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# Manipulation of Chemical Properties in Soil under Wetland Rice through Industrial Effluents

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#### Authors' contributions

This work was carried out in collaboration among all authors. Author MRI designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author GKMMR managed the analyses of the study. Author MAS managed the literature searches. All authors read and approved the final manuscript.

#### Article Information

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## ABSTRACT

A laboratory experiment was conducted in Soil Science Division of Bangladesh Rice Research Institute (BRRI) during 2010-11 aimed to determine the effects of different industrial effluents on some soil chemical properties under long-term industrial wastewater irrigated rice field. Effluents irrigation created some differences in soil pH, electrical conductivity and organic carbon. The pH in all soil depth was higher with wastewater irrigated rice field. Irrigation with wastewater increased in all the effluents irrigated rice fields; the electrical conductivity (EC) was remarkable higher with all soil depth than the control field. In all the rice fields soil (Control + effluents irrigated fields), the organic carbon content (%) started to decrease sharply with the increase in soil depth. Organic carbon content was slightly higher with wastewater irrigated rice soils. Exchangeable cations (Ca, Mg, K and Na), trace elements (Zn, Fe, Mn and Cu) and heavy metals (Pb, Cd, Cr and Ni) were increased through irrigation with wastewater in rice–rice cropping pattern. Keywords: Wetland rice; industrial waste; plant nutrients; heavy metals.

#### **1. INTRODUCTION**

Growing industrial establishments increased sharply in Bangladesh without proper attention to pollution control. Farmers' of industrial areas are growing crops in their field by using industrial wastewater for many years. The use of different wastewaters (industrial effluents as well as municipal sewage) for irrigation has emerged in the recent past as an important way of the utilization of wastewater taking the advantage of the presence of considerable quantities of nitrogen and phosphorus along with some other essential elements. Another advantage of wastewater irrigation includes an important aspect of pollution removal. The pollutants are partly taken up by the plants and partly transformed in the soil without causing any damage. Nevertheless, the use of wastewaters for agriculture is marred by several constraints due to various problems like soil salinity, the interaction of chemical constituents of the wastes with the uptake of nutrients and changes in soil property and microflora [1]. Darvishil et al. [2] reported that effluents change the soil chemical properties like pH, EC, soil organic matter, primary, secondary nutrient elements including heavy metals. The addition of sewage sludge to a coarse-textured sandy and calcareous soils was reported to have improved the water holding capacity, cation exchange capacity, increase the availability of N, P, K, Cu, Zn, Fe, Mn, Na but with reduced biochemical oxygen demand (BOD) [3]. Lim and Ping [4] recorded an increase in pH, K, Ca, Mg and organic matter content with the application of palm oil mill effluent. This necessitates a detailed scientific study before any specific waste can be used for irrigation for a particular crop with particular soil and climate. Since crop plants are increasingly being exposed to the effluent discharge in the industrial area, an attempt has been done to study the effects of different industrial effluents on some soil chemical properties.

#### 2. MATERIALS AND METHODS

#### 2.1 History of Soil Sample

Soil samples were collected from Mouchak area of Gazipur district (middle part of Bangladesh; Madhpur tract; AEZ 28) which has a long cropping history under rice–rice systems. The sampling area represents two kinds of farmers' managed rice fields (i) irrigated with underground freshwater (control soil) and (ii) irrigated with effluents water for 8-10 years. The distance between control and effluents irrigated field was 500 meters. The locations of different plots are shown in Fig. 1.

#### 2.2 Soil Sample Collection

The samples were collected through auger from control (rice cultivated with fresh water) and industrial wastewater treated plots in December 2010. Thirty soil samples from ten plots (six from 2 control plots and 24 from 8 effluent water receiving plots) were collected from the depth 0-10 cm, 10-20 cm and 20-30 cm, respectively. The control and effluent irrigated plot soils were denoted by C and I, respectively. The collected samples were composited to make about 1/2 kg and samples were brought in Soil Science Division net house of Bangladesh Rice Research Institute (BRRI), air-dried, crushed and sieved through 2-mm sieve prior to analysis.

#### 2.3 Soil Analytical Methods

Analytical methods that are used for soil samples have been presented in Table 1.

#### 2.4 Statistical Analysis

The obtained data were statistically analyzed following IRRISTAT version 4.3 [9].

#### 3. RESULTS AND DISCUSSION

#### 3.1 Soil pH

The pH of collected soil samples varied from 4.26 to 6.37 at 0-10 cm, from 4.86 to 6.57 at 10-20 and from 4.75 to 6.39 at 20-30 cm soil depth (Fig. 2). The control soil gave a pH of 4.78 at 0-10 cm depth. At 0-10 cm depth,  $I_1$  plot gave 0.98 and  $I_4$  plot gave 0.47 unit's higher pH than that of control plot. At 0-10 cm depth,  $I_5$ ,  $I_6$  and  $I_7$  plots showed an increase in pH than the control soil by 0.57, 0.42 and 0.53 units, respectively. A remarkable increase in pH was found in the  $I_2$  plot. The  $I_2$  plot showed a pH of 6.37 at 0-10 cm depth. However, the  $I_3$  plot recorded 0.52 and  $I_8$  plot recorded 0.11-unit lower pH as compared to the control plot at 0-10 cm depth.



Fig. 1. Locations of soil profiles and different plot soils under study area

Table 1. Analytical methods used for soil	analysis
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Soil property	Methods
pH (H₂O)	1:2.5 soil-water ratio, using a glass electrode method [5]. Ten g of air-dried soil
	sample was taken in 50 ml of a beaker and 25 ml of distilled water was added. The
	suspension was stirred with a glass-rod at regular interval for 30 minutes. A glass
	electrode pH meter (WPA Linton Cambridge, UK) calibrated with buffer pH 7.0 and
	4.0 measured the pH of the soil suspension.
Electrical	A portion of 20 gm of air-dried soil sample was taken in a 250 ml of the conical
Conductivity	flask and then 100 ml of distilled water was added. It was shaken for 30 minutes
(dS/m)	and filtered through Whatman # 42 filter paper. Electrical conductivity was
	measured from the filtered sample using a conductivity meter (YSI Model 32) [5].
Organic	Walkley and Black wet digestion method Nelson and Sommers [6] was followed to
Carbon (%)	determine organic carbon. The sieved soil was again passed through 0.5 mm
	sieve to determine organic carbon. One gm soil sample was taken in a 500 ml
	conical flask, and then 10 ml of 1 N $K_2Cr_2O_7$ solution and 20 ml of conc. $H_2SO_4$
	was added. Flask was then kept for 30 minutes for completion of oxidation. Then
	200 ml of distilled water, 10 ml of $H_3PO_4$ and 2 ml of di-phenyl amine indicator
	solution were added. The sample was then titrated with 1N FeSO <sub>4</sub> solution until the
	green colour appeared. A blank sample was also taken to calculate the results.
Exchangeable	Thomas [7] method was followed to determine exchangeable cations. A portion of
Ca, Mg, K	ten g of air-dried sieved soil sample was taken in a 125 ml of the conical flask, then
and Na	50 ml of extracting solution (1 N CH <sub>3</sub> COONH <sub>4</sub> , pH 7.0) was added. It was shaken
(cmol/kg)	for 10 minutes and filtered through Whatman # 42 filter paper. In the case of
	exchangeable K and Na direct reading was taken from atomic absorption
	spectrophotometer at 766.5 nm and 589 nm wavelengths, respectively. For

Soil property	Methods
	Exchangeable Ca was determined by diluting a portion of 2 ml of aliquot with 1 ml
	of $La_2O_3$ and 7ml of distilled water into 25 ml test tube and atomic absorption
	Spectrophotometer reading was taken at 422.7 nm wavelength. For Mg, 1 ml
	aliquot was diluted in 19 ml of distilled water into 25 ml test tube and atomic
	absorption Spectrophotometer reading was taken at 285.2 nm wavelength.
Trace	Lindsay and Norvell [8] method was followed to determine trace elements. A
elements (Zn,	portion of ten g of air-dried sieved soil sample was taken in a 125 ml of the conical
Fe, Mn and	flask, then 20 ml of extracting solution (EDTA-Diethylenetriaminepentraacetic acid)
Cu) (mg/kg)	was added. It was shaken for 2 hours and filtered through Whatman # 42 filter
	paper. Concentrations of Zn, Fe, Mn and Cu were determined by atomic
	absorption Spectrophotometer with respective wavelength.
Heavy metals	Heavy metals analysis involved digestion of 0.5 g of soil sample with concentrated
(Pb, Cd, Cr	$HNO_3$ and $HClO_4$ (5:2) at 120 <sup>o</sup> C following the procedure described by Lindsay and
and Ni)	Norvell [8]. Finally, the digest was filtered through Whatman # 42 filter paper and
(mg/kg)	diluted to 50 ml with distilled water prior to analysis. Concentrations of Pb, Cd, Cr
	and Ni were determined by atomic absorption Spectrophotometer with respective
	wavelength (AAS; Model: Varian 55B).

At 10-20 cm depth, the control plot gave a pH of 4.86. At 10-20 cm depth,  $I_1$ ,  $I_4$ ,  $I_5$ ,  $I_6$  and  $I_7$  plots showed an increase in pH than the control soil by 1.05, 0.52, 1.0, 0.47 and 0.65 units, respectively. The  $I_3$  and  $I_8$  plots gave equal pH in the soil as that of control soil. A remarkable increase in pH was found in the  $I_2$  plot at 10-20 cm depth. The  $I_2$  plot gave a pH of 6.51 at 10-20 cm depth.

At 20-30 cm depth, the control plot gave a pH of 4.75. At 20-30 cm depth,  $I_1$  plot gave 1.05 and  $I_4$ plot gave 0.45-unit higher pH than that of control. The I<sub>6</sub> plot showed an equal pH to that of the I<sub>4</sub> plot. However, the  $I_3$  and  $I_8$  plots gave the equal pH to that of control plot at 20-30 cm depth. The  $I_5$  and  $I_7$  plots showed an increase in pH than the control soil by 0.31 and 0.61 units, respectively. A remarkable increase in pH was found in the  $I_2$ plot. The I<sub>2</sub> plot had a pH of 6.39 at 20-30 cm depth. In all the fields, the highest soil pH was found at 10-20 cm depth and the lowest was observed in 0-10 cm depth. Effluents irrigated plots showed the highest pH value compared to control indicating that effluents irrigated plots accumulated more Ca and Mg that is responsible to increase in soil pH and decrease in exchangeable acidity. This report was similar to the findings of [10,11].

# 3.2 Electrical Conductivity (EC)

The EC of tested soil samples ranged from 1.3 to 5.5 dS/m at 0-10 cm, from 1.0 to 4.5 dS/m at 10-20 cm and from 0.8 to 4.0 dS/m at 20-30 cm soil depth (Fig. 3). At 0-10 cm depth, the control plot showed EC of 1.3 dS/m. The  $I_1$  plot gave 4.2 and  $I_3$  plot gave 3.5 folds higher EC than that of control plot. The  $I_2$  plot showed the equal EC to

that of  $I_1$  plot. At 0-10 cm depth,  $I_4$ ,  $I_5$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots showed an increase in EC content than the control plot by 3.2, 2.6, 2.7, 3.3 and 3.4 folds, respectively.

At 10-20 cm depth, the control plot gave EC of 1.0 dS/m. The  $I_1$  plot had 4.5 and  $I_3$  plot had 3.7 folds higher EC than that of control plot. The  $I_2$  plot showed the equal EC to that of  $I_1$  plot at 10-20 cm depth. The  $I_4$ ,  $I_5$ ,  $I_6$  and  $I_7$  plots showed an increase in EC in soil than the control by 3.9, 3.0, 3.1 and 4.0 folds, respectively. The  $I_8$  plot found a similar EC value to that of  $I_7$  plot.

At 20-30 cm depth, the control plot had EC of 0.8 dS/m. At 20-30 cm depth,  $I_1$  plot had 5.0 folds and  $I_3$  plot had 4.3 folds higher EC compared to control plot. The  $I_2$  plot had a similar EC to that of  $I_1$  plot. At 20-30 cm depth,  $I_4$ ,  $I_5$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots showed an increase in EC content than the control plot by 4.5, 3.2, 3.3, 4.4 and 3.8 folds, respectively. A tremendous increase in EC was found with effluents irrigated plots compared to the control plot may be deposition of salts, especially Na salt and heavy metals from effluents. Similar results were also reported by Begum [12] Saif et al. [13].

# 3.3 Organic Carbon (OC)

The OC content of tested soil samples varied from 1.13 to 1.28% at 0-10 cm, from 0.86 to 1.02% at 10-20 cm and from 0.71 to 0.88% at 20-30 cm soil depth (Fig. 4). At 0-10 cm depth, the control plot recorded OC content of 1.13%. The  $I_1$  plot gave 4% and  $I_2$  plot gave 2% higher OC than that of control. The  $I_5$  plot showed a similar OC content to that of  $I_2$  plot at 0-10 cm

depth. The  $I_3$ ,  $I_4$  and  $I_6$  plots showed an increase in OC content than the control plot by 5, 3 and 5%, respectively. A considerable increase in OC was found in the  $I_7$  and  $I_8$  plots. The  $I_7$  plot had OC content of 1.28% and that in the  $I_8$  plot was 1.24%.



Fig. 2. Distribution of soil pH in effluents and control water irrigated rice soils







Fig. 4. Distribution of soil OC (%) in effluents and control water irrigated rice soils

At 10-20 cm depth, the control plot gave OC content of 0.86%. The I<sub>1</sub> plot showed 8% and I<sub>2</sub> plot showed 10% higher OC content compared to the control plot. At 10-20 cm depth, I<sub>3</sub>, I<sub>4</sub>, I<sub>5</sub> and I<sub>6</sub> plots tended to increase in OC content than the control plot by 3, 13, 2 and 5%, respectively. A considerable increase in OC content was found in the I<sub>7</sub> and I<sub>8</sub> plots. The I<sub>7</sub> plot had OC content of 1.02% and that in the I<sub>8</sub> plot was 0.99%

At 20-30 cm depth, the control plot recorded OC content of 0.74%. At 20-30 cm depth, I1 plot had 7% and I<sub>4</sub> plot had 11% higher OC content than that of control plot. The  $I_2$  and  $I_3$  plots gave similar OC content to that of control plot. The I<sub>5</sub> plot decreased 3% while I<sub>6</sub> plot increased 4% OC content in soil compared to the control plot. A considerable increase in OC content was found in the I<sub>7</sub> and I<sub>8</sub> plots. The I<sub>7</sub> plot had OC content of 0.88% and that in the  $I_8$  plot was 0.87%. In all the fields, the highest OC was found at 0-10 cm soil depth and the lowest was obtained in 20-30 cm depth. The greater concentration of organic carbon content in 0-10 cm soil depth compared to 10-20 and 20-30 cm depth may be due to the accumulation of organic residues left out in former. Sood and Kanwar [14] earlier reported that the organic carbon content decreased with the depth of soils in Himachal Pradesh of India. However, OC content was the highest with effluents irrigated plots than the control plot. It might be due to the high total solid present in the effluent.

# 3.4 Exchangeable Cations (Ca, Mg, K and Na)

The exchangeable Ca content of collected soil samples varied from 5.62 to 8.08, from 5.04 to 7.84 and from 3.23 to 6.09 cmol/kg at 0-10, 10-20 and 20-30 cm soil depths, respectively (Fig. 5). At 0-10 cm depth, the control plot obtained Ca content of 5.62 cmol/kg. The  $I_1$  plot gave 0. 76 and  $I_2$  plot gave 1.35 units higher Ca content in soil than that of control plot. At 0-10 cm depth,  $I_3$ ,  $I_4$ ,  $I_5$ ,  $I_6$  and  $I_7$  plots showed an increase in Ca content than the control plot by 0.36, 0.24, 1.93 and 1.52 cmol/kg, respectively. The  $I_7$  plot gave the equal Ca content to that of  $I_5$  plot. A considerable increase in Ca content was found in the  $I_8$  plot at 0-10 cm depth. The  $I_8$  plot had a Ca content of 8.08 cmol/kg.

At 10-20 cm depth, the control plot gave Ca content of 5.04 meq/100 g soil. The  $I_1$  plot gave 0. 53 and  $I_2$  plot gave 1.23 units higher Ca content in soil compared to control plot. The  $I_3$ ,

 $I_4$ ,  $I_5$ ,  $I_6$  and  $I_7$  plots showed an increase in Ca content than the control plot by 0.23, 0.18, 1.87, 1.58 and 1.81 cmol/kg, respectively. A remarkable increase in Ca content was found in the  $I_8$  at 10-20 cm depth. The  $I_8$  plot obtained a Ca content of 7.84 meq/100 g soil.

At 20-30 cm depth, the Ca content of 3.23 cmol/kg was found in the control plot. The I<sub>1</sub> plot gave 0. 64 and I<sub>2</sub> plot gave 1.05 units higher Ca content compared to control plot. The I<sub>3</sub> plot showed the equal Ca content to that of I<sub>1</sub> plot at 20-30 cm depth. At 20-30 cm depth, the  $I_4$ ,  $I_5$ ,  $I_6$ and I<sub>7</sub> plots tended to increase in Ca content than the control plot by 0.29, 1.92, 1.93 and 2.04 cmol/kg, respectively. Like 10-20 cm depth, a considerable increase in Ca content was found in the I<sub>8</sub>. The I<sub>8</sub> plot obtained a Ca content of 6.09 cmol/kg. The Ca content was found the higher in effluents irrigated plots as compared to the control plot. It might be due to the higher accumulation of Ca by effluents irrigated plots as because effluents were rich in Ca salt. A similar result was reported by Lim CA and Ping [4]. They recorded an increase in Ca in soil with the application of palm oil mill effluent. The concentration of Ca was decreased at deeper soil depth. It might be due to leaching related translocation.

The exchangeable Mg content of collected soil samples varied from 0.53 to1.06, from 0.48 to1.0 and from 0.38 to 0.86 cmol/kg at 0-10, 10-20 and 20-30 cm soil depths, respectively (Fig. 6). The control plot gave Mg content of 0.53 cmol/kg soil at 0-10 cm depth. The  $I_1$  and  $I_2$  plots increased Mg content in soil than the control by 0.49 and 0.46 cmol/kg, respectively. The  $I_3$ ,  $I_4$ ,  $I_5$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots tended to increase in Mg content than the control plot by 0.53, 0.44, 50, 0.43, 0.41 and 0.16 cmol/kg, respectively.

At 10-20 cm depth, the control plot obtained Mg content of 0.48 cmol/kg. The  $I_1$  and  $I_2$  plots increased Mg content in soil than the control by 0.51 and 0.45 cmol/kg, respectively. The  $I_4$  plot gave the equal Mg content to that of  $I_2$  plot at 10-20 cm depth. At 10-20 cm depth, the  $I_3$ ,  $I_5$ ,  $I_6$  and  $I_8$  plots showed an increase in Mg content than the control plot by 0.52, 0.50, 0.42 and 0.19 cmol/kg, respectively. The  $I_7$  plot obtained the equal Mg content to that of  $I_6$  plot at 10-20 cm depth.

At 20-30 cm depth, the control plot obtained Mg content of 0.38 cmol/kg. At 20-30 cm depth,  $I_1$  plot gave 0. 38 while  $I_2$  plot gave 0.40 cmol/kg

higher Mg content than that of control plot. The  $I_3$ ,  $I_4$ ,  $I_5$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots showed an increase in Mg content than the control plot by 0.48, 0.35, 0.23, 0.13, 0.22 and 0.14 cmol/kg, respectively. In all the depths, the exchangeable Mg was found the higher in effluents irrigated plots than that of control plot might be due to the higher accumulation of Mg from effluents. A similar result was reported by Lim and P'ng [4]. They recorded an increase in Mg in soil with the application of palm oil mill effluent.

The exchangeable K content of collected soil samples varied from 0.16 to 0.38, from 0.10 to 0.35 and from 0.07 to 0.27 cmol/kg at 0-10, 10-20 and 20-30 cm soil depths, respectively (Fig. 7). The control plot showed Mg content of 0.16 cmol/kg at 0-10 cm depth. The I<sub>1</sub> plot gave 2 and I<sub>2</sub> plot gave 2.4 folds higher K content in soil than that of control plot. The I<sub>3</sub>, I<sub>4</sub>, I<sub>5</sub> and I<sub>8</sub> plots gave almost the equal K content to that of I<sub>1</sub> plot at 0-10 cm depth. However, at 0-10 cm depth, the I<sub>6</sub> and I<sub>7</sub> plots showed the equal K content to that of I<sub>2</sub> plot.

At 10-20 cm depth, the control plot obtained K content of 0.10 cmol/kg. The  $I_1$  and  $I_2$  plots increased K content in soil than that control plot by 2.1 and 2.9 folds, respectively. At 10-20 cm depth, the  $I_3$ ,  $I_4$ ,  $I_6$  and  $I_8$  plots showed an increase in K content than the control plot by 3, 2.8, 3.5 and 2.7 folds, respectively. The  $I_5$  plot obtained the equal K content to that of  $I_4$  plot while  $I_7$  obtained equal K content to that of  $I_6$  plot.

At 20-30 cm depth, the K content 0.07 cmol/kg was found in the control plot. At 20-30 cm depth,  $I_1$  plot gave 2.3 and  $I_2$  plot gave 3.1 folds higher K content compared to control plot. The  $I_8$  plot gave the equal K content to that of  $I_2$  plot at 20-30 cm depth. At 20-30 cm depth, the  $I_3$  and  $I_4$  plots showed an increase in K content than the control plot by 3.3 and 3.0 folds, respectively. A remarkable increase in K content was found in the  $I_6$  and  $I_7$  plots at 20-30 cm depth. The  $I_6$  plot had K content of 3.7 and that in the  $I_7$  plot was 3.9 folds higher than that of control plot. The effluents irrigated plots showed the highest K







Fig. 6. Distribution of Exch. Mg (cmol/kgl) in effluents and control water irrigated rice soils



Fig. 7. Distribution of Exch. K (cmol/kgl) in effluents and control water irrigated rice soils

concentration in the whole soil profile than the control plot. It might be due to the higher K salt accumulation from effluents because effluents were rich in K.

The exchangeable Na content of tested soil samples varied from 0.77 to 3.14, from 0.58 to 2.71 and from 0.43 to 2.17 cmol/kg at 0-10, 10-20 and 20-30 cm soil depths, respectively (Fig. 8). The control plot showed Na content of 0.77 cmol/kg at 0-10 cm depth. At 0-10 cm depth,  $I_1$  plot gave 3.5 and  $I_2$  plot gave 3.7 folds higher Na content than that of control plot. The  $I_3$ ,  $I_4$ ,  $I_5$  and  $I_6$  plots showed an increase in Na content than the control plot by 3.8, 4.1, 3.3 and 3.1 folds, respectively. The  $I_7$  plot gave the equal Na content to that of  $I_6$  plot while the  $I_8$  gave the equal Na content to that of  $I_5$  plot at 0-10 cm depth.

At 10-20 cm depth, the control plot obtained Na content of 0.58 cmol/kg. The  $I_1 I_2$  plots increased Na content compared to control by 4.1 and 4.2 folds, respectively. The  $I_3$ ,  $I_4$ ,  $I_5$  and  $I_6$  plots tended to increase in Na content than the control plot by 4.5, 4.7, 3.9 and 3.6 folds, respectively. The  $I_7$  plot gave the equal Na content in soil to that of  $I_6$  while  $I_8$  plot gave the equal Na content to that of  $I_5$  plot at 10-20 cm depth.

At 20-30 cm depth, the control plot gave Na content of 0.43 cmol/kg. The  $I_1$  and  $I_2$  plot recorded the equal Na content which was 4.6 folds higher than that of the control plot. At 20-30 cm depth, the  $I_5$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots showed an increase in Na content than the control plot by 4.4, 3.8, 4.2 and 4.3 folds, respectively. A tremendous increase in Na content was found in

the  $I_3$  and  $I_4$  plots. The  $I_3$  plot had Na content of 4.8 and that in the  $I_4$  plot was 5.0 folds higher than that of control. The exchangeable Na concentrations were more prominent throughout the soil depths with effluents irrigated plots than the control plot. The exchangeable Na was obtained the highest with effluents irrigated plots compared to the control plot might be due to the accumulation of salt from effluents. A similar result was made by Begum [12].

#### 3.5 Trace Elements (Fe, Zn, Mn and Cu)

Effluents irrigation was affected by the trace elements concentration in soil depths. The Fe content of tested soil samples varied from 53 to 99 mg/kg at 01-10 cm, from 34 to 83 mg/kg at 10-20 cm and from 1 to 47 mg/kg at 20-30 cm soil depth (Fig. 9). At 0-10 cm depth, the control plot gave Fe content of 53 mg/kg. The I<sub>1</sub> plot had 14 and I<sub>2</sub> plot had 23-unit higher Fe content than that of control. The I<sub>3</sub>, I<sub>4</sub>, I<sub>5</sub> and I<sub>7</sub> plots showed an increase in Fe content than the control plot by 40, 30, 33 and 27 units, respectively. A remarkable increase in Fe content was found in the I<sub>6</sub> and I<sub>8</sub> plots at 0-10 cm depth. In both plots, the Fe content had 46 units higher than the control.

At 10-20 cm depth, the control plot obtained Fe content of 34 mg/kg. The  $I_1$ ,  $I_2$ ,  $I_3$ ,  $I_4$ ,  $I_6$  and  $I_7$  plots tended to increase in Fe content compared to control plot by 19, 29, 36, 27 and 33 units, respectively. The  $I_5$  plot gave similar Fe content to that of  $I_3$  plot at 10-20 cm depth. A considerable increase in Fe content was found in the  $I_6$  and  $I_8$  plots at 10-20 cm depth. The  $I_6$  plot had Fe content of 125% and that in  $I_8$  plot was 144% higher than that of control.

At 20-30 cm depth, the control plot obtained Fe content of 1 mg/kg. The I<sub>1</sub>, I<sub>2</sub>, I<sub>3</sub>, I<sub>4</sub>, I<sub>7</sub> and I<sub>8</sub> plots showed an increase in Fe content than the control plot by 7, 13, 16, 26, 23 and 13 units, respectively. A remarkable increase in Fe content was found in the I<sub>5</sub> and I<sub>6</sub> plots at 20-30 cm depth. The I<sub>5</sub> plot had Fe content of 39 mg/kg and that in I<sub>6</sub> plot was 46 mg/kg than the control. In all the soil depths, the Fe content was obtained the higher with effluents irrigated plots than control. However, in both types of plots, the Fe content was decreased with increasing the soil depth, indicating that the Fe enrichment at the surface.

Industrial effluent irrigation was affected by the zinc status in soil depths. The Zn content of collected soil samples varied from 8 to 47 mg/kg at 0-10 cm, from 2 to 9 mg/kg at 10-20 cm and from 2 to 8 mg/kg at 20-30 cm soil depth (Fig. 10). The control plot had Zn content of 8 mg/kg

at 0-10 cm depth. The  $I_1$  plot gave equal Zn content to that of the control plot. The  $I_2$  plot gave 2 and  $I_4$  plot gave 3 folds higher Zn content than that of control plot. The  $I_3$  and  $I_8$  plots obtained the equal Zn content to that of  $I_2$  plot. However, the  $I_7$  plot gave similar Zn content to that of  $I_4$  plot at 0-10 cm depth. A remarkable increase in Zn content was found in the  $I_5$  and  $I_6$  plots at 0-10 cm depth. The  $I_5$  plot had Zn content of 40 mg/kg and that in the  $I_6$  plot was 47 mg/kg than that of control soil.

At 10-20 cm depth, the control plot obtained Zn content of 2 mg/kg. The  $I_1$  and  $I_2$  plots showed an increase in Zn content than the control plot by 3 and 4 folds, respectively. The  $I_4$ ,  $I_6$  and  $I_7$  plots gave the equal Zn content to that of  $I_1$  plot. However, the  $I_3$  plot obtained the equal Zn content to that of  $I_2$  plot at 10-20 cm depth. The  $I_5$  and  $I_8$  plots obtained 2 folds higher Zn content than that of control plot.



Fig. 8. Distribution of Exch. Na (cmol/kgl) in effluents and control water irrigated rice soils





Fig. 9. Distribution of available Fe (mg/kg) in effluents and control water irrigated rice soils

At 20-30 cm depth, the control plot obtained Zn content of 2 mg/kg. The  $I_1$ ,  $I_2$  and  $I_5$  plots showed an increase in Zn content than the control plot by 3, 4 and 2 folds, respectively. The  $I_4$  and  $I_7$  plots gave similar Zn content to that of  $I_1$  plot while the  $I_6$  and  $I_8$  plots gave similar Zn content to that of  $I_5$  plot at 20-30 cm depth. Zinc concentrations were found to decrease with increasing the soil depths in both effluents irrigated and control field soils, indicating that deposition of Zn at the surface soil.

The Mn content of collected soil samples varied from 47 to 72, from 43 to 66 and from 33 to 51 mg/kg at 0-10, 10-20 and 20-30 cm soil depths, respectively (Fig. 11). The control plot gave Mn content of 72 mg/kg at 0-10 cm depth. The  $I_1$  plot had 11 and  $I_2$  plot had 22 units lower Mn content than that of control plot. The  $I_7$  and  $I_8$  plots gave equal Mn content in soil to that of  $I_2$  plot. The  $I_3$ ,  $I_4$ and  $I_6$  plots tended to decrease in Mn content than the control plot by 19, 15 and 25 units, respectively.

At 10-20 cm depth, the control plot obtained Mn content of 66 mg/kg. The  $I_1$  plot gave 9 and  $I_2$  plot gave 21 units lower Mn content than that of control. The  $I_6$ ,  $I_7$  and  $I_8$  plots showed the equal Mn content to that of  $I_2$  plot. At 10-20 cm depth, the  $I_3$ ,  $I_4$  and  $I_5$  plots tended to decrease in Mn content than the control plot by 18, 13 and 17 units, respectively.

At 20-30 cm depth, the control plot obtained Mn content of 51 mg/kg. The  $I_1$ ,  $I_2$ ,  $I_3$  and  $I_5$  plots decreased in Mn content than the control plot by 16, 19, 15 and 18 units, respectively. The  $I_6$  plot

gave the equal Mn content to that of  $I_1$  plot while the  $I_7$  and  $I_8$  plots gave the equal Mn content to that of  $I_5$  plot. In all the soil depths, the Mn content was found the higher with control soil than the effluents irrigated soils indicating that effluents irrigation had no effect on soil Mn. In both the soils, the Mn content was found to decrease with increasing the soil depth, meaning that enrichment of Mn at the surface.

The Cu content of collected soil samples varied from 4 to 9 mg/kg at 0-10 cm, from 3 to 8 mg/kg at 10-20 cm and from 2 to 4 mg/kg at 20-30 cm soil depth (Fig. 12). The Cu content mg/kg was found in the control plot at 0-10 cm depth. The  $I_1$  plot gave 2 and  $I_2$  plot gave 3 units higher Cu content than that of control plot. The  $I_5$  and  $I_8$  plots gave the equal Cu content to that of  $I_1$  plot at 0-10 cm depth, the  $I_3$  and  $I_6$  plots recorded the similar Cu content to that of  $I_3$  plot. The  $I_4$  and  $I_7$  plots showed an increase in Cu content than that control plot.

At 10-20 cm depth, the control plot gave Cu content of 3 mg/kg. The  $I_1$  and  $I_3$  plots had 3 while the  $I_2$  and  $I_6$  plots had 4 units higher Cu content than that of control plot. The  $I_4$ ,  $I_5$  and  $I_8$  plots showed an increase in Cu content than the control by 5, 2 and 1 units, respectively. The  $I_7$  plot gave the equal Cu content to that of  $I_5$  plot at 10-20 cm depth.

At 20-30 cm depth, the control plot obtained Cu content of 2 mg/kg. The  $I_1$ ,  $I_3$  and  $I_8$  plots had 2 higher while in  $I_5$  and  $I_6$  plots had 1-unit higher Cu content compared to control plot. The  $I_2$ ,  $I_4$  and  $I_7$ 



Fig. 10. Distribution of available Zn (mg/kg) in effluents and control water irrigated rice soils



Fig. 11. Distribution of available Mn (mg/kg) in effluents and control water irrigated rice soils

plots showed the equal Cu content to that of control plot. The Cu concentration was found to decrease with increasing the soil depth in both types of soils, indicating that the Cu accumulated at the surface soil.

Trace elements (Fe, Zn, Mn and Cu) were obtained the higher at 0-10 cm soil depth than that of 10-20 cm and 20-30 cm soil depth. The affinity of metals to the organic matter could be responsible for this deposition because of the relatively high organic carbon concentration in the topsoil. Agbenin [15] reported that the trace elements accumulated in the soil surface.

## 3.6 Heavy Metals (Pb, Cd, Cr and Ni)

The total Pb content of collected soil samples varied from 23 to 27 at 0-10 cm, from 22 to 26 at 10-20 cm and from 19 to 22 mg/kg at 20-30 cm soil depth, respectively (Fig. 13). The control plot gave Pb content of 25 mg/kg at 0-10 cm depth. The  $I_1$  and  $I_2$  plots showed an increase in Pb content than the control plot by 8 and 4%, respectively. The  $I_3$  and  $I_4$  plots gave the equal Pb content to that of  $I_2$  plot while  $I_5$  plot gave the equal Pb content to that of control plot at 0-10 cm depth. The  $I_6$  and  $I_7$  plots gave 4 while  $I_8$  plot gave 8% lower Pb content in soil than that of control plot.

At 10-20 cm depth, the control plot recorded Pb content of 24 mg/kg. The  $I_1$  and  $I_2$  plots showed an increase in Pb content than the control plot by 8 and 4%, respectively. The  $I_3$ ,  $I_4$  and  $I_5$  plots gave the equal Pb content to that of  $I_2$  plot at 0-10 cm depth. However,

the  $I_7$  plot gave equal Pb content to that of the control plot. At 10-20 cm depth, the  $I_6$  and  $I_8$  plots decreased Pb content than the control by 4 and 8%, respectively.

At 20-30 cm depth, the total Pb content 19 mg/kg was found in the control plot. The  $I_1$  and  $I_2$  plots showed an increase in Pb content than the control plot by 16 and 11%, respectively. The I<sub>3</sub>,  $I_4$  and  $I_5$  plots gave the equal Pb content to that of I<sub>2</sub> plot while I<sub>7</sub> plot gave similar Pb content to that of  $I_1$  plot. At 20-30 cm depth, the  $I_6$  and  $I_8$ plots had 5% higher Pb content than that of the control plot. In some soil samples, the Pb content was found slightly the higher in effluents irrigated soils than the control soil while in others it was found the lowest that indicates effluents had slight or no effect on Pb content in soil depth. However, the Pb concentration was found the higher at 0-10 cm depth compared to other two depths indicating that the Pb accumulated at the soil surface. Similar result was reported by Abdu et al. [16]. The concentration of Pb in waste water irrigated soil ranged from 44 to 52 mg/kg in industrial areas of Bangladesh [17].

Among the heavy metals, the Cd content was found the lowest in soil. The total Cd content of collected soil samples varied from 0.22 to 0.26 mg/kg at 0-10 cm, from 0.20 to 0.25 mg/kg at 10-20 cm and 0.18 to 0.22 mg/kg at 20-30 cm soil depth (Fig. 14). At 0-10 cm depth, the control plot had Cd content of 0.22 mg/kg. The I<sub>1</sub> and I<sub>2</sub> plots showed an increase in Cd content than the control plot by 9 and 14%, respectively. The I<sub>5</sub> and I<sub>6</sub> plots had the equal Cd content to that of I<sub>2</sub> plot while I<sub>4</sub> and I<sub>7</sub> plots had the equal Cd content to that of I<sub>2</sub> plot. At 0-10 cm depth, the I<sub>3</sub> and I<sub>8</sub> plots gave 18% higher Cd content than the control plot.

At 10-20 cm depth, the control plot obtained Cd content of 0.20 mg/kg. The  $I_1$  plot gave 20% and  $I_2$  plot gave 15% higher Cd content than that of control plot. The  $I_3$  and  $I_8$  plots had the equal Cd content to that of  $I_1$  plot. However, the  $I_4$  and  $I_7$  plots had equal Cd content to that of  $I_2$  plot. The  $I_5$  and  $I_6$  plots showed an increase in Cd content compared to control by 10%.

At 20-30 cm depth, the control plot had Cd content of 0.18 mg/kg. The  $I_1$  and  $I_3$  plots increased Cd content than that of control by 22 and 11%, respectively. The  $I_2$ ,  $I_4$  and  $I_8$  plots gave the equal Cd content to that of  $I_1$  plot while the  $I_6$  plot gave the equal Cd content to that of  $I_3$  plot. The  $I_5$  and  $I_7$  plots showed an increase in Cd content than the control plot by 17 and 6%, respectively. In all the depth soils, the Cd content was found the higher with effluents irrigated soils

compared to control soil might be due to the accumulation of Cd from the effluents.

The total Cr content of collected soil samples varied from 48 to74 mg/kg at 0-10 cm, from 44 to 67 mg/kg at 10-20 cm and from 43 to 61 mg/kg at 20-30 cm soil depth (Fig. 15) which was higher than the values (34-68 mg/kg) reported by Ahmed [17]. At 0-10 cm depth, the Cr content 48 mg/kg was found in the control plot. The  $I_1$  plot had 24 and  $I_2$  plots had 14 unit's higher Cr content than that of control plot. The  $I_3$ ,  $I_4$ ,  $I_5$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots showed an increase in Cd content than the control plot by 22, 26, 15, 17, 11 and 5 units, respectively.

At 10-20 cm depth, the control plot obtained Cr content of 44 mg/kg. The  $I_1$  plot had 20 and  $I_2$  plot had 11 unit's higher Cr content than that of control plot. The  $I_3$ ,  $I_4$ ,  $I_5$ ,  $I_7$  and  $I_8$  plots increased in Cr content than the control plot by 19, 23, 12,



Fig. 12. Distribution of available Cu (mg/kg) in effluents and control water irrigated rice soils



Fig. 13. Distribution of available Pb (mg/kg) in effluents and control water irrigated rice soils

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Fig. 14. Distribution of available Cd (mg/kg) in effluents and control water irrigated rice soils



Fig. 15. Distribution of available Cr (mg/kg) in effluents and control water irrigated rice soils



Fig. 16. Distribution of total Ni (mg/kg) in effluents and control water irrigated rice soils.

9 and 4 units, respectively. The  $I_6$  plot gave similar Cr content to that of  $I_5$  plot at 10-20 cm depth.

At 20-30 cm depth, the control plot gave Cr content of 43 mg/kg. The  $I_1$  and  $I_2$  plot increased in Cr than the control by 16 and 9 units, respectively. The  $I_5$  plot gave equal Cr content to that of  $I_2$  plot. At 20-30 cm depth, the  $I_3$ ,  $I_4$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots showed an increase in Cr content than the control plot by 18, 17, 7, 8 and 2 units, respectively. The Cr concentration was obtained the highest at 0-10 cm soil depth as compared to the other two depths indicating that the Cr enrichment at 0-10 cm soil depth. [16] reported that the Cr content decrease with the increasing soil depth in three African cities.

Industrial effluents irrigation affected the Ni status in soil depth. The total Ni content of collected soil samples varied from 51 to 67 mg/kg at 0-10 cm, from 48 to 64 at 10-20 cm and from 45 to 58 mg/kg at 20-30 cm soil depth (Fig. 16). Ahmed and Goni [17] reported that the Ni concentration ranged from 36 to 74 mg/kg in wastewater irrigated soil in industrial areas of Bangladesh. At 0-10 cm depth, the control plot gave total Ni content of 51 mg/kg. The I<sub>1</sub> plot had 16 and I<sub>2</sub> plots had 11 unit's higher Ni content than that of control plot. The I<sub>3</sub>, I<sub>4</sub>, I<sub>5</sub>, I<sub>6</sub>, I<sub>7</sub> and I<sub>8</sub> plots showed an increase in Ni content than the control plot by 13, 14, 15, 7, 12 and 3 units, respectively.

At 10-20 cm depth, the control plot obtained total Ni content of 48 mg/kg. The  $I_1$  and  $I_2$  plots increased in Ni concentration than the control by 16 and 12 units, respectively. The  $I_3$ ,  $I_4$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots showed an increase in Ni content than the control plot by 11, 14, 5, 9 and 3 units, respectively. The  $I_5$  plot gave the equal Ni content to that of  $I_3$  plot at 10-20 cm depth.

At 20-30 cm depth, the control plot gave Ni content of 45 mg/kg. The  $I_1$  plot had 13 and  $I_2$  plot had 12 unit's higher Ni content compared to control. The  $I_3$ ,  $I_4$ ,  $I_6$ ,  $I_7$  and  $I_8$  plots tended to increase in Ni content than the control plot by 10, 13, 7, 2 and 4 units, respectively. The  $I_5$  plot obtained the equal Ni content to that of  $I_3$  plot at 20-30 cm depth. The Ni concentration was obtained the highest at 0-10 cm soil depth as compared to the other two depths indicating that the Ni deposition at 0-10 cm soil depth. A similar result was reported by Abdu et al. [16].

#### 4. CONCLUSION

Results of this experiment showed that the soil chemical properties were affected through effluents irrigation. Effluents irrigation created some differences in soil pH, electrical conductivity and organic carbon. Exchangeable cations (Ca, Mg, K and Na), trace elements (Zn, Fe, Mn and Cu) and heavy metals (Pb, Cd, Cr and Ni) were increased in soils with effluents irrigation.

#### **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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