of soil water with an increase in waste application rate. An increase in WHC at low tensions such as field capacity (FC) was primarily due to increased number of small pores caused by the improvement in aggregation in the soil [54]. Barzegar et al. [8] observed that water content of soil did not change with the rate and type of organic matter. Organic matter supplied through the sludge and other kind of wastes also lowered the bulk density as stated by Ramulu [60].
### Table 1. Physico-chemical and microbiological and heavy metal characteristics of control (Bore well water) and Star paper mill effluent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Effluent concentration</th>
<th>BIS for Drinking water</th>
<th>BIS for Irrigation water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 (BWW)</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>TDS (mg L$^{-1}$)</td>
<td>345.64±2.18</td>
<td>860.24±6.75</td>
<td>1420.82±7.28</td>
</tr>
<tr>
<td>EC (m S$^{-1}$)</td>
<td>0.54±0.11</td>
<td>1.34±0.19</td>
<td>2.22±0.24</td>
</tr>
<tr>
<td>pH</td>
<td>7.50±0.24</td>
<td>7.54±0.23</td>
<td>7.65±0.24</td>
</tr>
<tr>
<td>DO (mg L$^{-1}$)</td>
<td>8.24±2.65</td>
<td>5.36±4.28</td>
<td>4.22±2.44</td>
</tr>
<tr>
<td>BOD (mg L$^{-1}$)</td>
<td>5.88±1.37</td>
<td>145.00±5.16</td>
<td>283.00±4.16</td>
</tr>
<tr>
<td>COD (mg L$^{-1}$)</td>
<td>3.83±0.59</td>
<td>70.39±3.70</td>
<td>129.00±6.22</td>
</tr>
<tr>
<td>Cl$^-$ (mg L$^{-1}$)</td>
<td>15.68±2.50</td>
<td>64.50±7.00</td>
<td>104.25±8.02</td>
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<tr>
<td>HCO$_3^-$ (mg L$^{-1}$)</td>
<td>282.00±13.95</td>
<td>264.96±5.88</td>
<td>275.67±4.92</td>
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<tr>
<td>CO$_3^{2-}$ (mg L$^{-1}$)</td>
<td>105.75±5.91</td>
<td>119.70±2.74</td>
<td>130.41±3.28</td>
</tr>
<tr>
<td>Na$^+$ (mg L$^{-1}$)</td>
<td>9.65±1.25</td>
<td>34.87±5.19</td>
<td>62.51±3.85</td>
</tr>
<tr>
<td>K$^+$ (mg L$^{-1}$)</td>
<td>5.54±2.25</td>
<td>19.42±2.31</td>
<td>23.06±2.84</td>
</tr>
<tr>
<td>Ca$^{2+}$ (mg L$^{-1}$)</td>
<td>23.46±4.16</td>
<td>60.47±3.50</td>
<td>70.68±3.62</td>
</tr>
<tr>
<td>Mg$^{2+}$ (mg L$^{-1}$)</td>
<td>12.15±1.50</td>
<td>19.24±2.17</td>
<td>22.08±2.80</td>
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<tr>
<td>TKN (mg L$^{-1}$)</td>
<td>24.27±5.08</td>
<td>33.02±3.34</td>
<td>37.46±4.14</td>
</tr>
<tr>
<td>NO$_3^-$ (mg L$^{-1}$)</td>
<td>25.17±4.16</td>
<td>50.03±3.23</td>
<td>64.43±3.81</td>
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<tr>
<td>PO$_4^{3-}$ (mg L$^{-1}$)</td>
<td>0.04±0.00</td>
<td>8.75±0.80</td>
<td>18.37±3.26</td>
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<tr>
<td>SO$_4^{2-}$ (mg L$^{-1}$)</td>
<td>17.64±2.57</td>
<td>51.31±3.66</td>
<td>79.12±5.23</td>
</tr>
<tr>
<td>Fe$^{2+}$ (mg L$^{-1}$)</td>
<td>0.28±0.04</td>
<td>0.70±0.01</td>
<td>1.64±0.15</td>
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<tr>
<td>Zn (mg L$^{-1}$)</td>
<td>0.06±0.02</td>
<td>0.32±0.07</td>
<td>0.67±0.04</td>
</tr>
<tr>
<td>Cd (mg L$^{-1}$)</td>
<td>0.01±0.00</td>
<td>0.13±0.01</td>
<td>0.32±0.03</td>
</tr>
<tr>
<td>Cu (mg L$^{-1}$)</td>
<td>0.04±0.01</td>
<td>0.10±0.01</td>
<td>0.23±0.08</td>
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<tr>
<td>Pb (mg L$^{-1}$)</td>
<td>0.02±0.01</td>
<td>0.05±0.01</td>
<td>0.09±0.01</td>
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<tr>
<td>Cr (mg L$^{-1}$)</td>
<td>0.04±0.02</td>
<td>0.06±0.00</td>
<td>0.18±0.01</td>
</tr>
<tr>
<td>MPN (MPN100 ml$^{-1}$)</td>
<td>2.56x10$^{15}$±15.25</td>
<td>3.42x10$^{10}$±236</td>
<td>4.78x10$^2$±342</td>
</tr>
<tr>
<td>SPC (SPC ml$^{-1}$)</td>
<td>6.3±6.20</td>
<td>6.42x10$^{10}$±162</td>
<td>7.69x10$^2$±156</td>
</tr>
</tbody>
</table>

*Mean ± of four values; BWW - Borewell water; BIS - Bureau of Indian standard*
Table 2. Physico-chemical characteristics of soil before and after irrigation with Star paper mill effluent.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before effluent irrigation (control)</th>
<th>After irrigation</th>
<th>F-calculated</th>
<th>Critical difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Effluent concentration (%)</td>
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<tr>
<td></td>
<td></td>
<td>5</td>
<td>10</td>
<td>25</td>
</tr>
<tr>
<td>Soil moisture (%)</td>
<td>61.08±6.21</td>
<td>60.82±2.50 (±0.42)</td>
<td>56.61±2.26 (-7.32)</td>
<td>53.83±2.90 (-11.86)</td>
</tr>
<tr>
<td>Soil texture</td>
<td>Loamy Sand</td>
<td>Loamy Sand</td>
<td>Loamy Sand</td>
<td>Loamy Sand</td>
</tr>
<tr>
<td>WHC (%)</td>
<td>45.98±3.03</td>
<td>45.31±4.44 (-1.46)</td>
<td>44.15±4.14 (-3.98)</td>
<td>42.79±3.37 (-6.94)</td>
</tr>
<tr>
<td>BD (gm cm⁻³)</td>
<td>1.42±0.08</td>
<td>1.41±0.07 (-0.70)</td>
<td>1.38±0.07 (-2.82)</td>
<td>1.37±0.07 (-3.52)</td>
</tr>
<tr>
<td>pH</td>
<td>8.02±0.19</td>
<td>8.10±0.10 (+0.99)</td>
<td>8.17±0.29 (+1.87)</td>
<td>8.25±0.31 (+2.87)</td>
</tr>
<tr>
<td>EC (dS m⁻¹)</td>
<td>2.08±0.07</td>
<td>2.43±0.05 (+16.82)</td>
<td>2.61±0.06 (+25.48)</td>
<td>2.73±0.04 (+31.25)</td>
</tr>
<tr>
<td>ECEC (cmol kg⁻¹)</td>
<td>12.00±1.03</td>
<td>13.19±2.97 (+9.92)</td>
<td>15.63±2.59 (+30.25)</td>
<td>21.52±2.48 (+79.33)</td>
</tr>
<tr>
<td>CI (mg Kg⁻¹)</td>
<td>88.18±1.68</td>
<td>107.37±5.07 (+21.76)</td>
<td>116.43±5.46 (+32.06)</td>
<td>143.37±6.30 (+62.58)</td>
</tr>
<tr>
<td>OC(mg Kg⁻¹)</td>
<td>0.43±0.10</td>
<td>1.56±0.22 (+262.79)</td>
<td>2.98±0.52 (+593.02)</td>
<td>4.20±0.18 (+876.74)</td>
</tr>
<tr>
<td>HCO₃⁻(mg Kg⁻¹)</td>
<td>382.39±4.23</td>
<td>391.56±5.10 (+2.92)</td>
<td>400.04±8.59 (+4.61)</td>
<td>415.24±8.91 (+8.59)</td>
</tr>
<tr>
<td>CO₂⁻(mg Kg⁻¹)</td>
<td>228.40±4.16</td>
<td>236.17±5.81 (+3.40)</td>
<td>241.10±6.69 (+5.56)</td>
<td>245.60±7.20 (+7.53)</td>
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<tr>
<td>Na⁺ (mg Kg⁻¹)</td>
<td>17.56±2.51</td>
<td>24.72±3.89 (+40.77)</td>
<td>26.84±3.73 (+52.84)</td>
<td>29.00±3.96 (+65.14)</td>
</tr>
<tr>
<td>K⁺ (mg Kg⁻¹)</td>
<td>154.09±5.80</td>
<td>164.54±2.38 (+6.78)</td>
<td>173.59±3.73 (+12.65)</td>
<td>187.11±4.71 (+21.43)</td>
</tr>
<tr>
<td>Ca²⁺ (mg Kg⁻¹)</td>
<td>14.11±2.69</td>
<td>37.09±5.75 (+162.86)</td>
<td>40.05±5.31 (+183.84)</td>
<td>75.60±2.39 (+435.79)</td>
</tr>
<tr>
<td>Mg²⁺(mg Kg⁻¹)</td>
<td>1.68±0.51</td>
<td>4.05±0.36 (+141.07)</td>
<td>5.23±0.46 (+211.31)</td>
<td>10.08±0.91 (+500.00)</td>
</tr>
<tr>
<td>TKN(mg Kg⁻¹)</td>
<td>30.96±4.09</td>
<td>55.83±5.31 (+80.33)</td>
<td>64.19±3.26 (+107.33)</td>
<td>123.84±3.88 (+300.00)</td>
</tr>
</tbody>
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<tr>
<td></td>
<td>5</td>
<td>10</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>NO$_3^-$ (mg Kg$^{-1}$)</td>
<td>38.07±4.34</td>
<td>42.87±3.84 (+12.61)</td>
<td>44.07±3.58 (+15.76)</td>
<td>46.89±4.48 (+23.16)</td>
</tr>
<tr>
<td>PO$_4^{3-}$ (mg Kg$^{-1}$)</td>
<td>51.75±4.79</td>
<td>67.40±2.67 (+30.24)</td>
<td>73.87±3.60 (+42.74)</td>
<td>95.44±2.70 (+84.42)</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (mg Kg$^{-1}$)</td>
<td>73.12±2.37</td>
<td>78.36±3.74 (+7.16)</td>
<td>81.34±3.42 (+11.24)</td>
<td>83.12±3.37 (+13.67)</td>
</tr>
<tr>
<td>Fe$^{2+}$ (mg Kg$^{-1}$)</td>
<td>2.63±0.85</td>
<td>3.69±0.73 (+31.55)</td>
<td>3.69±0.30 (+11.24)</td>
<td>5.33±0.43 (+13.67)</td>
</tr>
<tr>
<td>Zn (mg Kg$^{-1}$)</td>
<td>0.765±0.16</td>
<td>1.942±0.15 (+153.86)</td>
<td>2.241±0.12 (+192.94)</td>
<td>2.419±0.11 (+216.20)</td>
</tr>
<tr>
<td>Cd (mg Kg$^{-1}$)</td>
<td>0.040±0.06</td>
<td>0.177±0.02 (+126.92)</td>
<td>0.177±0.02 (+126.50)</td>
<td>0.147±0.01 (+270.00)</td>
</tr>
<tr>
<td>Cu (mg Kg$^{-1}$)</td>
<td>2.02±0.33</td>
<td>3.138±0.30 (+55.11)</td>
<td>3.441±0.41 (+70.09)</td>
<td>5.205±0.23 (+157.29)</td>
</tr>
<tr>
<td>Pb (mg Kg$^{-1}$)</td>
<td>0.016±0.01</td>
<td>0.125±0.02 (+606.25)</td>
<td>0.125±0.02 (+681.25)</td>
<td>0.136±0.05 (+750.00)</td>
</tr>
<tr>
<td>Cr (mg Kg$^{-1}$)</td>
<td>0.104±0.06</td>
<td>0.236±0.04 (+126.92)</td>
<td>0.310±0.05 (+198.07)</td>
<td>0.523±0.05 (+402.88)</td>
</tr>
</tbody>
</table>

Mean ± of four values; Significant F -**P > 0.1%, *P > 5% level; % Increase or decrease in comparison to control given in parenthesis; a - significantly different to the control; NS - Not Significant; BWW - Borewell water.
The recent studies by Miller and Turk [12] have indicated that the moisture content of soil is useful and an important factor which affects the pH, availability of nutrients to plant and aeration. Presence of large soil particles reduces the soil moisture content. The water holding capacity is the amount of water, which is absorbed and retained by the given amount of 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. Bulk density of 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 soil, which is useful for root development. It is used for determining the amount of pore space and water storage capacity of the soil.

During the present study, the soil moisture content was found to decrease (61.08 to 49.57%) on irrigation with different concentrations of the paper mill effluent (PME). The increasing dose of effluent reduced the bulk density of the surface soil (Table 2). The BD was decreased from (1.42 g cm$^{-3}$) in control soil to (1.34 g cm$^{-3}$) in 100% of PME followed by 75%, 50%, 25%, 10% and 5%. The WHC was decreased from its control soil 45.98% to 39.88% with 100% concentration of PME (Table 2).

The ANOVA analysis on data showed that the soil moisture content, WHC and BD were recorded to be insignificantly (P>0.05) affected with different concentrations of PME in comparison to control irrigated soil (Table 2). The soil characteristics were found to change on irrigation with PME. The soil particle size depicted that the experimental soil was of loamy sand (65% sand, 15% clay and 20% silt) type and there was no change in the soil texture (Table 2). The reduction in BD (uniformly repacked) was due to higher organic matter content in the treatments where PME was added in higher doses.

3.2.2. pH and EC

Charman and Murphy [51] reported that 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 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 (Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$) becomes lower due to leaching. Mohan et al. [58] found that soil having pH value 8.5 and above is expected to have more Na in the exchange complex and when unaccompanied by the presence of soluble salts, is classified as an alkaline soil. They also concluded that the EC of water and wastewater 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 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 dS m$^{-1}$ and SAR >13 or ESP >15) high enough to control a soil’s chemical attributes, they are known as sodic soils.

During present study, the soil pH was recorded to be alkaline (8.02) at initial level and it turned to more alkaline (8.54) with 100% concentration of PME. The effluent concentrations of 50%, 75% and 100% of PME showed significant (P<0.05) effect on soil pH in comparison to control
irrigated soil (Table 2). 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 cause for the stability of the soil reaction.

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 5% to 100% concentration of PME in comparison to control soil. The effluent treated pots registered significantly higher EC (3.14 dS m\(^{-1}\)) than control (2.08 dS m\(^{-1}\)) this was due to very high salt load (6.17 dS m\(^{-1}\)) EC of the PME. Similar findings were also reported by Chonker et al. [49] and Raverkar et al. [32]. The build-up of salt concentration with PME application, particularly at higher rate of application, is a cause of concern for its application. In the long run indiscriminate application of PME may create problem of soil salinity.

3.2.3. Effective cation exchange capacity

Carter [68] reported that 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 isomorphic 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.

During present study, the ECEC was found to increase in the PME irrigated soil. It increased significantly from initial level 12.00-25.41 cmol kg\(^{-1}\) in 100% of PME. The ECEC of the PME irrigated soil was found to be significantly (P<0.001) different with different concentrations (25% to 100%) of PME (Table 2).

3.2.4. Chlorides

Chloride is generally considered to be a hydrologically and chemically inert substance. Past research suggests that Cl\(^-\) participates in a complex biogeochemical cycle involving the formation of organically bound chlorine. Generally cation K\(^+\) is usually considered as one of the major plant nutrients; the accompanying anion Cl\(^-\) has been generally referred to as undesirable but unavoidable. However, Cl\(^-\) is now considered as an essential micronutrient for optimal growth. Both K\(^+\) and 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 K and Cl is related to the opening and closing of stomata [24; 37; 50].

In the present study, the chlorides in the PME irrigated soil increased with the increase in PME concentrations. The PME concentrations 5, 10, 25, 50, 75 and 100% showed significant (P<0.001) effect on chlorides of the soil in comparison to control soil (Table 2). Chlorides in the PME irrigated soil were increased significantly from initial level of 88.18-177.71 mg Kg\(^{-1}\) in 100% of PME.
3.2.5. **Organic carbon**

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. Organic matter is the source of 90-95% of the nitrogen in unfertilized soil. It can also be the major source of 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 [12; 60; 65; 66].

The present study showed that organic carbon content of the soil increased considerably with the application of PME. It increased from an initial level of 0.43–9.95 mg Kg⁻¹ in 100% of PME. The soil organic carbon was found to be significantly (P<0.001) different with 5% to 100% concentrations of PME (Table 2). Addition of organic matter through effluent could be the probable reasons for the improvement in organic carbon content particularly in high PME treated pots.

3.2.6. **Bicarbonates and carbonates**

Thompson *et al.* [25] has concluded that 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 higher concentration of Na in soil after effluent irrigation is associated with presence of higher concentration of carbonate, bicarbonate in the effluent.

During present study, the bicarbonates and carbonates content of the soil increased significantly with the appliance of PME. It increased from an initial level of 382.39–442.25 mg Kg⁻¹ and 228.40–284.69 mg Kg⁻¹ in 100% of PME respectively. The effluent concentration 5% to 100% of PME showed significant (P<0.001) affect on bicarbonates and carbonates in the PME irrigated soil (Table 2). The findings were supported by Vinod and Chopra [65; 66].

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

Ajmal and Khan [40] reported that various concentrations (25%, 50%, 75% and 100%) of brewery effluent were rich in ammonia nitrogen, nitrate-nitrogen, phosphorus and potassium, its application to the soil increased the 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 CaCO₃ content of the soil irrigated with 100% and 75% effluent, while it increased with 50% and 25% effluent. The highest perturbance 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. Ajmal and Khan [41] reported that various concentrations (25%, 50%, 75% and 100%) of textile effluent
increased the electrical conductivity, cation-exchange capacity, pH, NH$_3$-N, phosphorus, organic matter extractable Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ of the soil. The greatest changes were recorded with 100% effluent, the most marked increase being in the organic matter of soil, followed by NH$_3$-N, Na$^+$, K$^+$, Ca$^{2+}$ and Mg$^{2+}$ of the soil.

Higher concentration of Na causes the decrease the bulk density as well as water holding capacity by decrease the 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. Calcium and potassium are also an essential fertilizers element. They are vital for photosynthesis for protein synthesis, for starch formation and for the 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 reported by Patterson et al. [59].

Miller and Turk [12] reported that 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 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.

In present study, irrigation with PME, the exchangeable sodium, potassium and calcium were found to change with different concentrations of the effluent. The effluent concentrations 10%, 25%, 50%, 75% and 100% of PME 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 Na, K, and Ca were also recorded to be significantly (P<0.001) different with 5% concentration of PME (Table 2). The content of exchangeable sodium, potassium, calcium and magnesium were increased significantly from an initial (control) level of 17.56-37.41 mg Kg$^{-1}$, 154.09-228.47 mg Kg$^{-1}$, 14.11-151.99 mg Kg$^{-1}$ and 1.68-22.45 mg Kg$^{-1}$ in 100% of PME respectively (Table 2). The findings were supported by Vinod and Chopra [65; 66].

3.2.8. Total nitrogen, nitrate, phosphate and sulphates
Nitrate is the most essential and available form of nitrogen to plants because plant roots take up nitrogen in the form of NO$_3^-$ 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 [7; 22; 31]. 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 [31; 62].

The present study showed that the content of total nitrogen, nitrate, phosphate and sulphates increased significantly from an initial (control) level of 30.96-286.96 mg Kg$^{-1}$, 38.07-66.61 mg Kg$^{-1}$, 51.75-125.09 mg Kg$^{-1}$ and 73.12–114.79 mg Kg$^{-1}$ in 100% of PME respectively. The effluent concentrations 10%, 25%, 50%, 75% and 100% of PME showed significant (P<0.001) change in total nitrogen, nitrate, phosphate and sulphates of the soil. It was quite interesting to note that the total nitrogen and phosphate of soil were also recorded to be significantly different with 5% concentration of PME.

3.2.9. Micronutrients

Kaushik et al. [4] reported that 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.

Beligh et al. [42] reported that olive mill wastewater irrigation in agriculture affected the characteristics of soil and plant in Mediterranean countries. The influence of agronomic application of olive mill wastewater (30, 60, 100 and 150 m$^3$ ha$^{-1}$) significantly increase in organic C, C/N ratio, extractable phosphorus and exchangeable potassium. Biswas et al. [2] reported that 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. Jeremy et al. [39] observed the variability of soil pH, organic matter (OM), cation exchange capacity (CEC), total nitrogen (TN), total phosphorus (TP), available phosphorus and available potassium of Cambosols and Anthrosols in Zhangjiagang County, China due to increase the annual application of N and P fertilizer rates. Fertilizer input rates are causing nutrient imbalances, contributing to acidification in Anthrosols, and decreasing C/N ratios.

Mohammadi et al. [6] 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. The application of 2% sludge (based on soil dry mass) remarkably increased shoot dry matter and P, K, Fe, Mn, K and P uptake. Osadebamwen [30] observed that on treatment of the soil 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.

In present study, the concentration of micronutrients viz. Fe, Zn, Cd, Cu, Pb, and Cr were recorded to be significantly (P<0.001) affected with 10% to 100% concentration of PME. It was quite interesting to note that the concentration of Zn, Cu, Fe, Cd, and Cr were also found to be significantly (P<0.001) different with 5% concentration of PME irrigated soil (Table 2). Among the micronutrients, the maximum enrichment factor (Ef) was shown by Pb (10.68) while the minimum by Cu (3.31) and it was in order of Pb>Cr>Cd>Zn>Cu after irrigation with PME (Fig.1).
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 [51]. The content of Fe, Zn, Cd, Cu, Pb and Cr were increased significantly with the application of PME. It increased from an initial (control) level of 2.63–5.99 mg Kg\(^{-1}\), 0.765–2.790 mg Kg\(^{-1}\), 0.040–0.176 mg Kg\(^{-1}\), 2.023–6.695 mg Kg\(^{-1}\), 0.016–0.171 mg Kg\(^{-1}\) and 0.104–0.933 mg Kg\(^{-1}\) in 100% of PME respectively. This is in agreement with what was reported by other workers that organic wastes contain high amounts of macro and micronutrients [15; 19; 20; 65; 66].

**CONCLUSION**

The present study concluded that different concentrations of the Paper mill effluent altered the soil properties differently [6; 13; 16; 33; 49; 59] as in present study also. The effluents decreased the moisture content, WHC and bulk density and increased it, pH, EC, ECEC, Cl\(^-\), OC, HCO\(_3\)\(^-\), CO\(_3\)\(^2-\), Na\(^+\), K\(^+\), Ca\(^2+\), Mg\(^2+\), Fe\(^2+\), TKN, NO\(_3\)\(^-\), PO\(_4\)\(^3-\), SO\(_4\)\(^2-\), and Zn, Cd, Cu, Pb and Cr of the soil. The micronutrients such as Fe, Zn, Cu, Pb and Cr were also recorded to be higher in the soil irrigated with PME which may lead to toxicity of soil at higher concentration in comparison to control irrigated soil. All effluent concentrations were better than the control (BWW) in nutrient accumulation. Among the micronutrients the maximum enrichment factor (Ef) was that of Pb (10.68) while the minimum in case of Cu (3.31) and it was in order of Pb>Cr>Cd>Zn>Cu irrigation with PME. The nutrients and trace elements of paper mill effluent irrigation contributed significant changes in pH, EC, ECEC, Cl\(^-\), OC, HCO\(_3\)\(^-\), CO\(_3\)\(^2-\), Na\(^+\), K\(^+\), Ca\(^2+\), Mg\(^2+\), Fe\(^2+\), TKN, NO\(_3\)\(^-\), PO\(_4\)\(^3-\), SO\(_4\)\(^2-\), and Zn, Cd, Cu, Pb and Cr of the soil and affected the natural composition of the soil. Such alterations may improve the fertility and enhance the nutrients status of soil at lower concentration of effluent irrigation. Thus application of PME to the agricultural field, as an amendment, might be a viable option for the safe disposal of this industrial waste with concomitant enhancement in yield and 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.

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