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HAZARDOUS POLLUTANTS IN POTABLE GROUNDWATER SOURCES OF PUBLIC SCHOOLS, SOUTHERN PUNJAB (PAKISTAN)

Contaminantes peligrosos en fuentes subtarráneas de agua de escuelas públicas, Punjab del sur (Pakistán)

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ABSTRACT

Drinking water quality is considered to be of vital importance for all human beings and animals but its significance is much more heightened when consumer is a teenager. In view of foregone, groundwater quality assessment of 150 public schools situated in flooded areas of Southern Punjab, Pakistan, was carried out. Analysis results revealed that 49 and 37 % water samples are contaminated with coliform and faecal coliforms, respectively. On the other hand chemicals constituents in samples, including calcium (43 %), magnesium (11 %), potassium (37 %), sodium (31 %), sulphate (39 %), hardness (31 %), total dissolved solids (TDS) (35 %) and chloride (15 %) were higher than World Health Organization (WHO) limits. The situation is more serious as fluoride, iron and arsenic were also found in high concentration in 15, 60 and 58 % samples, respectively. Health risk assessment data indicated that mean chronic daily intake (CDI) values for children and adults were 0.592 and 0.537 µg/kg/day for arsenic and 0.012 and 0.011 µg/kg/day for iron, respectively. Calculated arsenic health risk index (HRI) > 1 for 88 and 58 % water samples for children and adults respectively, which highlights possible health risks associated with intake of contaminated water.

Palabras clave: contaminación, calidad del agua, evaluación de riesgo a la salud, metales traza, ingesta diaria crónica

RESUMEN

La calidad del agua potable se considera de vital importancia para todos los seres humanos y animales, pero su importancia aumenta mucho más cuando el consumidor es un adolescente. En vista de lo anterior, se llevó a cabo una evaluación de la calidad de las aguas subterráneas de 150 escuelas públicas ubicadas en áreas inundadas del sur de Punjab, Pakistán. Los resultados del análisis revelaron que 49 y 37% de las muestras de agua están contaminadas con coliformes y coliformes fecales, respectivamente. Por otro lado, los componentes químicos en las muestras que incluyen calcio (43 %), magnesio (11 %), potasio (37 %), sodio (31 %), sulfato (39 %), dureza (31 %), sólidos disueltos totales (TDS) (35 %) y cloruro (15 %)en 43, 11, 37, 31, 39, 31, 35 y 15% de las muestras fueron mayores que los límites de la Organización Mundial de la Salud (OMS). La situación es más ya que el fluoruro, el hierro y el arsénico también se encontraron en altas concentraciones en 15, 60 y 58% de las muestras, respectivamente. Los datos de evaluación de riesgo para la salud indicaron que los valores medios de ingesta crónica diaria (CDI, por sus siglas en inglés) para niños y adultos fueron de 0.592 y 0.537 µg/kg/día para arsénico y 0.012 y 0.011 µg/kg/día para el hierro, respectivamente. El índice de rieso, calculado para el arsénico, (HRI, por sus siglas en inglés) fue > 1 para 88 y 58% de muestras de agua para niños y adultos, respectivamente, lo que destaca los posibles riesgos para la salud asociados con la ingesta de agua contaminada.

INTRODUCTION

One third of world's population have no other option than groundwater for their drinking use (Nickson et al. 2005) whereas in Pakistan about 70 % people rely on groundwater for their household use (Malik et al. 2010). Various types of materials on seepage routes, general human activities including use of fertilizers and pesticides, natural disasters, the dissolved solids and domestic and industrial wastes disposal system adversely affect groundwater quality (Phiri et al. 2005). It has been reported that severe contamination of drinking water with various hazardous pollutants and microorganisms was resulted due to floods in different areas of Pakistan, which caused waterborne diseases like diarrhoea, cholera, typhoid fever, food poisoning, dysentery, gastroenteritis, and other serious infections (Baig et al. 2012, Muhammad et al. 2013).

Literally, drinking water must not have any objectionable aesthetic parameter and should be free from organic and inorganic material and pathogens exerting adverse physiological effects on human health (Qadeer 2004). Literature shows that infectious diarrhoea caused by poor sanitation, hygiene and water quality, resulted in 2.2 million deaths per year around the world (WHO 2000). Furthermore, 90 % of these deaths were in children and unfortunately all cases were reported in developing countries (Ashbolt 2004). Waterborne diseases such as dysentery, diarrhoea, tooth decay, anemia and hepatitis in children contribute nearly 80 % of total existing diseases (Memon et al. 2011) and the situation is much more deteriorated in emergencies like floods. In Pakistan, over 40 % deaths in urban areas are attributed to the diseases caused by consumption of water drawn from polluted sources. An investigation conducted in three districts (Badin, Thar and Thatta) of southern Sindh, Pakistan, revealed that consumption of polluted drinking water was the main cause of diseases like diarrhoea, gastroenteritis, dysentery, kidney problems, etc. (Memon et al. 2011).

From a physical and chemical point of view, although the major ions in drinking water are essential nutrients for humans, beyond certain limit these pose serious health hazards. It was observed that high level of total dissolved solids (TDS), fluoride, nitrate, calcium, and total hardness is associated with frequent prevalence of renal gravels and renal stones (Mohamed et al. 2015). Through a number of studies, it has been established that concentrations of different minerals, chemicals and substances in drinking water exceed the World Health Organization (WHO) guideline values (GVs), as found in Cambodia, Zimbabwe, Ghana, Pakistan and Bangladesh (WHO 2004, Wakida et al. 2005, Laluraj et al. 2006, WHO 2010, Memon et al. 2011).

Trace elements if ingested in excess can cause serious health implications. Therefore, it is of vital importance to estimate potential health impact by calculating health risk associated with various contaminants in aquatic ecosystems. Evaluation of heavy metal concentration and health risk assessment have been carried out in various studies which reveal that overall excess concentration of all these metals is toxic (Adepoju-Bello et al. 2005, Venkatramanan et al. 2015). In order to evaluate physical, chemical and microbiological quality of drinking water and estimate associated health risks, a large number of other investigations have also been conducted revealing contamination of most of the water samples analyzed either with chemical and/or microbiological contaminants (Khan et al. 2001, Imitiaz, et al. 2004, Akhter et al. 2010, Mohsin et al. 2013, Shakoor et al. 2015, Rasool et al. 2016, Alamgir et al. 2016).

In continuation of our previous studies (Sarfraz et al. 2016, Sarfraz et al., 2018a, 2018b), we have designed the present project to evaluate microbiological, physical and chemical quality of drinking water sources available in public schools of Southern Punjab, Pakistan.

MATERIALS AND METHODS

Dera Ghazi Khan and Rajanpur districts are located in between the Koh-Suleman range of mountains and the river Indus at 30º 3′ 22″ N to 70º 38″ 04″ E and 29º 6″ 12″ N to 70º 19″ 30″ E respectively, whereas Muzaffargarh district is located in between DG Khan and Multan districts at 30º4′ 13″ N to 71º11′ 36″ E. Water samples from 150 hand pumps situated in public schools of flood affected rural areas of Muzaffargarh, DG Khan and Rajanur districts (**Fig.1**) were collected for water quality assessment. From each sampling site, three water samples have been collected carefully in clean polypropylene bottles (600 mL) for evaluation of physical, chemical, trace metals and aesthetic parameters. In addition, sterilized glass bottles (250 mL) were used for collection of water samples for microbiological analysis, which were stored in ice boxes and immediately shifted to the laboratory.

Fig. 1. Graphical presentation of studied area

Analytical grade reagent and chemicals were made available and all instruments used were calibrated prior to analysis of water samples collected. Few water quality parameters such as taste, color, electrical conductivity (EC) and turbidity were estimated by using field testing kits. Membrane filtration technique was used for analysis of microbiological parameters like coliform and faecal coliform (Clesceri et al. 2005). Detailed evaluation of other chemical indicators including alkalinity, hardness, sodium (Na^+), calcium (Ca^{+2}), magnesium (Mg^{+2}), iron (Fe), potassium (K^+), sulphate (SO_4^{2-}), chloride (Cl^-), fluoride (F^-), nitrate (NO_3^-), TDS and arsenic (As) have been carried out in a water quality laboratory by using the American Public Health Association (APHA) standard methods (Clesceri et al. 2005).

In short, total coliform and faecal coliform were determined by using M-Endo Agar and M-FC Agar media, respectively. Plates were incubated at 35 ºC and 44.5+0.2 ºC for 24 hours. Appearance of pink to dark red color with metallic surface sheen colonies for total coliform and blue colored colonies for faecal coliform bacteria as CFU/100 mL were calculated. Alkalinity including carbonates and bicarbonates were determined by titration with hydrochloric acid using phenolphthalein and methyl orange as indicators. Calcium and hardness assessment was made by volumetric titration with ethylenediaminetetracetic acid using murioxide and eriochrome black T as indicator, respectively. The concentration of NO_3, SO_4 and Fe was determined by using spectrophotometric method with barium chloride and HCl as reagents. Fluoride was estimated by colorimetric method using spadns solution whereas, Cl^- was quantified by argentometric titration with $AgNO_3$ using potassium chromate as an indicator. Atomic absorption spectrophotometer (AAS) was used for determination of As using air-acetylene flame for combustion with single-element hollow cathode lamp. Estimation of Na and K was carried out by using flame photometer. Finally, TDS was calculated by addition of cations and anions (Clesceri et al. 2005). Other instruments and methods used for current study includes Louibond PC_H63739 Germany turbidity meter, EC meter of Hannna HI 99300 (Italy), pH meter of Jenway 350, flame photometer (Italy), colorimeter Hach DR 2800, Optizen 2120 UV plus spectrophotometer (Korea).

Chronic daily intake (CDI) and health risk assessment (HRI) for As and Fe was calculated by using equations 1and 2 (Shah et al. 2012, Muhammad et al. 2010):

$$CDI = \frac{Lw \times Mc}{Wb}, \qquad HRI = \frac{CDI}{RfD} \times 0.001$$

where Mc (µg/L) represents the concentration of metal in water and Lw (L/day) presents amount of water consumed daily that may be considered as 1 L/day for child and 2 L/day for adults, whereas Wb (kg) is body weight of respective consumer that can be assumed as 32.7 kg and 72 kg for child and adult respectively (Khan et al. 2010). RfD shows the reference dose of trace metals for oral toxicity which is 0.0003 and 0.7 mg/kg/day for As and Fe respectively and 0.001 is the multiplication factor for converting the RfD from mg to µg. Water samples having measured HRI<1 will be considered as safe for consumption.

RESULTS AND DISCUSSION

Analysis of aesthetic and physical parameters such as color, taste, odor and turbidity showed that 25 % water samples have saline taste which may be attributed to excess of chemicals. Analysis data of major water quality parameters as range and average values is presented in **table I.** Microbiological analysis data revealed that 49 % water samples were contaminated with total coliforms bacteria whereas 37 % were found to have faecal coliforms **(Fig. 2)** which may be attributed to pathogens associated with agricultural waste and human excreta. As per WHO standard, each type of coliform organisms should be absent in water intended to be used for drinking purpose (WHO 1963). Nabeela et al. 2014 showed that drinking water samples contaminated with microbial organisms (total coliforms and faecal coliforms) pose serious impact on public health in Pakistan (Nabeela et al. 2014). Natural disasters like floods and earthquakes are considered among the main water pollution sources due to which human and animal wastes as well as industrial contaminants are liable to enter the main water body through surface water sources and unprotected bore holes (Baig et al. 2012).

pH measurement indicates acidic or alkaline nature of water. If pH value is less than 7, water is considered as acidic whereas pH above 7 shows alkaline nature of water. pH controls measured chemical parameters and affects corrosion process in water (Imitiaz et al. 2004). The present study shows that pH varied from 7.0 to 8.38 as compared to WHO permissible limits (6.5-8.5) (Rice et al. 2012). EC is an indicator of ionic concentration and dissolved solids in a water sample. EC of water samples in the present study varied from as low as 324 µS/cm to as high as 16890µS/cm. Calcium and Mg are among essential micronutrients but causes hardness of water, resulting digestive system problems and clothes cleaning issues if their concentration is higher than the permissible limit (Khan et al. 1999). Present analysis data (**Fig.2**) showed that 43, 11 and 31 % water

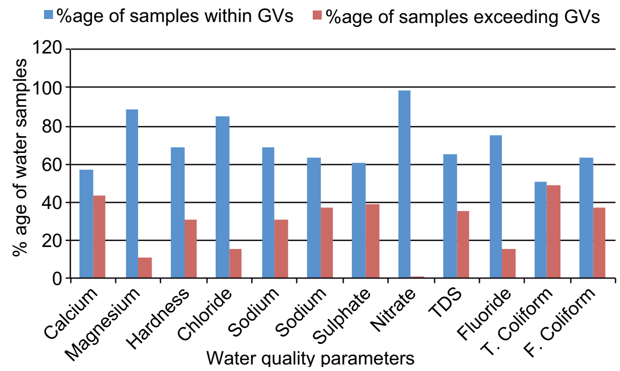

Fig. 2. Comparison of studied water parameters (%age) with GV

TABLE I. DISTRICT WISE RANGE AND AVERAGE VALUES OF STUDIED PARAMETERS

District		Overall (n=150)		Muzafargarh (n=50)		Dera Ghazi Khan (n=50)		Rajinpur (n=50)	
Parameter	GV	Range	Average	Range	Average	Range	Average	Range	Average
Ec (µS/cm)	NGVS	263-16890	2218	324-9055	1410	263-6686	1520	331-16890	3723
Hard (mg/L)	<500	60-4300	613	100-1650	305	100-2500	528	60-4300	60
Cl (mg/L)	<250	14-3010	235	14-1680	126	17 - 367	85	21-3010	495
Alk (mg/L)	NGVS	80-1500	329	80-1500	353	100-780	285	130-1240	348
SO4 (mg/L)	<250	13-3480	456	18-1560	201	13-2520	389	44-3480	779
NO3 (mg/L)	<12	0.01-20.4	1.8	0.6-20.4	2.4	0.1-8.9	1.4	0.01-19.5	1.8
TDS (mg/L)	<1000	177-10773	1368	231-4928	845	177-4499	980	222-10773	2280
Ca (mg/L)	<75	08-1080	125	08 -136	48	20 - 500	114	16 - 1080	213
Mg (mg/L)	<150	4.8 - 510	73	9.7 - 318	45	12 - 303	59	4.9 - 510	115
Na (mg/L)	<200	12 - 2840	259	14 - 1050	186	12 - 900	145	25 - 2840	446
K (mg/L)	<12	03 - 70	13	03 - 70	16	03 - 43	10	04 - 65	14
Fe (mg/L)	<0.3	0.1-1.5	0.4	0.1-1.5	0.4	0.1-1	0.4	0.2-0.5	0.2
F (mg/L)	<1.5	0.01-10	1.1	0.01-4.5	1.1	0.1-10	1.0	0.32-6.5	1.3
As (µg/L)	<10	5-100	19.3	5-100	23.6	5-100	18.6	5 - 45	15.8
Coliform/CFU	Absent	0-71	18	0-45	15	0-71	22	0-63	18
Faecal Coliform/CFU	Absent	0-48	16	0-43	12	0-48	19	0-46	17

GV = guideline values, NGVS = no guideline value set, CFU = colony forming unit samples have high levels of Ca, Mg and hardness as compared to WHO guideline values (WHO 2004). It has been shown that laxative effect may appear due to consumption of drinking water having high concentration of both, Mg and SO_4 (WHO 2010).

Chlorides are present naturally in water, higher content may impart saline taste in drinking water along with creating problems in throat and digestive system (Khan et al. 2000). Analysis data revealed that 15 % water samples have Cl content higher than WHO permissible limits (**Fig. 2**). Alkalinity, an important parameter of water quality affects a number of chemical and biological reactions in a human body. Alkalinity varied from 80 to 1500 mg/L, higher concentration may have adverse problems like gas trouble, kidney stones, hardness and damage of metallic pipes (Kudryavtseva 1999). Sodium is also an important mineral element but intake of water with elevated concentration may increase blood pressure. A study conducted on 4^{th} and 5^{th} grade school children revealed that drinking of water with high Na concentrations have led to an increase in mean arterial and systolic blood pressure (Pomeranz et al. 2002). Present analysis data indicate that 31, 37 and 39 % water samples have high concentration of Na, K and SO_4^- respectively (**Fig. 2**). A number of waterborne diseases like diarrhoea, respiratory illness, gastrointestinal disorder, weight abatement and dehydration are linked with elevated concentration of SO_4 in drinking water (Mazloomi et al. 2009). TDS is a measure of total ion concentration and contribute towards taste, corrosion properties, tendency to incrustation and hardness. Present study indicates that TDS value of 35 % water samples exceed guideline value. Various natural and anthropogenic origins are considered as the main sources of water contamination including industrial, municipal and domestic disposal system, agricultural runoff containing organic and inorganic fertilizers and pesticides (Ritter et al. 2002).

Fluoride is an important micronutrient but higher concentration may contribute towards dental and skeletal fluorosis and other body joints problems (Iqbal et al. 2000). Presented study shows that 15 % water samples have F content higher than recommended value of 1.5 mg/L. It was estimated that consumption of drinking water with F concentrations $\geq$4.32 ppm for the long term may increase the risk of bone along with hip fractures (Li et al. 2001). Arsenic is a trace element whose high concentration for long term may cause problems like mental retardation, epilepsy, severe hearing loss and other brain damage (Spencer 2000). A number of studies about source, distribution and human health implications of arsenic in different parts of the world have been carried out (McArthur et al. 2001, Smedley et al. 2002, Ayotte et al. 2003, Camacho et al. 2011). Our results show that 87 (58 %) water samples have high level of As in comparison to guideline value (10 ppb) as shown in **Fig. 3**. It has been reported that lungs, skin, kidneys, intestine and liver are among the major body organs affected by high concentration of As due to its involvement in As absorption, accumulation and excretion (Ötleş et al. 2010).

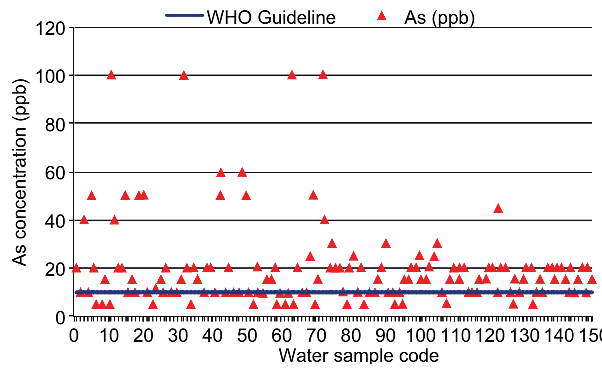

Fig. 3. Illustration of As content in comparison to WHO GV

Research showed that term low birth weight in newborns is associated with chronic exposure to Fe through drinking water (Grazuleviciene et al. 2009). Present study indicates high level of Fe contamination in ground water of southern Punjab as 60 % water samples showed iron content higher than guideline value as shown in **Fig. 4**. Due to the interaction of water with biosphere and geosphere as a result of hydrological cycle, the ground and surface water sources are generally liable to contain natural organic matter (NOM) to some extent, but during

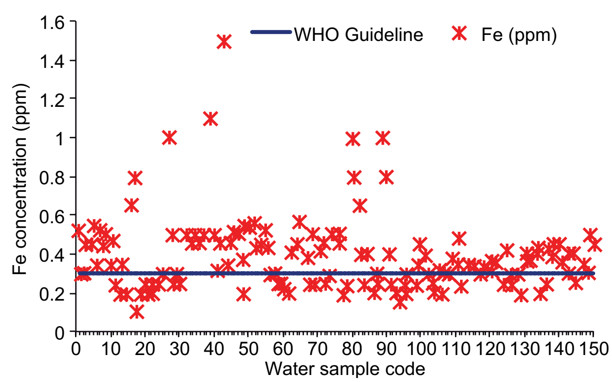

Fig. 4. Illustration of Fe content in comparison to WHO GV

rains and floods amount of NOM increases much more, which is considered to inhibit oxidation of iron as it is reduced from Fe^{+3} to Fe^{+2}, and resultantly Fe concentration is increases in water. Literature showed that the anthropogenic and geogenic activities are responsible for masking Fe concentration in underground water system as is evident from relatively higher concentration of Fe in some water samples collected from tube wells located near municipal waste waters (Achary 2014).

CDI and HRI were calculated, for children as well as adults, on the basis of concentration of trace elements in drinking water (**Table II** and **III**). Calculated CDI values for As ranged from 0.153 to 3.058 and 0.139 to 2.778 µg/kg/day and for Fe from 0.003 to 0.046 and 0.003 to 0.042 µg/kg/day for children and adults respectively. Mean CDI values of As and Fe were higher for water samples collected from Muzaffargarh district as compared to DG Khan and Rajanpur for both, adults and children as highlighted in **table II**.

Calculated HRI values were high for As, ranging from 0.510 to 10.194 (mean HRI = 1.972) for children and from 0.463 to 9.259 (mean HRI = 1.791) for adults. Overall HRI was > 1 in 88 % water samples for children and 58 % for adults. Mean HRI of water samples collected from Muzaffargarh district was higher than those collected from other two districts as shown in **table II**. HRI for Fe ranged from 4.37E-06 to 6.55E-05 and 3.97E-06 to 5.95E-05 for children and adults respectively indicating overall HRI < 1 for Fe. As in ground water of public schools of Southern Punjab is higher than Fe as shown by HRI calculations. Literature highlights correlation of As with Fe and other heavy metals and high carcinogenic and non-carcinogenic health risk associated with elevated concentration of As in drinking water (Van Halem et al. 2010). Sultana et al. (2014) investigated water

TABLE II. COMPARISON OF CALCULATED CHRONIC DAILY INTAKE (CDI) RANGE AND MEAN VALUES

District		As CDI		Fe CDI	
		Children	Adults	Children	Adults
Overall n=150	Range	0.53-3.058	0.139-2.778	0.003-0.046	0.003-0.042
	Mean	0.592	0.537	0.012	0.011
Muzafargarh n=50	Range	0.153-3.058	0.139-2.778	0.003-0.046	0.003-0.042
	Mean	0.723	0.657	0.013	0.012
Dera Ghazi Khan n=50	Range	0.153-3.058	0.139-2.778	0.005-0.031	0.004-0.028
	Mean	0.569	0.517	0.012	0.011
Rajanpur n=50	Range	0.153-1.376	0.139-1.250	0.006-0.015	0.006-0.014
	Mean	0.483	0.439	0.010	0.009

TABLE III. COMPARISON OF CALCULATED HEALTH RISK INDEX (HRI) RANGE AND MEAN VALUES

District		As HRI		Fe HRI	
		Children	Adults	Children	Adults
Overall n=150	Range	0.510-10.194	0.463-9.259	4.37E-06 to 6.55E-05	3.97E-06 to 5.95E-05
	Mean	1.972	1.791	1.70E-05	1.55E-05
Muzafargarh n=50	Range	0.510-10.194	0.463-9.259	4.37E-06 to 6.55E-05	3.97E-06 to 5.95E-05
	Mean	2.410	2.189	1.91E-05	1.73E-05
Dera Ghazi Khan n=50	Range	0.510-10.194	0.463-9.259	6.55E-06 to 4.37E-05	5.95E-06 to 3.97E-05
	Mean	1.896	1.722	1.73E-05	1.57E-05
Rajanpur n=50	Range	0.510-4.578	0.463-4.167	8.74E-06 to 2.18E-05	7.94E-06 to 1.98E-05
	Mean	1.611	1.463	1.48E-05	1.34E-05

quality of Lahore, Punjab and concluded that 87 % water samples have HQ values greater than 1.00 (HQ = 2.3-48.6) (Sultana et al. 2014).

In order to reduce bacterial contamination, it is suggested that disinfection campaign should be launched among the residents for mitigation of microbiological risks. Boiling of drinking water is considered as the most effective means of water disinfection, which destroys all the coliform bacteria. Alternatively, use of solar rays could be considered as a cheaper method but it does not eliminate microbial load completely. However, granular activated carbon filtration is the most suitable technique for decreasing microbial content of the drinking water. Concerned authorities should launch public awareness scheme about waterborne diseases and undertake the initiative to encourage the culture of hygiene and sanitation among people of the area.

Keeping in view the physical and-chemical results of water samples analyzed, it is recommended that any treatment process should be implemented so that high concentration of Na, K, SO_4, F, Fe and As may be reduced. It is also recommended that use of available household water treatment techniques for As and Fe should be encouraged among the inhabitants. A more comprehensive study should be carried out in the region to identify and designate safe drinking water sources in near about areas of public schools so that students may have access to safe drinking water. Moreover, periodical water quality analysis of pre-identified and designated water sources is very important.

CONCLUSION

Water quality assessment of public schools in flood affected area of Southern Punjab revealed that most of water samples were highly contaminated with total coliform (49 %), faecal coliform (37 %), Fe (60 %), As (58 %), SO_4 (39 %) and TDS (35 %) posing serious threat to healthy lives of youngsters, which may contribute toward a severe health dilemma. In addition, a number of sampling sites were contaminated with other chemicals constituents like Ca, Mg, F, Na, K and Cl as well. It is concluded that drinking water quality in public schools is substandard, as is evident from high level of microbial contamination and other chemicals constituents. It is recommended to devise a concrete policy for purification of drinking water and addressing post-flood environmental effects so that safety from harmful effects of bacterial contamination and other toxic pollutants may be ensured.

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