SEASONAL VARIATIONS OF TRACE ELEMENTS AND HEAVY METAL CONCENTRATIONS IN PHULELI CANAL WATER (SINDH), PAKISTAN

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ABSTRACT

Phuleli Canal (Sindh), Pakistan is one of the irrigation canals of the Kotri Barrage which provides water for irrigation as well as for drinking purpose. Quality of the canal deteriorates while passing through Hyderabad city, 2nd largest city of Sindh, Pakistan because highly toxic effluent from plastic factories, illegal cattle pens, slaughterhouses and municipal sewage water are directly discharged into the Phuleli Canal without any treatment. That polluted water has put lives of millions of people at risk living at downstream in district Tando Muhammad Khan. Human health problems due to waterborne diseases are commonly reported in newspapers in Phuleli Canal Command area. Present study was thus conducted to investigate the effect of disposal of untreated domestic and industrial sewage water and waste into Phuleli canal on the quality of canal water. The study was conducted during the year 2008-2009 to observe seasonal variation of trace and heavy metals at different location (reduced distance, RD = 1000 ft.) along the length of Phuleli Canal. Water samples were collected during four seasons (summer, autumn, spring and winter) with three replications each from seven locations (RD-0, RD-30, RD-50, RD-70, RD-90, RD-110 and RD-130). The samples collected were analyzed for their trace elements and heavy metal concentrations including zinc, manganese, copper, iron, cadmium, chromium, lead and arsenic. The water analysis results were then compared with international organizations i.e. FAO and WHO standards of water for irrigation and human consumption respectively. Fe, Cd and Cr concentrations in water were higher than WHO permissible limits, and Cu and Mn were greater than FAO permissible limit at downstream of the canal. Comparatively heavier metals viz. Cd, Cr, Pb and As were higher towards downstream reaches as compared to upstream reaches during winter. As the season changed the values of these parameters showed decreasing trend (autumn > spring > summer).

Key words: water quality standards, WHO/FAO, pollution, discharge, contamination, longitudinal flow and reduced distances (RD)

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INTRODUCTION

Water is a vital component for existence of flora and fauna in the biosphere (Kakar et al., 2010). It is a fact that over two thirds of the earth’s surface is covered with water which is undoubtedly the most precious 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 become a scarce commodity globally (Rao, 2010). Polluted water consists of industrial discharged effluents, sewage water, and the industrial waste (Mahmood, 2006). When polluted water is consumed, it affects human health; and thus pollution makes the water unsuitable for the desired use. A little negligence on the part of civic bodies can result in the spread of many diseases (Mukhi and Srivastava, 1987). There is possibility of uptake of contaminants from irrigation water by crops thus affecting human health. In Pakistan, the problem of water pollution is growing at an alarming rate. The phenomenal increase in country’s population has brought unprecedented pressure on safe drinking water. Waterborne diseases account for 20 to 30% of all the hospital cases and 60% of infant deaths (GOP, 2000). In Pakistan, 64% of the population lives in rural area (WHO, 2012); most of them do not have the accessibility to good quality water; and due to use of polluted water, people face many diseases in such as typhoid, stomach infections, kidney problem, food poisoning and skin problem (Ilyas, 1998; Ilyas et al., 2008).

In most towns in Pakistan, which have a sewage disposal system, the wastewater is used for irrigation. Recent estimates reveal that about 26% of vegetable production comes from fields irrigated with wastewater (Jeroen et al., 2004). In the cases where there is no suitable disposal of wastewater, it is disposed off in the most convenient surface water bodies, which often are irrigation canals that often serve as the source of drinking water for people living along the banks of canal at downstream. Trace metal contaminations found in wastewater are important due to their potential toxicity for the environment and human beings (Gueu et al., 2007; Lee et al., 2007; Adams et al., 2008; Vinodhini and Narayanana, 2008). Some of the metals like Cu, Fe, Mn, Ni and Zn are essential as micronutrients for the life processes in animals and plants, while many other metals such as Cd, Cr, Pb and Co have no known physiological activities (Kar et al., 2008; Akhtar et al., 2010).
Metals are non-degradable and can accumulate in the human body system, causing damage to nervous system and internal organs (Lee et al., 2007).

Canal irrigated crops are affected by the poor water quality due to salt accumulation in the root zone (FAO, 1990). Contaminants in irrigation water may accumulate in the soil and, after a period of years, render the soil unfit for agriculture. Although the presence of pesticides or pathogenic organisms in irrigation water does not directly affect plant growth, the acceptability of the agricultural production for consumption is potentially affected. Quality criteria may also differ considerably from one country to another, due to different annual application rates of irrigation water (Akhtar et al., 2005).

Like other cities of Pakistan, Hyderabad is also facing a great problem of safe disposal of wastewater. 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 (Leghari, et al., 2004) as it passes through Hyderabad. As a result, Phuleli Canal has potentially put in jeopardy lives of millions of people in Hyderabad, Badin, Tando Muhammad Khan districts of Sindh Province of Pakistan because they use this contaminated water for drinking purpose (Dawn, 2006a, b; Guriro, 2009). The average quantity of wastewater discharged into Phuleli Canal from different sewage stations is reported as 225584.44 m$^3$ day$^{-1}$ (Watoo et al., 2004 and 2006). Sewage water having bulk volumes of organic and inorganic matter, changes the chemical characteristics of the water body by producing toxic substances and ultimately pollute the canal water (Watoo et al., 2004; Watoo et al., 2006). This untreated sewage water contains dissolved and suspended solids, inorganic and organic compounds, oils, solvents, greases, thermal discharge, etc. The sewage laden irrigation water of the canals also deteriorates the quality of irrigated crops. Therefore, it is imperative to protect the freshwater bodies of Sindh Province. The present study was thus conducted to analyse the variation in the concentrations of trace and heavy metals in the canal water during various seasons at different locations in the Phuleli canal.

MATERIALS AND METHODS

Phuleli is a non-perennial canal of Sindh (Pakistan) which was constructed in 1955 on the left bank of river Indus at the upstream of Ghulam Muhammad barrage to meet the irrigation and drinking water requirements of the Hyderabad, Tando Muhammad Khan and Badin districts. The canal has the discharge capacity of 14,350 cusecs with total cultureable commanded area (CCA) of 929358 acres. The industries are concentrated in Hyderabad city which is located towards the upstream of the canal. The water of the canal is used mainly for agricultural purpose and also for domestic use at downstream of canal.

In Pakistan, monsoon season starts in summer from July to September which contributes about 70% of the total annual rainfall. About 30% of total rain falls in winter while spring and autumn are dry seasons However, winter rains contributes. Sindh province has arid climate hence agriculture is not possible without supplemental irrigation (Rasul, 2012). In this situation, usually contaminant concentration in canal becomes low during rainy season which might be due to the dilution effect of rainfall whereas the higher concentration of these metals are found during winter when canal flow is low (Das et al., 2011).

Water quality of Phuleli Canal, Sindh (Pakistan) in terms of trace and heavy metals were monitored seasonally (summer, autumn, winter and spring) during 2008-2009 at seven locations of the canal viz. Reduced distance (RD = 304.8 m) 0, 30, 50, 70, 90, 110 and 130). These locations start from Kotri Barrage (Ghulam Muhammad Barrage) RD-0 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 area are shown in Figure 1.

<table>
<thead>
<tr>
<th>Locations</th>
<th>Village</th>
<th>Taluka / Tehsil</th>
<th>District</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD-0</td>
<td>Kotri</td>
<td>Jamshoro</td>
<td>Jamshoro</td>
</tr>
<tr>
<td>*RD-30</td>
<td>Expo-Center Pretabad</td>
<td>Hyderabad</td>
<td>Hyderabad</td>
</tr>
<tr>
<td>RD-50</td>
<td>Harsheg Patel</td>
<td>Hyderabad</td>
<td>Hyderabad</td>
</tr>
<tr>
<td>RD-70</td>
<td>Near City Hosri</td>
<td>Latifabad</td>
<td>Hyderabad</td>
</tr>
<tr>
<td>RD-90</td>
<td>Near Katiar</td>
<td>Latifabad</td>
<td>Hyderabad</td>
</tr>
<tr>
<td>RD-110</td>
<td>Mohd Moosa Rindh</td>
<td>Tando Muhammad Khan</td>
<td>Tando Muhammad Khan</td>
</tr>
<tr>
<td>RD-130</td>
<td>Hussain Khan Leghari</td>
<td>Bulri Shah Karim</td>
<td>Tando Muhammad Khan</td>
</tr>
</tbody>
</table>

*RD (Reduced distance) = 304.8 m

Canal water samples were collected from the sides near banks and center by standing in the middle of the stream using boat during summer, autumn, winter and spring. Care was taken to keep the bottle well above the bed of the stream to avoid unwanted bed material going into the sample following the procedures given by National
Water Quality Monitoring Programme (Kahlown et al., 2002). The samples for determination of heavy/trace metals were kept in glass bottles prewashed with detergent, diluted HNO₃ and doubly de-ionized distilled water as described by Akoto and Adiyiah (2007) and Wattoo et al. (2004). 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 HNO₃ per liter was added in the samples and kept in refrigerator at 4°C for laboratory analysis as described by Wattoo et al. (2004) and Akoto and Adiyiah (2007). The trace and heavy metal status was then compared with WHO and FAO standards for drinking and irrigation purposes respectively. Heavy metals and trace elements were determined by direct air acetylene flame method using Atomic Absorption Spectrophotometer (Marry and Franson, 1992).

The data collected were subjected to statistical analysis using analysis of variance technique. Least Significant Differences (LSD) test was applied to compare the individual treatment means as per the statistical methods developed by Gomez and Gomez (1984). The statistical analyses were performed using MSTAT-C Computer Software.

RESULTS AND DISCUSSION

Seasonal variability of trace and heavy metal concentrations in Phuleli Canal water were studied and the results are given in Table 2. The Table shows that all the trace and heavy metals viz. Zn, Fe, Cu, Mn, Cd, Cr, Pb and As in Phuleli Canal water during different seasons of the year varied significantly at 5% probability level. The analysis of water samples collected during winter showed higher Zn (0.032 mg L⁻¹), Fe (1.72 mg L⁻¹), Cd
(0.0032 mg L\(^{-1}\)), Cr (0.059 mg L\(^{-1}\)), Pb (0.038 mg L\(^{-1}\)) and As (0.31 µg L\(^{-1}\)) compared to those collected during autumn, spring and summer seasons. However, concentrations of Cu (0.51 mg L\(^{-1}\)) and Mn (0.32 mg L\(^{-1}\)) in water were higher during summer. The concentration of Fe and Pb in Phuleli Canal water were higher than the WHO safe limits throughout all seasons. But concentration of Cd was higher during winter and Cr was higher during winter and autumn seasons, which are not within permissible limit of WHO for human consumption/drinking purpose. The water utilization for agriculture purpose showed that concentration of Zn, Fe, Cd, Cr and Pb in water were higher in all seasons, and Cu in winter was within the permissible limits of FAO except of other seasons for irrigation/crop production. However, Mn was higher in all seasons and not within the permissible limit of FAO. But for human consumption, the concentration of Zn, Cu, Mn and As were within the permissible limit of WHO.

Table 2. Trace and heavy metals concentration in Phuleli Canal water in various seasons.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>SE (mg L(^{-1}))</th>
<th>LSD (5%)</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
<th>Spring</th>
<th>(^*)WHO (mg L(^{-1}))</th>
<th>(^*)*FAO (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.0021</td>
<td>0.0097</td>
<td>0.020 b</td>
<td>0.029 ab</td>
<td>0.032 a</td>
<td>0.025 ab</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0019</td>
<td>0.0095</td>
<td>0.73 d</td>
<td>1.11 b</td>
<td>1.72 a</td>
<td>0.92 c</td>
<td>0.3</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0022</td>
<td>0.0097</td>
<td>0.51 a</td>
<td>0.32 c</td>
<td>0.182 d</td>
<td>0.44 b</td>
<td>2.0</td>
<td>0.2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0018</td>
<td>0.0095</td>
<td>0.32 a</td>
<td>0.24 c</td>
<td>0.209 d</td>
<td>0.27 b</td>
<td>0.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.00217</td>
<td>0.0095</td>
<td>0.0014 a</td>
<td>0.0023 a</td>
<td>0.0032 a</td>
<td>0.002 a</td>
<td>0.003</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>0.00218</td>
<td>0.0098</td>
<td>0.03 c</td>
<td>0.05 ab</td>
<td>0.059 a</td>
<td>0.04 bc</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>Pb</td>
<td>0.0015</td>
<td>0.0097</td>
<td>0.021 b</td>
<td>0.029 ab</td>
<td>0.038 a</td>
<td>0.025 b</td>
<td>0.01</td>
<td>5.0</td>
</tr>
<tr>
<td>As (µg L(^{-1}))</td>
<td>0.0018</td>
<td>0.009821</td>
<td>0.138 d</td>
<td>0.23 b</td>
<td>0.31 a</td>
<td>0.20 c</td>
<td>0.01</td>
<td>0.1</td>
</tr>
</tbody>
</table>

In each row, means followed by common letter are not significantly different at 5% probability level.

* Max: permissible limit for drinking purpose/human consumption

** Recommended Maximum concentration for irrigation/crop production (Ayers and Westcot, 1985)

Table 3 shows the RD wise trace and heavy metal concentrations in Phuleli Canal water. It shows that at upstream reach (RD-0) the Zn (0.034 mg L\(^{-1}\)) concentration in canal water was higher which significantly decreased (0.019 mg L\(^{-1}\)) at mid and downstream reach (RD-50-130). The opposite trend was noted for Fe and Mn, which were low (0.79 and 0.158 mg L\(^{-1}\)) at upstream reach near RD-0 and suddenly increased (1.74 and 0.32 mg L\(^{-1}\)) near RD-30. The lowest concentration of Cu (0.156 mg L\(^{-1}\)), Cd (0.0013 mg L\(^{-1}\)), Cr (0.023 mg L\(^{-1}\)), Pb (0.022 mg L\(^{-1}\)) and As (0.109 µg L\(^{-1}\)) was recorded near upstream reach (RD-0) and the higher concentration of Cu (0.58 mg L\(^{-1}\)), Cd (0.0033 mg L\(^{-1}\)), Cr (0.067 mg L\(^{-1}\)), Pb (0.032 mg L\(^{-1}\)) and As (0.37 µg L\(^{-1}\)) was observed towards the downstream reach. The Zn, Cu and As concentration in canal water samples collected at different locations of Phuleli Canal was within the permissible limits of WHO for drinking purpose, while Fe and Pb concentration in water samples was found to be higher than the WHO permissible limits at all locations. While, the concentration of Mn was higher at midstream reach (RD-30 and RD-50) and was beyond the permissible limit of WHO. However, Cd was found maximum at downstream reach (RD-110 to RD-130), and Cr was higher at midstream to downstream reach near RD-70 to RD-130. Similar Pb was noted higher at downstream reach from RD-90 to RD-130. For drinking purpose, the concentrations of Cd, Cr and Pb at midstream to downstream reach were not within the permissible limits of WHO. Similarly, Mn and Cu were within the permissible limit of WHO at all locations. The concentration of Zn, Fe, Cd, Cr, Pb and As in water for irrigation purpose were found within the permissible limit of FAO. However, Cu and Mn at midstream to downstream reach were beyond the permissible limits of FAO.

Table 3. Trace and heavy metals concentration at various locations of Phuleli Canal water at various locations.

<table>
<thead>
<tr>
<th>Parameters (mg L(^{-1}))</th>
<th>SE</th>
<th>LSD (5%)</th>
<th>RD-0 (Regulator)</th>
<th>RD-30</th>
<th>RD-50</th>
<th>RD-70</th>
<th>RD-90</th>
<th>RD-110</th>
<th>RD-130</th>
<th>(^*)WHO (mg L(^{-1}))</th>
<th>(^*)*FAO (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.0026</td>
<td>0.0090</td>
<td>0.034 a</td>
<td>0.032 ab</td>
<td>0.029 ab</td>
<td>0.025 abc</td>
<td>0.024 abc</td>
<td>0.022 bc</td>
<td>0.019 c</td>
<td>3.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0026</td>
<td>0.0097</td>
<td>0.174 a</td>
<td>1.46 b</td>
<td>1.69 c</td>
<td>0.96 d</td>
<td>0.91 e</td>
<td>0.89 f</td>
<td>0.3</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.0028</td>
<td>0.0095</td>
<td>0.156 g</td>
<td>0.25 e</td>
<td>0.38 d</td>
<td>0.47 c</td>
<td>0.52 b</td>
<td>0.58 a</td>
<td>2.0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.0029</td>
<td>0.0098</td>
<td>0.158 f</td>
<td>0.30 b</td>
<td>0.26 d</td>
<td>0.28 c</td>
<td>0.25 d</td>
<td>0.23 e</td>
<td>0.5</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.0025</td>
<td>0.0096</td>
<td>0.0033 a</td>
<td>0.024 a</td>
<td>0.040 c</td>
<td>0.051 b</td>
<td>0.059 a</td>
<td>0.067 a</td>
<td>0.08</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.0028</td>
<td>0.0095</td>
<td>0.023 d</td>
<td>0.024 d</td>
<td>0.040 c</td>
<td>0.051 b</td>
<td>0.059 a</td>
<td>0.067 a</td>
<td>0.08</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.0027</td>
<td>0.0097</td>
<td>0.022 a</td>
<td>0.025 a</td>
<td>0.026 a</td>
<td>0.027 a</td>
<td>0.030 a</td>
<td>0.031 a</td>
<td>0.032 a</td>
<td>0.01</td>
<td>5.0</td>
</tr>
<tr>
<td>As (µg L(^{-1}))</td>
<td>0.0026</td>
<td>0.0098</td>
<td>0.109 g</td>
<td>0.177 c</td>
<td>0.21 d</td>
<td>0.25 c</td>
<td>0.27 b</td>
<td>0.37 a</td>
<td>0.01</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

In each row, means followed by common letter are not significantly different at 5% probability level.

* Max: permissible limit for drinking purpose/human consumption

** Recommended Maximum concentration for irrigation/crop production (Ayers and Westcot, 1985)
The interactive effect of seasons and locations for the trace and heavy metals concentration of Phuleli Canal water were statistically highly significant (P<0.05) as given in Table 4. The higher heavy metal concentration i.e. Cd (0.004 mg L⁻¹), Cr (0.082 mg L⁻¹), Pb (0.045 mg L⁻¹) and As (0.5 μg L⁻¹) was observed near downstream reach (RD-130) during winter. As the season changed, the values of these parameters reduced (autumn>spring>summer). Same was true for other locations which recorded higher values of these traits at RD-130>110>90>70>50>30>0. Overall results showed that the heavy metals were higher in the downstream reach as compared to that at regulator (RD-0).

Correlation coefficient (r) between trace and heavy metal content of Phuleli Canal area

The correlation between trace and heavy metal concentrations at various locations and seasons (Table 5) showed that Zn was negatively associated with Cd, Cr and As with ‘r’ value of -0.13, -0.24 and -0.14 respectively but positively associated with Pb (r =0.15). Iron was positively associated with Cd, Cr, Pb and As, with ‘r’ value of 0.22, 0.14, 0.51 and 0.21, respectively. Results showed that Fe had a non-significant difference at 5% probability level with Cd, Cr, and As, but, showed significant differences at 1% probability level with Pb.

Table 4. Interactive effect of seasons x locations of Phuleli Canal on trace and heavy metals concentration

<table>
<thead>
<tr>
<th>Seasons</th>
<th>Locations</th>
<th>Parameters (mg L⁻¹)</th>
<th>(μg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn</td>
<td>Fe</td>
</tr>
<tr>
<td>Summer</td>
<td>RD-0 (Regulator)</td>
<td>0.022 a-d</td>
<td>0.40 u</td>
</tr>
<tr>
<td></td>
<td>RD-30</td>
<td>0.027 a-d</td>
<td>1.57 i</td>
</tr>
<tr>
<td></td>
<td>RD-50</td>
<td>0.023 a-d</td>
<td>0.97 k</td>
</tr>
<tr>
<td></td>
<td>RD-70</td>
<td>0.020 b-d</td>
<td>0.68 o</td>
</tr>
<tr>
<td></td>
<td>RD-90</td>
<td>0.018 cd</td>
<td>0.55 r</td>
</tr>
<tr>
<td></td>
<td>RD-110</td>
<td>0.018 cd</td>
<td>0.50 s</td>
</tr>
<tr>
<td></td>
<td>RD-130</td>
<td>0.013 d</td>
<td>0.42 t</td>
</tr>
<tr>
<td>Autumn</td>
<td>RD-0 (Regulator)</td>
<td>0.039 ab</td>
<td>0.75 n</td>
</tr>
<tr>
<td></td>
<td>RD-30</td>
<td>0.035 a-c</td>
<td>1.83 c</td>
</tr>
<tr>
<td></td>
<td>RD-50</td>
<td>0.032 a-d</td>
<td>1.65 gh</td>
</tr>
<tr>
<td></td>
<td>RD-70</td>
<td>0.026 a-d</td>
<td>0.98 k</td>
</tr>
<tr>
<td></td>
<td>RD-90</td>
<td>0.026 a-d</td>
<td>0.88 l</td>
</tr>
<tr>
<td></td>
<td>RD-110</td>
<td>0.023 a-d</td>
<td>0.78 m</td>
</tr>
<tr>
<td></td>
<td>RD-130</td>
<td>0.021 b-d</td>
<td>0.88 l</td>
</tr>
<tr>
<td>Winter</td>
<td>RD-0 (Regulator)</td>
<td>0.041 a</td>
<td>1.35 j</td>
</tr>
<tr>
<td></td>
<td>RD-30</td>
<td>0.036 a-c</td>
<td>1.90 a</td>
</tr>
<tr>
<td></td>
<td>RD-50</td>
<td>0.035 a-c</td>
<td>1.86 ab</td>
</tr>
<tr>
<td></td>
<td>RD-70</td>
<td>0.031 a-d</td>
<td>1.81 d</td>
</tr>
<tr>
<td></td>
<td>RD-90</td>
<td>0.028 a-d</td>
<td>1.75 e</td>
</tr>
<tr>
<td></td>
<td>RD-110</td>
<td>0.026 a-d</td>
<td>1.71 f</td>
</tr>
<tr>
<td></td>
<td>RD-130</td>
<td>0.024 a-d</td>
<td>1.65 h</td>
</tr>
<tr>
<td></td>
<td>RD-0 Regulator</td>
<td>0.034 a-c</td>
<td>0.66 p</td>
</tr>
<tr>
<td>Spring</td>
<td>RD-30</td>
<td>0.028 a-d</td>
<td>1.67 g</td>
</tr>
<tr>
<td></td>
<td>RD-50</td>
<td>0.025 a-d</td>
<td>1.35 j</td>
</tr>
<tr>
<td></td>
<td>RD-70</td>
<td>0.023 a-d</td>
<td>0.88 l</td>
</tr>
<tr>
<td></td>
<td>RD-90</td>
<td>0.023 a-d</td>
<td>0.66 p</td>
</tr>
<tr>
<td></td>
<td>RD-110</td>
<td>0.020 b-d</td>
<td>0.65 p</td>
</tr>
<tr>
<td></td>
<td>RD-130</td>
<td>0.020 b-d</td>
<td>0.59 q</td>
</tr>
<tr>
<td>SE</td>
<td>0.0059</td>
<td>0.0057</td>
<td>0.0058</td>
</tr>
<tr>
<td>LSD (5%)</td>
<td>0.017</td>
<td>0.019</td>
<td>0.016</td>
</tr>
<tr>
<td>*WHO (mg L⁻¹)</td>
<td>3.00</td>
<td>0.30</td>
<td>2.0</td>
</tr>
<tr>
<td>**FAO (mg L⁻¹)</td>
<td>2.0</td>
<td>5.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

In each column, means followed by common letter are not significantly different at 5% probability level.
* Max: permissible limit for drinking purpose/human consumption
** Recommended Maximum concentration for irrigation/crop production (Ayers and Westcot, 1985)

Concentration of Cu was positively associated with Cd, Cr, and As, with ‘r’ value of 0.16, 0.27, 0.19, respectively. However, Cu was negatively associated with Pb (r = -0.17). Statistical results for Cu showed non-
significant differences at 5% probability level with these heavy metals concentration. Manganese was negatively associated with Cd, Cr, Pb and As having \( r \) value of -0.34, -0.33, -0.51 and -0.43, respectively. Statistical results for Mn showed non-significant differences at 5% probability level with Cd, but had significant differences at 1% probability level with Pb. Lead (Pb) was positively associated with Cd and As having \( r \) value of 0.87 and 0.89. The statistical results for Pb showed significant differences at 1% probability level with these metals. Whereas, Cd was positively associated with As with \( r \) value of 0.86. Statistical results for Cd showed significant differences at 1% probability level with As.

In canal water, the higher Zn concentrations were noted in the upper reach and lowest Zn was observed towards down reach during summer. The higher Fe was observed near upper reach during winter and had decreasing trend towards down reach during summer. Maximum Cu concentration was observed towards down reach during spring and decreased towards upper reach during winter. With regard to Mn, it was higher near upper reach during summer and was low at upper reach during winter. The Zn and Fe concentrations in canal water were within the permissible limits of FAO for irrigation/crop production in all seasons at all locations. The Cu was higher in all seasons except winter near up to mid-reach and was not within the permissive limits. However, Mn was higher in all seasons except upper reach where it was also within the permissible limit of FAO. With regard to canal water for human consumption/drinking purpose, the Zn, Cu, Mn concentration in canal water were within the permissible limit of WHO in all seasons and at all locations, however, Fe was found beyond permissible limit of WHO in all season and locations.

### Table 5. Correlation coefficient between trace and heavy metals concentration parameters of Phuleli Canal water

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Intercept</th>
<th>Slope</th>
<th>( r ) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn (mg L(^{-1})) vs Cd (mg L(^{-1}))</td>
<td>0.00</td>
<td>-0.019</td>
<td>-0.13 ns</td>
</tr>
<tr>
<td>Zn (mg L(^{-1})) vs Cr (mg L(^{-1}))</td>
<td>0.06</td>
<td>-0.67</td>
<td>-0.24 ns</td>
</tr>
<tr>
<td>Zn (mg L(^{-1})) vs Pb (mg L(^{-1}))</td>
<td>0.02</td>
<td>0.15</td>
<td>0.15 ns</td>
</tr>
<tr>
<td>Zn (mg L(^{-1})) vs As (µg L(^{-1}))</td>
<td>0.28</td>
<td>-2.19</td>
<td>-0.14 ns</td>
</tr>
<tr>
<td>Fe (mg L(^{-1})) vs Cd (mg L(^{-1}))</td>
<td>0.00</td>
<td>0.00</td>
<td>0.22 ns</td>
</tr>
<tr>
<td>Fe (mg L(^{-1})) vs Cr (mg L(^{-1}))</td>
<td>0.04</td>
<td>0.005</td>
<td>0.14 ns</td>
</tr>
<tr>
<td>Fe (mg L(^{-1})) vs Pb (mg L(^{-1}))</td>
<td>0.02</td>
<td>0.007</td>
<td>0.51**</td>
</tr>
<tr>
<td>Fe (mg L(^{-1})) vs As (µg L(^{-1}))</td>
<td>0.17</td>
<td>0.04</td>
<td>0.21 ns</td>
</tr>
<tr>
<td>Cu (mg L(^{-1})) vs Cd (mg L(^{-1}))</td>
<td>0.00</td>
<td>0.001</td>
<td>0.16 ns</td>
</tr>
<tr>
<td>Cu (mg L(^{-1})) vs Cr (mg L(^{-1}))</td>
<td>0.04</td>
<td>0.024</td>
<td>0.27 ns</td>
</tr>
<tr>
<td>Cu (mg L(^{-1})) vs Pb (mg L(^{-1}))</td>
<td>0.03</td>
<td>-0.006</td>
<td>-0.17 ns</td>
</tr>
<tr>
<td>Cu (mg L(^{-1})) vs As (µg L(^{-1}))</td>
<td>0.19</td>
<td>0.097</td>
<td>0.19 ns</td>
</tr>
<tr>
<td>Mn (mg L(^{-1})) vs Cd (mg L(^{-1}))</td>
<td>0.00</td>
<td>-0.005</td>
<td>-0.34 ns</td>
</tr>
<tr>
<td>Mn (mg L(^{-1})) vs Cr (mg L(^{-1}))</td>
<td>0.07</td>
<td>-0.092</td>
<td>-0.33**</td>
</tr>
<tr>
<td>Mn (mg L(^{-1})) vs Pb (mg L(^{-1}))</td>
<td>0.04</td>
<td>-0.054</td>
<td>-0.51**</td>
</tr>
<tr>
<td>Mn (mg L(^{-1})) vs As (µg L(^{-1}))</td>
<td>0.39</td>
<td>-0.67</td>
<td>-0.43*</td>
</tr>
<tr>
<td>Pb (mg L(^{-1})) vs Cd (mg L(^{-1}))</td>
<td>-0.00</td>
<td>0.122</td>
<td>0.87**</td>
</tr>
<tr>
<td>Pb (mg L(^{-1})) vs As (µg L(^{-1}))</td>
<td>-0.14</td>
<td>13.155</td>
<td>0.89**</td>
</tr>
<tr>
<td>Cd (mg L(^{-1})) vs AS (µg L(^{-1}))</td>
<td>0.02</td>
<td>90.508</td>
<td>0.86**</td>
</tr>
</tbody>
</table>

\( ns \) = non significant, * and ** significant at 5% and 1% probability level respectively

The use of polluted water in the surroundings of the big cities for 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 irrigation 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 health (Perveen et al., 2006). A variety of contaminants including toxic metals especially copper and zinc are reported to be ubiquitously present in rivers, reservoirs and are disadvantageous for aquatic organisms (Olsson, 1998). Trace elements are immobilized within the stream sediments and thus could be involved in-absorption, co-precipitation and complex formation (Mohiuddin et al., 2010; Okafor and Opuene, 2007). Sometimes they are co-adsorbed with other elements as oxides, hydroxides of Fe and Mn or may occur in particulate form (Awofolu et al., 2005; Mwiganga and Kansiime, 2005).

In this study, it was observed that canal had more trace elements in winter except Cu and Mn in summer. Abolude et al. (2009) while investigating trace elements in Kubanni Reservoir, detected trace elements viz. iron, manganese, zinc, chromium, copper in higher concentrations in dry season than the rainy season. The seasonal variations may be due to either anthropogenic causes, such as irrigate ion or wastewater discharge, or natural causes, such as water temperature, pH, redox condition, water flux, or activity of microorganisms (Papafilippaki...
et al., 2008). Abolude et al. (2009) investigated the Kubanni Reservoir in Zaria and reported that Fe, Zn, Cu and Mn had significant variations between the months, stations and seasons and found that these elements were higher than the permissible limits for drinking water. The accumulation of these elements in soils and crops may become health hazards to humans and/or animals. Therefore, continued monitoring of the concentrations of potentially toxic elements in soil and plants and/or treatment of sewage water before using for irrigation is needed (Brar et al., 2000). In this study, iron was higher in canal 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 (Rajappa et al., 2010; Vijaya Bhaskar et al., 2010).

In this study, Fe were found higher in winter compared to other season. Similar results were reported by Khan et al. (2006) that the levels of Fe were higher during winter as compared to summer. Contrary, Haq et al. (2005) observed lower Fe in winter than that in the summer. Mn content in canal water was higher during summer as compared to rest of the seasons. Khan et al., (2006) observed the levels of Mn were lower during winter than during summer.

The present study shows that Cu in water was higher than the permissible limits of FAO (Ayers and Westcot, 1985) for agriculture purpose/irrigation. Higher concentration of Cu in water is an index of pollution from effluents in the canals or water bodies (Vijaya Bhaskar et al., 2010). Its excessive amounts usually influence water as well as soil (Perveen et al., 2006). 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 (Mohammad et al., 2003), causes stomach and intestinal distress, liver and kidney damage, and anemia (USEPA, 2003).

The metal concentration of canal water viz. Cd, Cr, Pb and As were higher towards downstream reach as compared to upstream reach during winter. As the season changed the values of these parameters showed decreasing trend (autumn>spring>summer). As concentration in canal water was within the permissible limit of WHO for human consumption/drinking purpose in all seasons and locations. Pb concentration in canal water was not within permissible limit of WHO in all season and locations. The Cd in water was higher during winter, autumn and spring seasons in all locations and was not within permissible limit of WHO. The Cr was higher near mid to down reach during whole the year and was beyond the permissible limit of WHO. The permissible limits of FAO for heavy metal concentration viz. Cd, Cr, Pb and As in canal water.

Heavy metal accumulation was noted in canal, varied significantly in seasons and locations. The variation in concentration of heavy metals was due to the use of different raw materials and variation of production level (Das et al., 2011). Further, it was observed that lowest concentrations during rainy season which might be due to the dilution effect of rainfall whereas the highest concentration of these metals were found during dry periods (without rain) as industrial effluents are less diluted due to recede water in the river in this season. The heavy metal pollution of fresh water is the single most important environmental threat to the future (Rachna et al., 2011). 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. Pollution makes streams, canals and lakes waters unpleasant to look at, to smell, and to swim in. People who ingest polluted water can become ill, and, with prolonged exposure, may develop cancers or bear children with birth defects (Perveen et al., 2006).

The inter-metallic correlation coefficients in Phuleli Canal water with p<0.01 were: Fe-Pb, Fe-Cr, Pb-Cd, Pb-As, Cd-As. There are well defined relationships between various heavy and trace metals. These metals concentrations in effluents exhibited a strong positive correlation with those in surface water. So, metals found in the Phuleli Canal and around were mainly generated from various pollution sources viz. industrial and municipal liquid effluents.

CONCLUSION AND RECOMMENDATIONS

Cadmium, Cr, Pb and As of canal water increased considerably towards downstream (RD-130) during winter season. Cadmium, Cr and Pb concentration in canal and was found higher than WHO permissible limit and Cu and Mn were found above FAO limit. Heavy metal concentration in canal water samples were found higher in down-reach compared to up-reach may be due to discharge of industrial waste into canal. Trace and heavy metal concentration in the canal is higher usually during winter season due reduced discharge from Kotri Barrage into canal and reception of low rainfall in the area. The canal water contained highly toxic metals which were beyond the permissible limits of WHO and FAO for human consumption and agricultural crops, respectively. Hence, people using canal water, directly or indirectly at downstream reach of the canal are at risk. It is highly 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.
REFERENCES


Vijaya Bhaskar C., K. Kumar and G. Nagendrappa. 2010. Assessment of heavy metals in watersamples of certain locations situated around Tumkur, Karnataka, India. E-J. Chem. 7 (2), 349-352


