Seasonal Variability of Trace and Heavy Metals Concentration in Groundwater and its Quality for Drinking and Irrigation Purpose under Phuleli Canal Command Area (Sindh), Pakistan

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Abstract: The availability of good quality groundwater is a serious problem not only for drinking purpose but also for agriculture production. Human health problems due to waterborne diseases are commonly reported in Phuleli Canal Command area. In this context, a study was conducted to find out the existence of heavy metals as well as trace elements in groundwater of Phuleli Canal Command area, (Sindh) Pakistan which were affected by seasonal variability. The groundwater samples were collected from different seven locations i.e. RD-0, RD-30, RD-50, RD-70, RD-90, RD-110 and RD-130 throughout four seasons (summer, autumn, winter, and spring). Results of analysis of groundwater samples showed that Fe, Cd, Cr and Pb concentration in groundwater was higher than WHO permissible limit while Cu and Mn concentrations were greater than FAO limit. Comparatively heavy metals (Cd, Cr, Pb and As) concentrations in groundwater were higher towards downstream reach in winter as compared to upstream reach. Regarding seasons, the values of these parameters decreased in autumn>spring>summer. The results also showed increasing trend of heavy metal concentrations towards downstream reach (RD 130>110>90>70>50>30>0). It was concluded that groundwater in Phuleli Canal Command area contains highly toxic metals above the permissible limits of WHO and FAO for human consumption and agricultural crops respectively. Hence, people using groundwater, directly or indirectly, at downstream reach of the canal are at health risk.

Keywords: Trace metal, Heavy metal, Phuleli Canal, reduced distance (RD), WHO and FAO.

INTRODUCTION

The water is important for existence of life on the earth [1]. Over two thirds of the earth's surface is covered with water which is certainly the most valuable natural resource. Although it is a recognized fact, but it is disregarded by humans; and they are polluting rivers, lakes and oceans and thus, fresh water has turned into a scarce commodity globally [2]. The optimum utilization of water resources is of paramount importance because the world as a whole is suffering from water shortages [3, 4]. Pakistan is presently facing the situation that all its developed water resources are inadequate to meet the irrigation and other water requirements [5]. Groundwater is also a supplemental source for domestic use, agricultural and industrial sector now a day. In recent years increasing threats to groundwater quality due to human activities has become of immense importance. The adverse effects on groundwater quality are the over burden of the population pressure, unplanned population, unrestricted exploration, unintentionally by domestic, agriculture and industrial effluents and dumping of polluted water at inappropriate place enhance the infiltration/seepage of harmful compounds like trace and heavy metal to the groundwater [6-8]. Specially, trace metal pollution of water has emerged as serious health problem highlighted in published work [9]. Heavy metals are designating a group of elements that occur in natural system in minute concentration and when present in sufficient quantities, they are toxic to living organisms. The behavior of trace metals in groundwater is complicated and is related to source of group water and the bio-geochemical process in elemental conditions [10]. Some metals are essential for normal functioning of the human body, whereas others are non-essential [11]. Most of the metals are important for the growth, development and health of living organisms [12]. It is evident through document that the primary pathways of toxic metal accumulation in human are through ingestion of contamination water and food [13, 14]. Health related studies have shown that excessive intake of toxic trace metals results in neurological and cardiovascular diseases, as well arenal dysfunction [15, 16]. Therefore, the initial step towards assessment of health risks posed by metal pollution requires regular monitoring of water quality in terms of trace metal distribution and source identification [17].

Like other cities of Pakistan, Hyderabad is also facing a great problem of safe disposal of wastewater.

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ISSN: 1814-8085 / E-ISSN: 1927-5129/13

Highly toxic run-off from plastic factories, illegal cattle pens, slaughterhouses and sewage water is directly disposed off either by gravity flow or by means of pumping into Phuleli canal without any treatment [18] as it passes through Hyderabad. As a result, Phuleli canal has put in jeopardy lives of millions of people in Hyderabad, Badin, Tando Muhammad Khan and Matli towns of Sindh province of Pakistan because they use this contaminated water for drinking purpose [19-21]. This untreated sewage water contains dissolved and suspended solids, inorganic and organic compounds, oils, solvents, greases, thermal discharge, etc. Groundwater is in nature replenished by surface water from precipitation, streams and rivers. It is not as prone to pollution as surface water but once polluted restoration is difficult in long term [1, 22]. The groundwater is said to be polluted due to leachate of harmful chemicals and is considered unfit for drinking purpose and agriculture use. Therefore, it is imperative to protect the freshwater bodies of Sindh Province. Quality of groundwater with regard to trace and heavy metal may vary from place to place and from stratum to stratum. It also varies from season to season. The determination of appropriateness of groundwater would, therefore involve a description of the occurrence of the various constituents and their relation to the use to which water would be put [23]. The present study is therefore an attempt to analyze trace element and heavy metal seasonal distribution in groundwater for drinking and irrigation in command area of Phuleli Canal.

MATERIALS AND METHODS

Groundwater quality for trace and heavy metals were monitored during four seasons (summer, autumn, winter and spring) at seven locations (RD-0, RD-30, RD-50, RD-70, RD-90, RD-110 and RD-130) of Phuleli command area. These locations start from Kotri Barrage (Ghulam Muhammad Barrage) towards RD-30, RD-50, RD-70, RD-90 situated in Hyderabad district, while RD-110, RD130 fall in Tando Muhammad Khan district. The locations of the study are shown in Figure **1**. The trace and heavy status was then compared with WHO/FAO standards.

Sample Collection

For determination of trace and heavy metals concentration in groundwater, the water samples were obtained directly from the hand pump installed about 100-110 m away from Phuleli Canal near each location (Figure **1**). The purging was carried out by making one stroke for every foot of water depth [24]. The samples for determination of heavy/trace metals were kept in glass bottles prewashed with detergent, diluted HNO_3 and double de-ionized distilled water as described by [25, 26]. Collected samples were sent to the laboratories of Land and Water Management, Faculty of Agricultural Engineering, Sindh Agriculture University Tandojam and Drainage Research Center, Tandojam. For heavy metal determination, the 2 ml ultra HNO_3 per litre was added in the samples and kept in refrigerator at 4°C for laboratory analysis as described by [25, 26].

Determinations

The determinations of metals direct air acetylene flame method was adopted for water sample determination on Atomic Absorption Spectrophotometer [27].

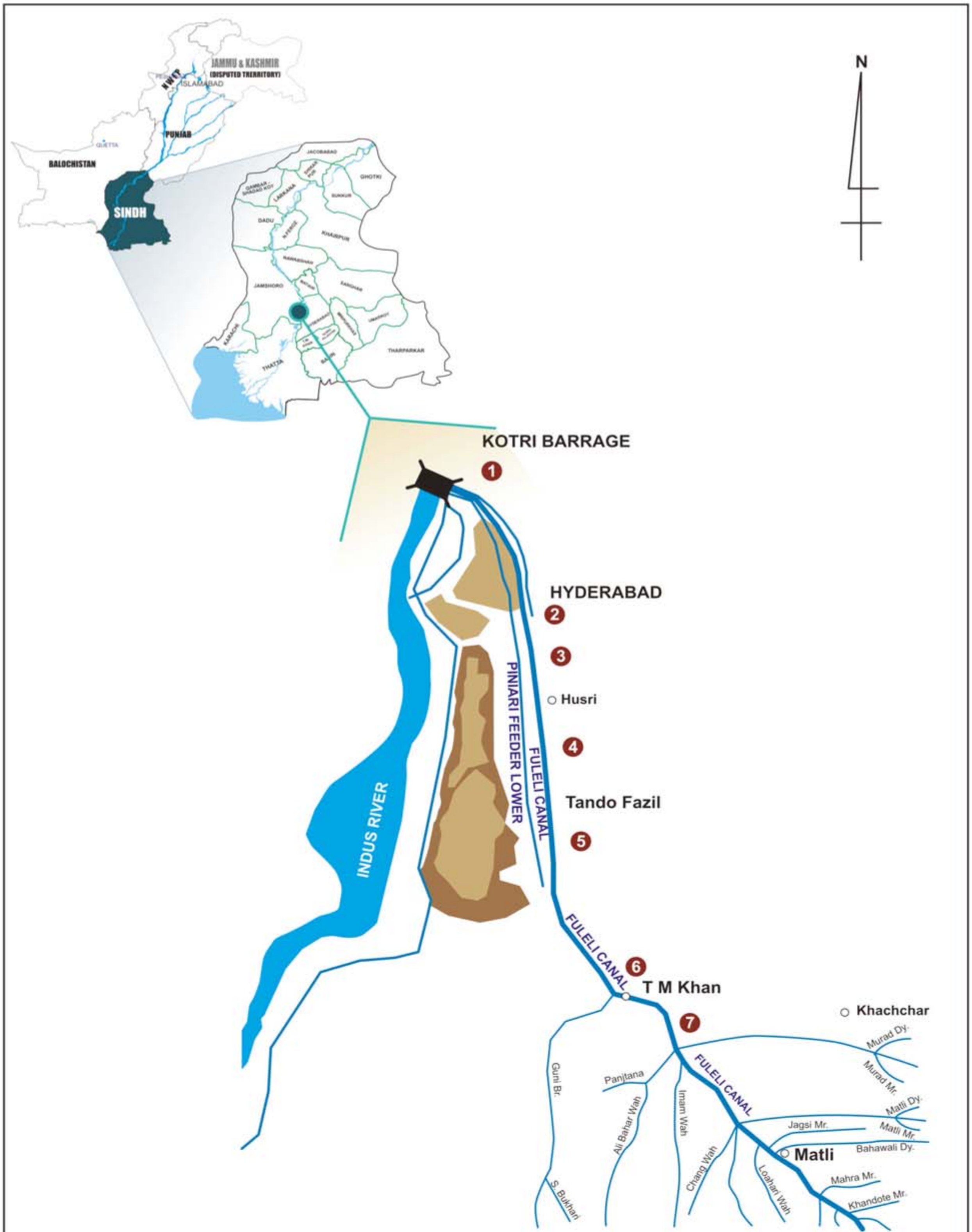
Statistical Analysis

The data collected were subjected to statistical analysis using analysis of variance technique. The LSD (Least Significant Differences) test was applied to compare the individual treatment means as per the statistical methods developed by [28]. The above statistical analyses were performed using MSTAT-C Computer Software.

RESULTS

Seasonal variability of trace and heavy metals concentration of groundwater revealed that the higher concentration of Zn (0.094 mg L^{-1}), Fe (2.89 mg L^{-1}), Cd (0.0059 mg L^{-1}), Cr (0.05 mg L^{-1}) Pb (0.53 mg L^{-1}) and As (3.727 ug L^{-1}) were present in groundwater of canal command area during winter than those collected during autumn, spring and summer seasons. However, Cu (0.61 mg L^{-1}) and Mn concentration (0.31 mg L^{-1}) were higher during summer (Table **1**). Comparing results with those recommended by WHO, it was noted that Zn, Cu, Mn and As concentration in groundwater was within the permissible limit for human consumption/drinking purpose, but Fe, Pb and Cr were not within permissible limit in all season. With regard to groundwater use for irrigation/crop production, the results indicated that Zn, Fe, Cd, Cr, Pb and As concentrations in groundwater were within the permissible limits of FAO in all seasons except Cu and Mn which were higher during summer and spring seasons.

Similarly, the trace and heavy metals concentration of groundwater were different at various locations



1	RD-0	Near Ghulam M. Barrage
2	RD-30	Expo-Center Hyderabad
3	RD-50	Harsheg Patel
4	RD-70	Near City Hosri
5	RD-90	Near Katiar
6	RD-110	Mohd Moosa Rindh
7	RD-130	Hussain Khan Laghari

Note: Reduced distance (RD)=304.8 m

Figure 1: Map showing locations along Phuleli Canal Command area from where groundwater samples were taken.

Table 1: Trace and Heavy Metals Concentration of Groundwater in Various Seasons as Affected by Water of Phuleli Canal

Parameters (mg L^{-1})	SE	LSD (5%)	Seasons				*WHO (mg L^{-1})	**FAO (mg L^{-1})
			Summer	Autumn	Winter	Spring		
Zn	0.0022	0.0098	0.026 d	0.061 b	0.094 a	0.042 c	3.0	2
Fe	0.0023	0.0096	1.400 d	2.14b	2.89 a	1.724 c	0.3	5
Cu	0.0019	0.0099	0.6045 a	0.36 c	0.27 d	0.50 b	2.0	0.2
Mn	0.0024	0.0095	0.31 a	0.15 c	0.065d	0.24 b	0.5	0.2
Cd	0.0018	0.0097	0.0019 d	0.0037 b	0.0059 a	0.003 c	0.003	0.01
Cr	0.0024	0.0096	0.026 c	0.042 ab	0.05 a	0.033 bc	0.05	0.10
Pb	0.0018	0.009	0.22 d	0.36 b	0.53 a	0.32 c	0.01	5.0
As (µg L^{-1})	0.06796	0.3059	2.08 d	3.18 b	3.727 a	2.65 c	0.01	0.1

In each row, means followed by common letter are not significantly different at 5% probability level.
*Max: permissible limit for drinking purpose/human consumption [56].
**Recommended Maximum concentration for irrigation/crop production [57].

(Table **2**). The upper reach (RD-0) showed higher Zn (0.15 mg L^{-1}) concentration, RD-30 indicated the higher Fe (2.98 mg L^{-1}) and Mn (0.32 mg L^{-1}) level. While, lower concentration of Zn (0.023 mg L^{-1}) was noted at down reach, RD-130 (Table **3**). Whereas, the down reach (RD-130) revealed the higher concentration of As, Cd, Cr, Cu and Pb (16.42 ug L^{-1}, 0.005, 0.06, 0.65 and 0.57 mg L^{-1}) which were minimum at upper reach RD-0.

However, Cd was found maximum in all locations which was statistically at par with reference to permissible limits of WHO for water usage for drinking purpose, the results for Zn, Cu, Mn and As concentration in groundwater at different locations were within the permissible limits. While, Fe and Pb were found higher at all locations.

With regard to permissible limits of water usage mentioned by FAO for agriculture/crop production/irrigation, the Zn, Fe, Cu, Cr, Pb and As in groundwater of canal command area were within the permissible limit of FAO. Cu was significantly higher than the permissible limit at mid to down reach (RD-50

Table 2: Trace and Heavy Metals Concentration of Groundwater at Various Locations as Affected by Water of Phuleli Canal

Parameters (mg L^{-1})	SE	LSD (5%)	Locations							*WHO (mg L^{-1})	**FAO (mg L^{-1})
			RD-0 (Regulator)	RD-30	RD-50	RD-70	RD-90	RD-110	RD-130		
Zn	0.0028	0.0098	0.15 a	0.084 b	0.042 c	0.04 cd	0.028 de	0.026 de	0.023 e	3.0	2
Fe	0.0129	0.0447	1.145 g	2.98 a	2.71 b	2.3c	1.99 d	1.67 e	1.51 f	0.3	5
Cu	0.0027	0.0097	0.15 g	0.17 f	0.45 e	0.49 d	0.52 c	0.61 b	0.65 a	2.0	0.2
Mn	0.0029	0.0098	0.097 f	0.32 a	0.31 b	0.21 c	0.18 d	0.12 e	0.12 e	0.5	0.2
Cd	0.0028	0.0096	0.002 a	0.003 a	0.003 a	0.004 a	0.004 a	0.005 a	0.005 a	0.003	0.01
Cr	0.0027	0.0099	0.02 f	0.025 ef	0.031 de	0.036 cd	0.042 bc	0.05 ab	0.06 a	0.05	0.10
Pb	0.0029	0.0098	0.13 g	0.19 f	0.22 e	0.36 d	0.50 c	0.52 b	0.57 a	0.01	5.0
As (ug L^{-1})	0.0899	0.3111	0.20 d	0.30 cd	0.48 cd	0.53 c	0.60 c	1.84 b	16.42 a	0.01	0.1

In each row, means followed by common letter are not significantly different at 5% probability level.
*Max: permissible limit for drinking purpose/human consumption [56].
**Recommended Maximum concentration for irrigation/crop production [57].

Table 3: Interactive Effect of Seasons x Locations of Groundwater on Trace and Heavy Metal Concentration as Affected by Water of Phuleli Canal

Seasons	Locations	Parameters (mg L^{-1})							µg L^{-1}
		Zn	Fe	Cu	Mn	Cd	Cr	Pb	As
Summer	RD-0 (Regulator)	0.05 fg	0.42 r	0.20 q	0.15 i	0.001 a	0.011 j	0.10 q	0.11 ij
	RD-30	0.041 f-h	2.27 h	0.25 p	0.46 b	0.001 a	0.015 ij	0.12 q	0.17 ij
	RD-50	0.03 h-j	2.15 i	0.62 h	0.54 a	0.002 a	0.018 h-j	0.11 q	0.29 ij
	RD70	0.02 h-j	1.65 l	0.72 d	0.35 c	0.002 a	0.03 g-j	0.12 q	0.32 ij
	RD-90	0.018 ij	1.44 m	0.76 c	0.29 d	0.002 a	0.033 f-i	0.35 k	0.33 ij
	RD-110	0.019 ij	0.99 o	0.82 b	0.20 f	0.003 a	0.035 e-h	0.37 j	1.36 fg
	RD-130	0.014 j	0.89 p	0.87 a	0.19 fg	0.003 a	0.041 c-g	0.40 i	12.00 d
Autumn	RD-0 (Regulator)	0.18 b	0.98 o	0.13 st	0.08 k	0.002 a	0.023 g-j	0.11 q	0.22 ij
	RD-30	0.10 d	3.47 b	0.13 t	0.29 d	0.003 a	0.027 f-j	0.21 p	0.34 ij
	RD-50	0.04 f-h	2.67 e	0.34 n	0.28 de	0.004 a	0.036 e-h	0.26 n	0.54 h-j
	RD70	0.04 g-i	2.41 fg	0.38 m	0.15 i	0.004 a	0.04 c-g	0.32 lm	0.63 h-j
	RD-90	0.03 g-j	1.98 j	0.43 l	0.12 j	0.004 a	0.042 c-g	0.50 f	0.65 h-j
	RD-110	0.024 h-j	1.76 k	0.54 k	0.07 kl	0.005 a	0.058 a-c	0.52 f	1.87 f
	RD-130	0.023 h-j	1.71 kl	0.57 j	0.07 kl	0.005 a	0.065 ab	0.61 e	18.00 b
Winter	RD-0 (Regulator)	0.29 a	2.41 fg	0.12 t	0.04 n	0.003 a	0.030 f-j	0.20 p	0.28 ij
	RD-30	0.13 c	3.70 a	0.130 t	0.19 fg	0.004 a	0.036 e-h	0.23 o	0.43 h-j
	RD-50	0.07 e	3.63 a	0.17 r	0.06 lm	0.006 a	0.042 c-g	0.32 l	0.65 h-j
	RD70	0.06 ef	3.04 c	0.29 o	0.05 mn	0.007 a	0.047 b-f	0.68 d	0.75 hi
	RD-90	0.04 f-h	2.84 d	0.33 n	0.04 n	0.007 a	0.053 a-e	0.72 c	0.98 gh
	RD-110	0.04 f-h	2.48 f	0.44 l	0.04 n	0.007 a	0.068 a	0.75 b	2.67 e
	RD-130	0.04 f-h	2.14 i	0.44 l	0.04 n	0.008 a	0.070 a	0.77 a	20.33 a
Spring	RD-0 (Regulator)	0.097 d	0.77 q	0.15 s	0.12 j	0.001 a	0.018 h-j	0.11 q	0.19 ij
	RD-30	0.07 e	2.48 f	0.18 r	0.35 c	0.002 a	0.023 g-j	0.20 p	0.25 ij
	RD-50	0.04 g-i	2.37 g	0.68 f	0.34 c	0.003 a	0.028 f-j	0.20 p	0.45 h-j
	RD70	0.03 g-j	2.01 j	0.59 i	0.28 d	0.003 a	0.032 f-i	0.31 m	0.43 h-j
	RD-90	0.02 h-j	1.71 kl	0.55 jk	0.26 e	0.004 a	0.038 d-g	0.42 h	0.45 h-j
	RD-110	0.02 h-j	1.43 m	0.66 g	0.18 gh	0.004 a	0.038 d-g	0.45 g	1.44 f-g
	RD-130	0.018 ij	1.30 n	0.70 e	0.17 h	0.004 a	0.057 a-d	0.52 f	15.33 c
SE		0.0058	0.0257	0.0056	0.0057	0.0059	0.0058	0.0056	0.1798
LSD (5%)		0.017	0.080	0.016	0.017	0.018	0.015	0.016	0.53
*WHO (mg L^{-1})		3.00	0.30	2.00	0.500	0.003	0.05	0.01	0.01
**FAO (mg L^{-1})		2	5	0.2	0.2	0.01	0.1	5	0.1

In each column, means followed by common letter are not significantly different at 5% probability level.
*Max: permissible limit for drinking purpose/human consumption [56].
**Recommended Maximum concentration for irrigation/crop production [57].

to RD-130). Mn was also higher at upper to mid-reach (RD-30 to RD-50) was not within the permissible limit of FAO.

The interactive effect of seasons x locations on trace and heavy metals concentration in groundwater was studied, the result indicated that the higher concentration of heavy metals Cd (0.008 mg L^{-1}), Cr (0.07 mg L^{-1}), Pb (0.77 mg L^{-1}) and As (20.33 ug L^{-}) in groundwater was recorded near upper reach (RD-130) during winter season. As the season changed concentration of these parameters decreased (autumn>spring>summer). Same was true with locations which had higher values of these traits at RD-130>110>90>70>50>30>0. Overall results showed that the heavy metals in groundwater were higher in the down reach as compared to upper reach (Table **3**).

Correlation Coefficient (r) Between Groundwater Trace and Heavy Metal Concentration of Phuleli Canal Command Area

The correlation trace and heavy metals concentration across various locations and various season of groundwater showed that Zn was negatively associated with Cd, Cr, Pb and As with 'r' value of -0.15, -0.28, -0.35 and -0.24 respectively. Statistical results showed that Zn had non significant differences at 5% of probability level (Table **4**). Fe was positively associated with Cd, Cr and Pb having 'r' value of 0.47, 0.18 and 0.14 respectively, but, showed negatively association with As (r=-0.20). Statistical results showed that Fe had non- significant differences at 5% probability level with the parameters Cr, Pb and As, but, showed significant differences at 1% probability level with Cd.

Cu was positively associated with Cd, Cr, Pb and As with 'r' value of 0.003, 0.27, 0.26 and 0.33 respectively. Statistical results showed that Cu had non- significant differences at 5% probability level with these metals concentration. Mn was negatively associated with Cd, Cr, Pb and As having 'r' value of -0.63, -0.61, -0.60 and -0.30 respectively. Statistical results showed that Mn had non-significant differences at 5% probability level with As, but, showed significant differences at 1% probability level with Cd, Cr and Pb (Table **4**). Whereas, Pb was positively associated with Cd and As with 'r' value of 0.89 and 0.53. Statistical

Table 4: Correlation Coefficient Between Groundwater Trace and Heavy Metals Concentration Phuleli Canal Command Area

Parameters	Intercept	Slope	R value
Zn (mg L^{-1}) v/s			
Cd (mg L^{-1})	0.00	-005	-0.15 ns
Cr (mg L^{-1})	0.04	-0.07	-0.28 ns
Pb (mg L^{-1})	0.43	-1.24	-0.35 ns
As (µg L^{-1})	4.25	-23.51	-0.24 ns
Fe (mg L^{-1}) v/s			
Cd (mg L^{-1})	0.00	0.001	0.47 **
Cr (mg L^{-1})	0.03	0.003	0.18 ns
Pb (mg L^{-1})	0.28	0.036	0.14 ns
As (µg L^{-1})	5.7	-1.37	-0.203 ns
Cu (mg L^{-1}) v/s			
Cd (mg L^{-1})	0.00	0.000	0.003 ns
Cr (mg L^{-1})	0.03	0.018	0.27 ns
Pb (mg L^{-1})	0.26	0.23	0.26 ns
As (µg L^{-1})	-0.58	8.01	0.33 ns
Mn (mg L^{-1}) v/s			
Cd (mg L^{-1})	0.01	-0.009	-0.63 **
Cr (mg L^{-1})	0.05	-0.071	-0.61 **
Pb (mg L^{-1})	0.54	-0.94	-0.6 **
As (µg L^{-1})	5.41	-12.98	-0.30 ns
Pb (mg L^{-1}) v/s			
Cd (mg L^{-1})	0.00	0.008	0.89**
As (µg L^{-1})	-2.3	14.6	0.53**
Cd (mg L^{-1}) v/s As (µg L^{-1})	-1.56	1202.18	0.40*

ns = non significant, and significant at 5% and 1% probability level respectively.

results for Pb showed significant differences at 1% probability level with these metals. Cd was positively associated with As having r value of 0.40. Statistical results for Cd showed significant differences at 5% probability level with As.

Linear Regression of Seasonal Effect at Various Locations on Trace and Heavy Metals Concentration of Phuleli Canal Command Area

Coefficient of Determination (R^2)

Regarding trace and heavy metals concentration of groundwater, the coefficient of determination (R^2) showed that total variation of Cu (87, 94, 95 and 66%), Cd (89, 88, 86 and 87%), Cr (96, 95, 97 and 90%), Pb (81, 97, 87 and 95%) and As (45, 44, 46 and 43%) in various locations was due to its association with Summer, Autumn, Winter and Spring seasons respectively (Figures **2-6**).

Regression Coefficient (b)

The regression coefficient revealed that a unit increase in locations resulted in correspondingly increase of trace and heavy metals concentration of Cu (0.12, 0.04, 0.03 and 0.09 mg L^{-1}), Cd (0.0004, 0.0005, 0.0008 and 0.0005 mg L^{-1}), Cr (0.005, 0.007, 0.006 and

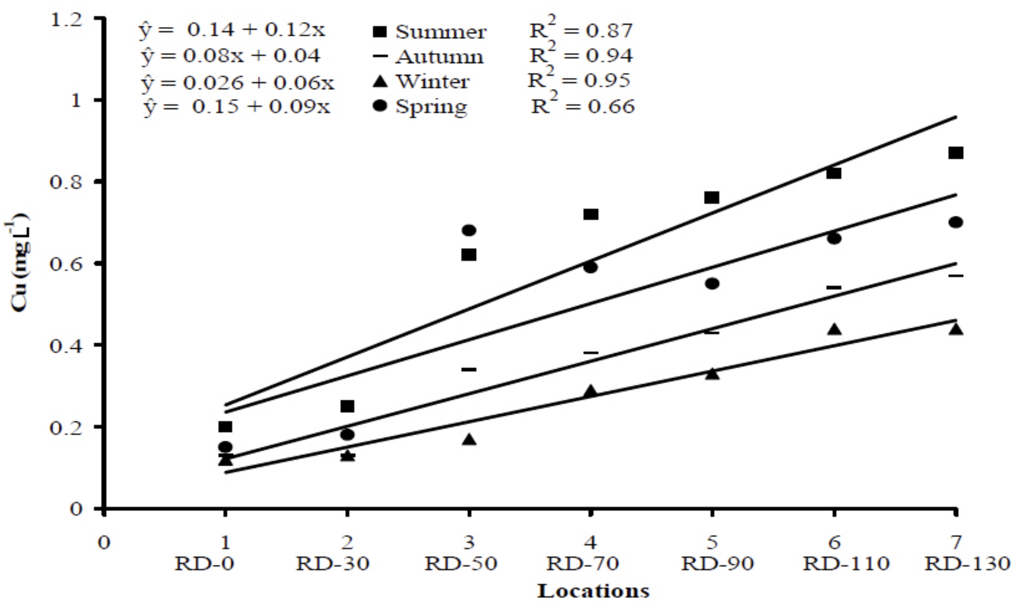


Figure 2: Linear regression of groundwater Cu (mg L^{-1}) between seasons and locations of Phuleli Canal Command area.

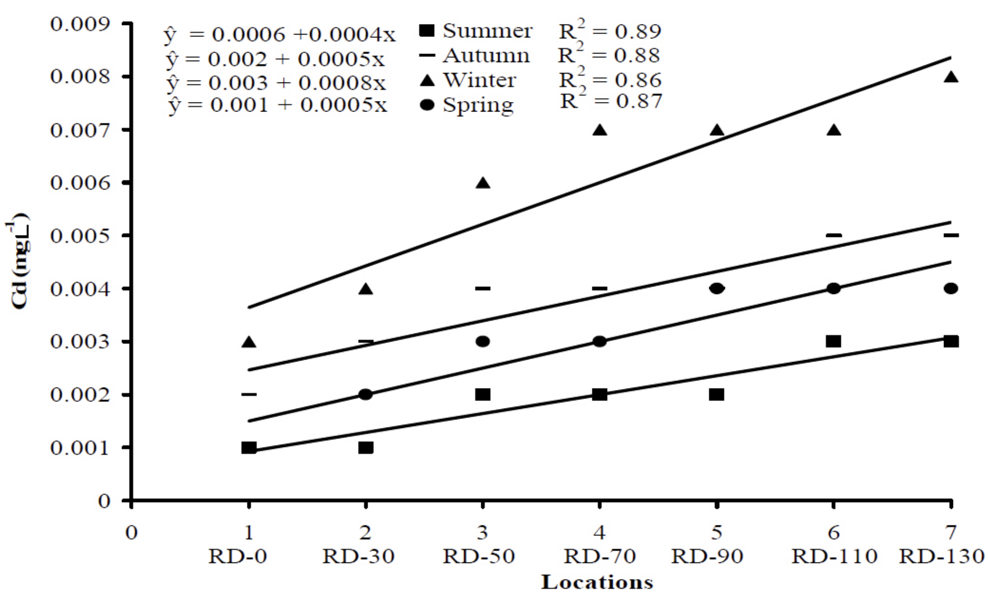


Figure 3: Linear regression of groundwater Cd (mg L^{-1}) between seasons and locations of Phuleli Canal Command area.

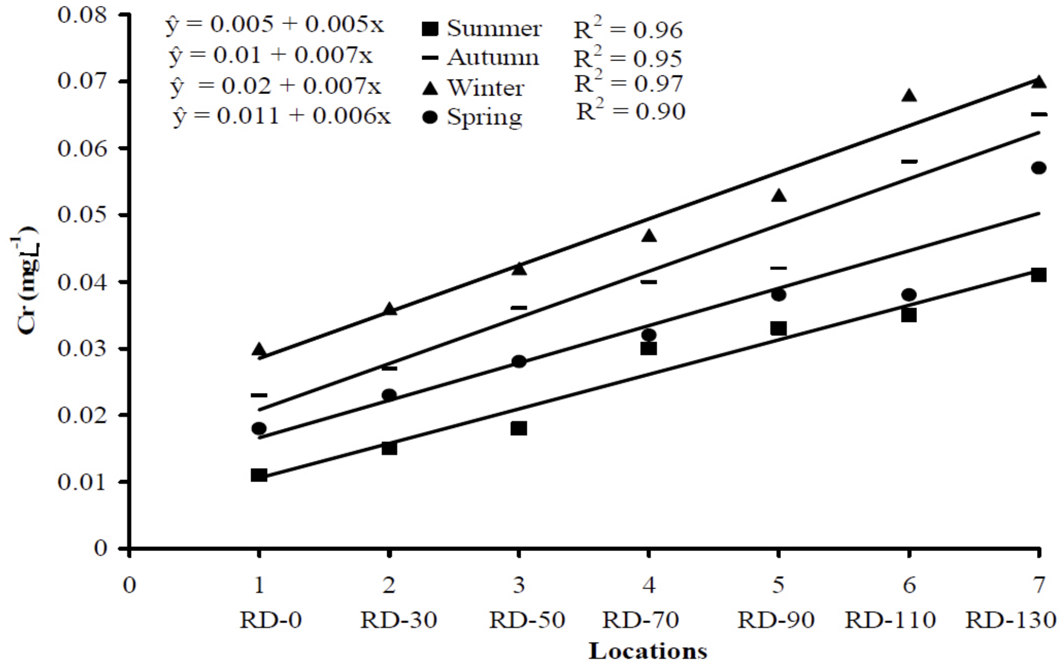


Figure 4: Linear regression of groundwater Cr (mg L^{-1}) between seasons and locations of Phuleli Canal Command area.

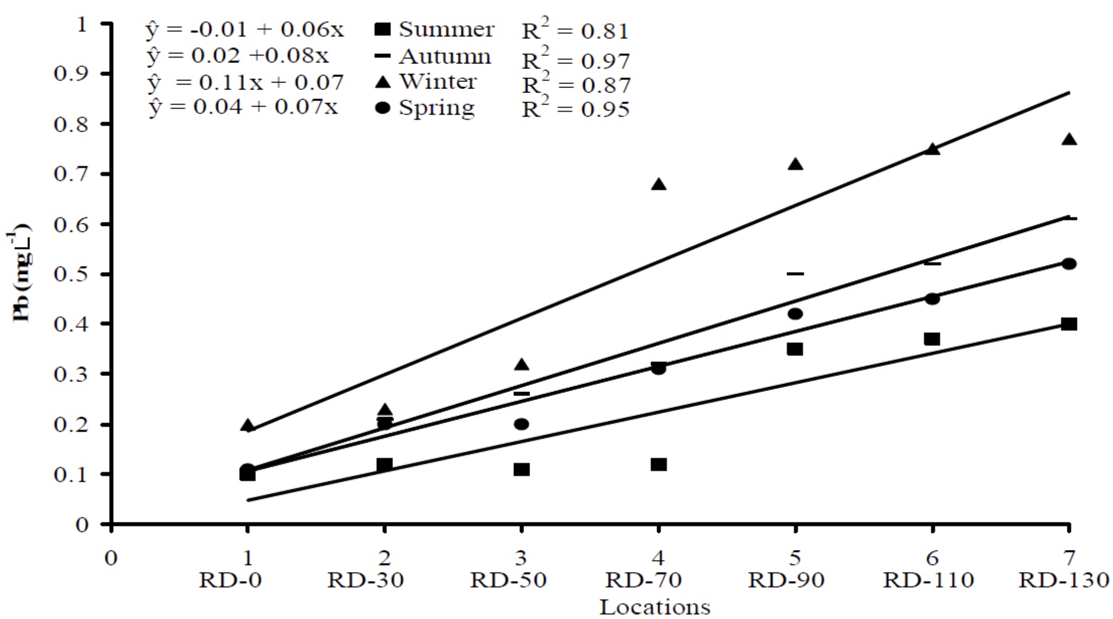


Figure 5: Linear regression of groundwater Pb (mg L^{-1}) between seasons and locations of Phuleli Canal Command area.

0.007 mg L^{-1}), Pb (0.06, 0.08, 0.07 and 0.07 mg L^{-1}) and As (1.36, 2.02, 2.32 and 1.71 µg L^{-1}) in Summer, Autumn, Winter and Spring seasons respectively (Figures **2-6**).

DISCUSSION

Trace Elements

The use of polluted water in the surroundings of the big cities for the growing of vegetables is a common practice in Pakistan. Although this water is considered to be a rich source of organic material and plants nutrients, yet it also contains sufficient amounts of soluble salts and metals like iron, manganese, copper, zinc, etc. When this water is used for the growing of crops for a long period, these metals may accumulate in soil and that may be toxic to the plants and also cause deterioration of soil [29, 30].

In this study, it was observed that trace elements in groundwater were more in winter except Cu and Mn in

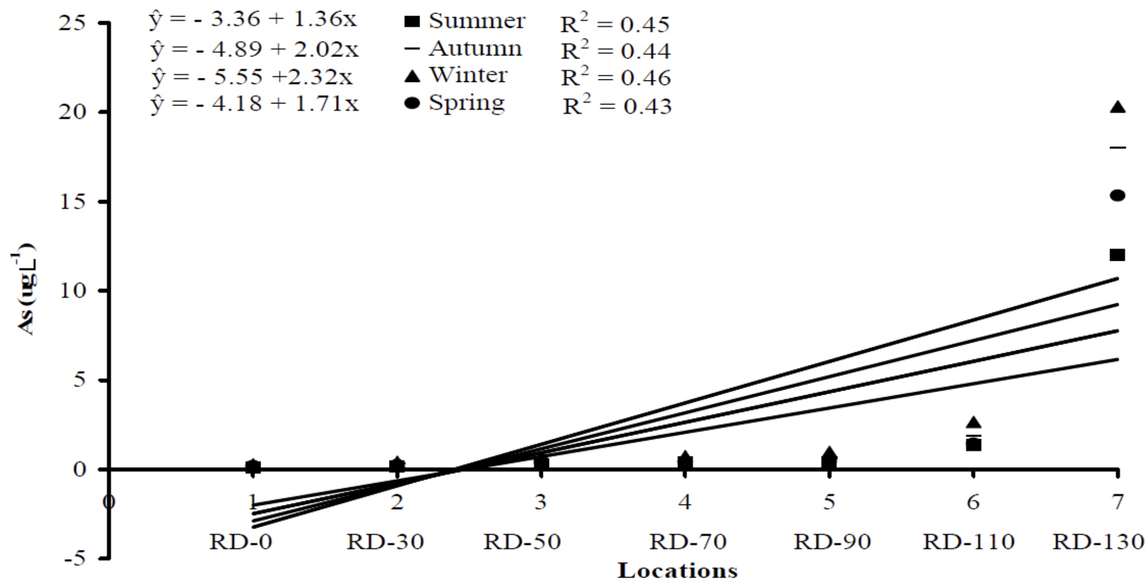


Figure 6: Linear regression of groundwater As (μg L^{-1}) between seasons and locations of Phuleli Canal Command area.

summer. The seasonal variations may be due to either anthropogenic causes, such as irrigation or wastewater discharge, or natural causes, such as water temperature, pH, redox condition, water flux, or activity of microorganisms [31].

The low concentration of zinc in groundwater could be due to the fact that pH of water samples was slightly alkaline and its solubility is a function of decreasing pH [32]. Low intake of zinc ultimately resulted in growth retardation, immaturity and anemia in human [33].

Iron is an essential element with no any significant health effect, but develops yellowish color and a peculiar taste when present in high concentration in water bodies [34]. In this study, iron was higher in groundwater and was higher than the permissible limit of WHO/FAO. Long term consumption of drinking water with high concentration of iron may lead to liver diseases [17, 33]. In this study, iron in water was lower in winter compared to other season. Similar results were reported by [35] that the levels of iron were higher during winter as compared to summer. Contrary, [36] observed lower Fe in winter than that in summer.

This study shows that Cu in water was higher than the permissible limits of FAO for agriculture purpose/irrigation. Higher concentration of Cu in water is an index of pollution from effluents in the canals or water bodies [33]. Its excessive amounts usually influence water as well as soil [30]. Though copper is not a cumulative systemic poison, large dose (>1.0 mg) is harmful and might cause central nervous system disorder, failure of pigmentation of hair, effects on Fe metabolism [37], causes stomach and intestinal distress, liver and kidney damage, and anemia [38].

This study show that Mn content in groundwater was higher during summer as compared to rest of the seasons. Similarly, observed the levels of manganese were lower during winter than during summer [35].

Heavy Metals

In this study groundwater concentration of heavy metals *viz.* Cd, Cr, Pb and As were higher towards down reach as compared to upper reach during winter. As the season changed the values of these parameters showed decreasing trend (autumn>spring>summer).

Heavy metal accumulation was noted in groundwater. The variation in concentration of heavy metals was due to the use of different raw materials and variation of production level [39]. The heavy metal pollution of fresh water is the single most important environmental threat to the future [40]. Water pollution, contamination of streams, canals and lakes by substances harmful to the living things is common when these supplies pass on through cities or populated area and by infiltration groundwater ultimately contaminate. People who ingest polluted water can become ill, and, with prolonged exposure, may develop cancers or bear children with birth defects [30, 41].

In comparison to rivers or streams, groundwater tends to move very slowly and with little turbulence. Groundwater is hidden from view; contamination can go undetected for years until the supply is tapped for use [42]. Studies conducted at Mexico shows that polluted water used for irrigation may account for up to 31% of heavy metal accumulation in soil surface [43]. Heavy metals by use of sewage water can affect sensitive plants which can also result in loss of soil productivity. Heavy metal accumulation in general is more in sewage sludge application than wastewater irrigation. Utilization of the canal water for irrigation and the mud for soil up gradation by local farmers; result in the spread of contaminants on both sides of the canal. Consequently, the soil and the groundwater in the command area were also contaminated by heavy metals [44].

This study shows that the mostly heavy metal concentration in underground. water towards down reach. Similarly, [45] also reported that canal flow transported the contaminants from source areas down reach, ultimately through seepage/turbulence increase contamination at down reach in groundwater. These heavy metals get into plants *via* adsorption which refers to binding of materials onto the surface or absorption which implies penetration of metals into the inner matrix [46]. However, in small concentrations these metals in plants are not the degree of metal pollution which could be assessed in terms of toxic [47]. Lead, cadmium and mercury are exceptions; they are toxic even in low concentrations [48].

The activities like; smelting operations, use of phosphate fertilizers, pigment, cigarettes smokes, automobiles etc. have contributed to the entry of cadmium into human and animal food chain [49, 50].

In addition to the immediate concern of As in drinking water, the arsenic contamination might have a detrimental effect on land and agricultural sustainability. Irrigation with As contaminated groundwater to crops may increase its concentration and eventually As may enter into food chain through crop uptake [51]. Continuous use of arsenic contaminated water over prolonged periods may cause health hazards [52, 53] cancer and symptoms of arsenicosis [34], carcinogenicity [53]. There are some point sources of arsenic contamination like pesticides, fossil fuel combustion, treated wood and smelting and mining wastes [54], application of phosphate fertilizer [55].

CONCLUSION

Cadmium, Cr, Pb and As in groundwater of Phuleli Canal Command area increased considerably towards down-reach during winter season at RD-130. While the values of these parameters decreased by following the trend of autumn>spring>summer. Fe, Cd, Cr and Pb concentrations in groundwater were higher than WHO permissible limit and Cu and Mn greater than FAO limit. Heavy metal concentration in groundwater samples were found higher in downstream reach compared to upstream reach may be due to discharge of industrial waste into Canal Command area. It was concluded that groundwater contains highly toxic metals above the permissible limits of WHO and FAO for human consumption and agricultural crops respectively. Hence, people using groundwater, directly or indirectly, at down-reach of the Canal Command area are at health risk. It is recommended that instead of discharging municipal sewage water directly into the Canal Command area, it should be partially treated and then used for propagation of urban agriculture. Regular monitoring of the canal water quality for contamination should be carried out. Awareness programs for local people should be initiated.

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Received on 25-08-2013 Accepted on 09-09-2013 Published on 12-09-2013

http://dx.doi.org/10.6000/1927-5129.2013.09.71