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Assessing Metallic Toxicity of Wastewater for Irrigation in Some Industrial Areas of Bangladesh

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Abstract

BACKGROUND: Wastewaters were collected from 25 sites of two industrial areas of Mymensingh and Gazipur in Bangladesh to assess metallic toxicity of wastewater for irrigation usage.
METHODS AND RESULTS: The analyzed wastewaters were slightly alkaline to alkaline in nature and were problematic for irrigation except 3 samples. As per TDS values, 9 samples were rated as fresh water and the rest 16 were classified as brackish water. EC and SAR reflected that all samples were medium salinity (C2), high salinity (C3), very high salinity (C4) and low alkalinity (S1) hazard classes expressed as C2S1, C3S1 and C4S1. Wastewaters of different industries were graded as excellent, good, permissible and doubtful for irrigation purpose as per SSP. According to hardness (H_T), wastewater were under moderately hard, hard and very hard classes. Cd, Cr and Cu ions were treated as toxicant for irrigating soils and crops. Zn was problematic for long-term irrigation. The concentrations of Pb, Fe and Na were far below the toxic levels. Synergistic relationships were observed between pH-EC, pH-TDS, EC-TDS, SAR-SSP and SSP-hardness.
CONCLUSION(s): If wastewater is applied for irrigation due to the fresh water shortage, it can contaminate soil due to some toxic metal ions.

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Key Words: H_T, Irrigation, Metallic Toxicity SAR, SSP, Wastewater

Introduction

Industrial wastewater is mostly used for the irrigation of crops due to its easy availability, disposal problems and scarcity of fresh water. Using wastewater to irrigate agricultural land is one of way to reuse the wastewater from urban and industrial areas. Wastewater irrigation has long been adopted in the developing countries like Bangladesh due to its high fertility and is also considered the best substitute of the freshwater shortages. While irrigation is a beneficial use of wastewater in water scarce regions, the contaminants present in it pose several environmental and health problems. Search for new water resources for irrigation is required among which is the reuse of wastewater for agricultural purposes because they contain a number of nutrients in much large amount than other compost material and can be a good source of organic matter (Mitra and Gupta, 1999; Aktar *et al.*, 2008). Irrigation with wastewater is said to have both beneficial and harmful effects (Singh *et al.*, 2004; Chen *et al.*, 2005). The use of wastewater for irrigation has been associated with a number of advantages such as increases in OC, N, P, K and Mg contents of the soil as compared to clean groundwater irrigation (Tiwari *et al.*, 2003).The utilization of wastewater resources is essential for meeting the everincreasing demand for irrigation water but on the other hand, it may lead to adverse health implications by heavy-metal contamination in agricultural production systems.

Irrigation with wastewater is known to contribute significantly to the heavy metals content of soil. Wastewater irrigation leads to accumulation of heavy metals in the soil (Singh *et al.*, 2004; Chen *et al.*, 2005; Mapanda *et al.*, 2005; Bahmanyar, 2008). Wastewater irrigation led to increase the heavy-metal concentrations in the soil and consequently to the plant (Arora *et al.*, 2008; Singh *et al.*, 2009). Excessive accumulation of heavy metals in agricultural soils through wastewater irrigation may not only result in soil contamination but also affect food quality and safety (Muchuweti *et al.*, 2006). It is, therefore, an urgent need to assess the quality of wastewater before utilization for irrigation. Considering the national importance, wastewater needs to be modified or improved in such a way that crop production will not be hampered. Systematic research has not yet been done on wastewater quality of these industrial areas and its impact on crop production as well as soil health. The objective of this study was to assess the status of toxic metals in order to categorize wastewater as per standard criteria for predicting the efficient use of wastewater for irrigation usage.

Materials and Methods

Exactly 25 wastewater samples were collected from some selected industrial areas of Bhaluka, Mouchak, Chandra and Tongi during January, 2010 following the sampling techniques as outlined by Sincero and Sincero (2004) and American Public Health Association (2005) depending on the degree of intensity of industrial pollution. Wastewater sampling sites have been presented in Fig. 1. Wastewater samples were filtered through filter paper (Whatman No. 1) to remove undesirable solid and suspended materials before chemical analysis. pH was measured by pH meter (Model: WTW pH522) and EC was estimated by conductivity meter (Model: WTW LF521) according to the technique as described by Singh *et al.* (1999). Total dissolved solids (TDS) were measured by evaporating water samples to dryness (Chopra and Kanwar, 1980). The contents of Ca and Mg were determined by EDTA titrimetric method (American Public Health Association, 2005). The quantities of K and Na were determined by flame photometric method (Tandon, 1995). The concentrations of Zn, Cu, Fe, Mn, Pb, Cd and Cr were analyzed by atomic absorption spectrometric method (American Public Health Association, 2005). The following parameters were considered in judging wastewater quality by the interpretation of obtained analytical results:

Fig. 1. Wastewater sampling sites in the industrial areas of Bangladesh.

i) Sodium adsorption ratio (SAR)

$$= \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

ii) Soluble sodium percentage (SSP)

$$= \frac{Na^{+} + K^{+}}{Ca^{++} + Mg^{++} + Na^{+} + K^{+}} \times 100$$

iii) Hardness $(H_T) = 2.5 \times Ca^{++} + 4.1 \times Mg^{++}$

Where, ionic concentrations were expressed as me/L in all parameters but as mg/L in case of hardness.

Results and Discussion

The chemical constituent and the quality classification of wastewater for irrigation have been presented in Tables 1-3. In the study areas, metallic constituents such as Ca, Mg, K, Na, Zn, Cu, Fe, Mn, Pb, Cd and Cr were analyzed and major metal ions like Ca, Mg, K and Na were dominant but the remaining metal ions were also detected in minor amounts in all wastewater samples. The obtained analytical results have been discussed under the following headings:

pH, EC and TDS

pH values of all wastewater samples ranged from 7.73 to 10.25 indicating slightly alkaline to alkaline in nature (Table 1). The acceptable pH range for irrigation is usually from 6.5 to 8.4 (Ayers and Westcot, 1994). Accordingly, 22 wastewater samples were problematic for long-term irrigation and these waters might be harmful for soils and crops except 3 samples (Sample nos: 11, 12 & 23). These findings were in agreement the findings of Tiwari *et al.* (2003). The electrical conductivity (EC) of all samples was within the limit of 550 to 3260 μS/cm with an average of 1708 μS/cm (Table 1). The highest EC value (3260 μS/cm) was recorded in Givency Group Ltd. (Sample no.: 15) and the lowest value (550 μS/cm) was obtained in Bengal Horiken Textile Ltd. (Sample no.: 14). According to Richards (1968), only 2 (Sample nos.: 14 & 21) samples were rated as medium salinity class which might be applied with moderate leaching, 18 samples were graded as high salinity class and the rest 5 samples were classified as

Table 1. pH, EC and TDS of wastewater samples

Sample No.	Name of the Industry	Location		pH	EC μS/cm	TDS mg/L
		District	Industrial area			
01	Shepherd Yarn Industries Ltd.	Mymensingh	Bhaluka	9.38	2220	1487
02	Consumer Knitex Ltd.			8.67	2308	1546
03	Becon Pharmaceuticals			9.15	1620	1085
04	Square Textile Ltd.			8.69	1935	1296
05	Yarn Dying Ltd			8.89	2025	1357
06	Adv. Knit Composite Ltd.			8.48	1960	1313
07	Shahin Textile Ltd.			8.88	1932	1294
08	Color Master Yarn Dying			8.52	1530	1025
09	Mark Limited	Gazipur	Mouchak	8.73	1384	927
10	Mark Washing & Dying Ltd.			9.20	2720	1822
11	One Composite Ltd.			7.73	875	586
12	Utah Kniting & Dying Ltd.			8.28	988	662
13	Golden Harvest Ltd. (Food)		Chandra	8.95	2670	1789
14	Bengel Horiken Textile Ltd.			8.82	550	369
15	Givency Group Ltd.			9.63	3260	2184
16	Lily Food Industries		Tongi	8.55	1894	1269
17	Pacific Knit & Febric Ltd.			8.95	1314	880
18	Uttara Food Industries Ltd.			8.84	980	657
19	Eshan Fasion Ltd.			10.25	2941	1970
20	Picas Ltd.			8.53	822	551
21	SR Fabrics Ltd.			8.96	614	411
22	Finix Home Textile Ltd.			9.13	1634	1095
23	Insaf Fabrics Ltd.			8.36	873	585
24	SAP Fabrics Ltd.			9.22	1892	1268
25	Biopharma Laboratories Ltd.			9.60	1775	1189
			Range	7.73 to 10.25	550 to 3260	369 to 2184
			Mean		1708	1145
			SD		733	492
			CV (%)		42	43

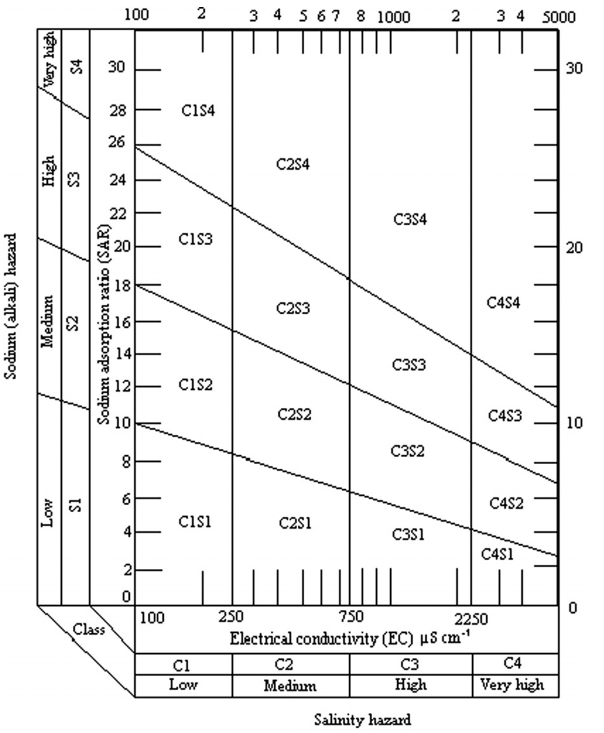

Fig. 2. Diagram for classifying irrigation water proposed by Richards (1968).

very high salinity which were treated as unsuitable for irrigation as presented in Fig. 2. The total dissolved solids (TDS) values varied from 369 to 2184 mg/L with a mean value of 1145 mg/L (Table 1). TDS values of 11 samples were less than their respective mean value while the rest 7 samples were higher than the average value. Based on this, 9 samples were considered as fresh water (TDS <1000 mg/L) and the rest 16 samples were considered as brackish water (TDS= 1,000-10,000 mg/L) in quality as per the classification suggested by Freeze and Cherry (1979). It is clearly demonstrated that irrigating fields by brackish waters would affect the osmotic pressure of soil solution and cell sap of the plants.

Ca and Mg

The concentrations of Ca and Mg in all samples ranged from 1.10 to 7.13 and 1.12 to 5.00 me/L with mean values of 2.45 me/L and 2.77 me/L, respectively (Table 2). The contribution of Ca in water was largely dependent on the solubility of $CaCO_3$, $CaSO_4$ and rarely on $CaCl_2$ (Karanth, 1994). According to Ayers and Westcot (1994), irrigation water containing less than 20 me/L Ca and 5 me/L Mg is suitable for irrigating crops. On the basis of Ca and Mg contents, all samples of Ca and Mg could safely be used for irrigation without any harmful impact on soil environment.

K and Na

The status of K in all wastewater samples was within the range of 0.04 to 0.78 me/L with a mean value of 0.23 me/L (Table 2). The detected level of K in all samples had no significant influence on water quality for irrigation (Ayers and Westcot, 1994). The content of Na was recorded within the limit of 0.34 to 7.97 me/L with an average value of 2.59 me/L (Table 2). According to Ayers and Westcot (1994), irrigation water containing less than 40 me/L Na is suitable for irrigating crops. The content of Na was far below this specified limit and could safely be applied for long-term irrigation.

Zn, Cu, Fe and Mn

The content of Zn ranged from 0.04 to 2.02 mg/L with an average value of 0.78 mg/L (Table 2). Maximum permissible limit of Zn in irrigation water is 2.00 mg/L (Ayers and Westcot, 1994). Accordingly, 21 wastewater samples did not exceed maximum permissible limit indicating no toxicity for irrigation. On the other hand, the recorded concentration of Zn in 4 samples (sample nos.: 5, 10, 12 & 14) were above the legal limit and this metal was considered as troublesome ion for long-term irrigation. The concentration of Cu varied from 0.21 to 4.10 mg/L with a mean value of 1.20 mg/L (Table 2). The content of Cu in all samples was higher than the recommended limit (0.20 mg/L) as reported by Ayers and Westcot (1994). As per this limit, Cu was treated as toxic ion for irrigation. The concentration of Mn in all samples ranged from 0.14 to 1.59 mg/L with an average value of 0.68 mg/L (Table 2). All samples except two samples (sample nos.: 17 & 18) were not suitable for irrigation because maximum legal limit of Mn in water used for irrigation is 0.20 mg/L as per Ayers and Westcot (1994).The amount of Fe ranged from 0.07 to 1.96 mg/L with an average value of 0.82 mg/L (Table 2). Based on the Fe content, all samples were suitable for irrigation showing no ionic toxicity (Ayers and Westcot, 1994).

Pb, Cd and Cr

The status of Pb in wastewater samples ranged from 0.02 to 2.10 mg/ L with a mean value of 0.36 mg/L (Table 2) reflecting no toxicity for irrigation

Table 2. Metallic constituents of wastewater samples

Sample No.	Ca	Mg	K	Na	Zn	Cu	Mn	Fe	Pb	Cd	Cr
	me/L				mg/L						
1	1.86	1.34	0.29	3.10	0.12	0.26	0.42	1.64	1.20	0.83	1.16
2	1.54	2.26	0.30	1.88	0.04	0.28	0.24	0.96	0.13	0.07	0.26
3	3.00	1.60	0.24	1.23	0.05	0.22	0.71	0.58	0.07	0.13	0.34
4	2.06	3.30	0.21	1.30	1.08	1.14	1.53	0.73	0.08	0.06	0.20
5	1.97	2.80	0.27	2.04	2.10	0.79	0.23	0.08	0.18	0.07	0.24
6	1.60	2.44	0.26	1.17	0.63	0.89	0.22	1.32	0.02	0.10	0.32
7	1.80	2.32	0.24	7.76	0.30	0.79	0.82	0.85	0.03	0.25	0.40
8	1.14	3.60	0.05	0.34	0.15	0.53	0.27	0.09	0.10	0.03	0.14
9	1.34	1.66	0.06	6.46	0.87	0.69	0.78	0.78	0.04	0.08	0.18
10	1.10	1.86	0.28	7.97	2.20	0.98	0.85	1.96	0.53	0.76	1.10
11	1.46	2.26	0.23	2.36	0.73	1.72	0.78	0.62	0.75	0.40	0.74
12	1.67	2.46	0.20	0.56	2.50	1.00	0.81	0.59	0.10	0.30	0.62
13	1.33	3.20	0.20	0.77	0.50	3.00	0.58	0.57	0.08	0.12	0.32
14	3.80	5.00	0.05	2.07	2.40	0.29	0.39	1.14	0.04	0.07	0.20
15	2.07	3.40	0.06	1.77	0.62	0.88	0.87	0.72	0.08	0.08	0.22
16	4.22	2.90	0.11	2.75	0.73	1.92	0.23	0.07	0.79	0.59	0.84
17	1.67	3.52	0.78	0.43	0.59	2.32	0.18	0.10	0.62	0.72	1.00
18	7.13	1.96	0.55	0.44	1.14	0.21	0.14	0.84	0.09	0.82	1.14
19	3.13	2.26	0.33	0.74	0.57	0.26	0.64	1.78	2.10	1.02	1.50
20	2.04	4.36	0.18	1.30	0.64	0.23	1.32	0.08	0.21	0.77	1.12
21	3.20	2.31	0.23	4.83	0.06	0.52	0.84	0.88	0.07	0.62	0.84
22	1.40	1.12	0.26	1.51	0.92	4.10	1.12	1.56	0.04	0.79	0.90
23	2.20	2.86	0.30	3.70	1.59	3.10	0.83	1.32	0.25	0.09	0.24
24	3.60	3.65	0.04	6.65	0.07	0.72	1.59	0.72	0.75	0.54	0.82
25	5.02	4.40	0.05	1.75	0.06	3.21	0.71	0.68	0.87	0.05	0.18
Range	1.10 to 7.13	1.12 to 5.00	0.04 to 0.78	0.34 to 7.97	0.04 to 2.50	0.21 to 4.10	0.14 to 1.59	0.07 to 1.96	0.02 to 2.10	0.03 to 1.02	0.18 to 1.50
Mean	2.45	2.77	0.23	2.59	0.78	1.20	0.68	0.82	0.36	0.37	0.60
SD	1.42	1.03	0.16	2.32	0.67	1.11	0.40	0.54	0.49	0.33	0.42
CV (%)	57.95	37.18	69.56	89.57	85.89	92.50	58.82	65.85	136.11	89.18	70.00

use. As because, the detected concentration of Pb was far below the acceptable limit (5.00 mg/L) as mentioned by Ayers and Westcot (1994). The wastewater samples contained Cd ranging from 0.03 to 1.02 mg/L with an average value of 0.37 mg/L (Table 2). According to Ayers and Westcot (1994), maximum permissible limit of Cd in water used for irrigation is 0.01 mg/L. Accordingly, the recorded Cd content in all samples exceeded the permissible limit and this ion was treated as toxicant for irrigating soils and crops. The level of Cr ranged from 0.18 to 1.50 mg/L with an average value of 0.60 mg/L (Table 2). On the basis of detected Cr content (>0.10 mg/L), all samples were not suitable for irrigation and this metal ion was considered as toxicant for long-term irrigation (Ayers and Westcot, 1994).

Wastewater quality determining indices

The computed results in Table 3 indicated that the calculated SAR and SSP values of all collected wastewater samples varied from 0.21 to 6.60 and 7.60 to 73.86%, respectively. Wastewaters containing SAR less than 10 were considered as excellent in quality reflecting low alkalinity hazard (S1) and could be safely used for irrigation but might not be harmful for agricultural crops (Todd, 1980). Considering this

Table 3. Quality classification of wastewater samples for irrigation

Sample No.	SAR		SSP (%)		H_T (mg/L)		Alkalinity and salinity hazard classes
	Value	Class	Value	Class	Value	Class	
1	2.45	Ex.	51.44	Perm.	158.92	Hard	C3S1
2	1.36	Ex.	36.45	Good.	188.19	Hard	C4S1
3	0.81	Ex.	24.22	Good	228.72	Hard	C3S1
4	0.79	Ex.	21.98	Good	265.36	Hard	C3S1
5	1.32	Ex.	32.63	Good	236.26	Hard	C3S1
6	0.82	Ex.	26.14	Good	200.05	Hard	C3S1
7	5.41	Ex.	66.01	Doubt.	204.14	Hard	C3S1
8	0.22	Ex.	7.60	Ex.	234.12	Hard	C3S1
9	5.27	Ex.	68.49	Doubt.	148.67	MH	C3S1
10	6.60	Ex.	73.86	Doubt.	144.51	MH	C4S1
11	1.73	Ex.	41.05	Perm.	184.19	Hard	C3S1
12	0.39	Ex.	15.54	Ex.	204.53	Hard	C3S1
13	0.51	Ex.	17.64	Ex.	223.94	Hard	C4S1
14	0.96	Ex.	18.63	Ex.	458.63	VH	C2S1
15	1.07	Ex.	25.07	Good	270.78	Hard	C4S1
16	1.46	Ex.	28.66	Good	353.68	VH	C3S1
17	0.27	Ex.	18.91	Ex.	256.68	Hard	C3S1
18	0.21	Ex.	9.82	Ex.	452.93	VH	C3S1
19	0.45	Ex.	16.56	Ex.	267.69	Hard	C4S1
20	0.73	Ex.	18.78	Ex.	316.51	VH	C3S1
21	2.91	Ex.	47.87	Perm.	273.65	Hard	C2S1
22	1.35	Ex.	41.26	Perm.	125.10	MH	C3S1
23	2.33	Ex.	44.15	Perm.	250.71	Hard	C3S1
24	3.49	Ex.	47.99	Perm.	359.58	VH	C3S1
25	0.81	Ex.	16.04	Ex.	467.48	VH	C3S1

Legend: Ex. = Excellent, Perm. = Permissible, Doubt = Doubtful, MH = Moderately Hard, VH = Very Hard, C2 = Medium Salinity, C3 = High Salinity, C4 = Very High Salinity and S1 = Low Alkalinity

value, all water samples were graded as excellent for irrigation purpose. Based on SSP, 9 samples were classified as excellent (SSP=<20%), 7 samples were classified as good (SSP=60-80%), 6 samples were classified as permissible (SSP=40-60%) and the rest 3 samples were rated as doubtful classes (SSP=60-80%) according to water classification proposed by Todd (1980). The hardness values of all samples varied from 125.10 to 467.48 mg/L in which hardness categorized 3 samples as moderately hard (H_T =75-150 mg/L), 16 samples as hard (H_T=151-300 mg/L) and the rest 6 samples as very hard (H_T>300 mg/L) classes following the classification of Sawyer and McCarty (1967). Hardness of waters resulted due to the abundant of divalent cations like Ca^{2+} and Mg^{2+} (Todd, 1980).

Relationship between wastewater quality parameters

The relationship between six water quality parameters like pH, EC, TDS, SAR, SSP and hardness was established and out of 15 combinations, 5 were differed significantly at 1% level (Table 4). Synergistic relationships were observed between pH-EC, pH-TDS, EC-TDS, SAR-SSP and SSP-Hardness.

It is evident from the experimental findings that most of the wastewater samples were not found suitable for irrigation as these samples contained toxic metal ions like Cd, Cr, Cu and Mn as compared to the permissible limit. Before irrigating these contaminated wastewater samples for crop production, appropriate sustainable remediation technology should be adopted for treating these samples in the investigated area.

Table 4. Correlation matrix among wastewater quality parameter

Parameters	EC	TDS	SAR	SSP	Hardness
pH	0.614^{**}	0.614^{**}	0.039^{ns}	0.012^{ns}	0.163^{ns}
EC		0.980^{**}	0.118^{ns}	0.106^{ns}	0.281^{ns}
TDS			0.118^{ns}	0.105^{ns}	0.281^{ns}
SAR				0.947^{**}	0.364^{ns}
SSP					0.519^{**}

Legend: ** = Significant at 1 % level; ^{ns} = Not significant
Tabulated value of r with 23 df is 0.505 at 1% level of significance.

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