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Analysis of Water in the Area of District Sahiwal for Heavy Metals (A Case Study)

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Abstract. Current study was conducted to analyze the water in the area of Sahiwal district for toxic metals. This study gives information about the concentrations of three toxic metals, arsenic (As), lead (Pb) and chromium Cr(III). Total of 20 samples were collected, including tap, filter plant, hand pump and tubewell water. The levels of As(III) and Cr(VI) were determined using spectrophotometer while As_{total}, Cr_{total} and Pb concentrations were analysed by using inductively coupled plasma-mass spectrometry (ICP-MS). The results of chromium were above EPA recommended value (0.05 ppm) in all the samples. On the other hand, the concentrations of arsenic and lead were lower than Pak-EPA Standard limits. The mean level of chromium was 5.559 mg/L which was 111.18 times higher than WHO and local standard of 0.05 mg/L. Similarly, the mean level of arsenic and lead were 10.668 µg/L and 7.037 µg/L, respectively, which were 4.687 and 7.1053 times, respectively lower than Pak-EPA Standard value of 50 µg/L.

Keywords: Sahiwal area, arsenic, chromium, lead, ICP-MS, spectrophotometer

Introduction

Two basic requirements of each individual are sanitation and water supply (Ikhlaq *et al*., 2014). Some elements are supplied by water but when water is contaminated, it becomes the source of such substances which cause diseases in human beings. Most common diseases caused by polluted water are different kinds of cancer, teeth decay, cardiovascular, reproductive and neurological diseases. It has been observed that the rate of effects of toxic metals is greater in children than adults (Johnson and Hallberg, 2005).

Arsenic (As) and its compounds i.e., arsenicals are hazardous to human beings. Anthropogenically, they come in water from ceramic, glassware, metallurgic products, fertilizers, pesticide, petroleum and other industries. Some sources of arsenic are also natural like soil (Tareen *et al*., 2014). As arsenic belongs to non-essential group of elements, so its exposure for long time results in lungs, skin and bladder cancer (Modal and Suzuki, 2002; Morales *et al*., 2000). Sources of lead are polluted water, soil and air. Water becomes polluted with lead when it passes through lead solder, lead containing pipes and brass fixtures (Tareen *et al*., 2014). Lead (Pb) effects on normal functions of circulatory system, kidneys, reproductive and nervous system (Singh *et al*., 2010; Duruibe *et al*., 2007; Jarup, 2003). The sources of chromium (Cr) [i.e. Cr(III) and Cr(VI)] and its compounds in air, soil and water are natural as well as anthropogenic. They come in water from sewage and industrial effluents of leather and steel industries. Their compounds also come from procedures like electroplating and pigmentation (Venkateswaran *et al*., 2007; Nath *et al*., 2005). It has been shown from several studies that exposure to chromium (VI) compounds for longer time may result in lung cancer, ulcers, liver and kidney damage, convulsions, upset stomach and even death (Barceloux and Barceloux, 1999).

Arsenic poisoning is observed in Argentina, China, Chile, Canada, Mexico, Greece, Japan, Mongolia, South Africa, New Zealand, Taiwan, Philippines, Thiland and USSR states. Thus, contamination of water due to arsenic is rising as a world problem (Tahir *et al*., 2012). Arsenic and other toxic metals are also measured in various regions of Pakistan, recently. This study was carried out to assess the concentrations of As, Pb and Cr in drinking water of various regions of Sahiwal district because there was no significant data available on water quality in that area (Fig. 1).

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Fig. 1. Study area.

Materials and Methods

Reagents and standards for arsenic (III). ***Standard arsenic solution.*** Stock solution of arsenic was prepared by adding 173.33 mg sodium arsenite (Wako, analytical grade) in 100 mL deionized water from which required standards were prepared. 1% w/v KIO_3 (analytical grade, Merck) aqueous solution was prepared. 0.5 M hydrochloric acid (HCl, analytical grade, Merck) and 2 M sodium hydroxide (NaOH, Merck, analytical grade) were prepared. 250 mg Leucocrystal violet (LCV, analytical grade, Sigma), 3 mL phosphoric acid (85%, Merck, analytical grade) and 200 mL deionized water were added in 1 L flask for preparation of LCV solution. Shook them gently to dissolve dye and diluted upto the mark. The colour of solution was light yellow.

Reagents and standards for chromium (VI). ***Diphenylcarbazide-acetone solution.*** Diphenylcarbazide (Merck) solution (0.25%) in 50% acetone was prepared. Sulphuric acid (H_2SO_4, Merck, analytical grade) 3M and 0.0002 M standard stock solution of potassium dichromate ($K_2Cr_2O_7$, Sigma, analytical grade) were prepared. Required standards of $K_2Cr_2O_7$ were prepared from this stock solution.

Chemicals used in ICP-MS. ***Reagent water.*** High purity Milli-Q water was used for blank and standard solutions preparation, which was free of interferences obtained from Millipore deionizer system. <2% v/v nitric acid (HNO_3, Fluka, analytical grade) and 1% v/v highly pure HCl (Merck) were used for the preparation of blank and standard solutions. High purity (>99.99% purity) standard solutions of 100 mg/L were purchased from Analytika, which were of ICP/MS-grade used for calibrating curves and standards preparation.

Instruments. Spectrophotometer UV-1900 (BMS) was used for As(III) and Cr(VI) evaluation while ICP-MS (Agilent 7700x) was used for the evaluation of As_{total}, Cr_{total} and Pb with an autosampler of Agilent ASX-500.

Sampling. Water samples were collected according to the guidelines and standard protocol of collecting samples of 22nd edition of American Public Health Association (APHA). Sample's collection was carried out in polyethylene bottles which were washed by soaking for overnight with 10% HNO_3 (Merck, Suprapur grade), rinsed with deionized water and dried in an area free of metals (Fancesconi and Kuehnelt, 2004).

Sample sources, preservation and storage. Water samples were taken from four sources, i.e., tap water, hand pump, tubewell and filter plant. All samples were obtained from the depth of 60 to 90 feet below the surface. 40 precleaned bottles were labeled with permanent marker for 20 sampling points. The details of sampling points are given in Table 1. Two samples were taken from each sampling point. To avoid from contamination, the bottles were rinsed with water sample of particular point, three times. To measure the analytes exactly and accurately, 0.5 mL HNO_3 (Suprapur grade) was added as preservative. The samples were stored at 4 °C in refrigerator before analysis. The samples were divided into two portions, each portion had 20 samples. One portion was analysed by ICP-MS at PCSIR Research Laboratory of Pakistan. The other portion was analysed for the evaluation of As(III) and Cr(VI) quantitatively on spectrophotometer (UV-1900, BMS).

Methodology. A number of methods are used for the As evaluation, i.e., cathodic stripping voltammetry (CSV) (Ferreira and Barros, 2002), spectrophotometry (Dasgupta, 2002) hydride generation-atomic absorption spectrometry (Bundaleska *et al*., 2005), potentiometry (Gupta and Agarwal, 2005) and inductively coupled plasma-mass spectrometry (ICP-MS) (Shraim *et al*., 2013).

To determine arsenic quantitatively, detection limit of $\leq$1 ppb is desired which can only be achieved by using ICP. So, for precise and accurate calculation of arsenic, ICP-MS was used. As arsenic (III) is more toxic than arsenic (V) (Maria *et al*., 2013), so its calculation is

Table 1. Details of sampling points

Location	Detail
SLF1	Filter water of Tariq Bin Ziad Colony (TBZC)
SLH1	Hand pump of TBZC
SLT1(I)	Tap water of Government Commerce College for Females, TBZC
SLT1(II)	Tap water of Faridia park, TBZC
SLF2	Filter water of Bhutto Nagar
SLH2	Hand pump of Bhutto Nagar
SLH3	Hand pump of Ghalla Mandi
SLT3(I)	Tap water of Ghalla Mandi
SLT3(II)	Tap water of Government Mehmoodia High School, Ghalla Mandi
SLF4	Filter water of New Abadi
SLTW4	Tubewell water of New Abadi
SLT5	Tap water of 90/9-L
SLTW5	Tubewell water of 90/9-L
SLT6	Tap water of Sharif Colony
SLTW6	Tubewell water of Sharif Colony
SLF7	Filter water of Tehsil chock
SLT8(I)	Tap water of Government High School Urban area, Bilal Colony
SLT8(II)	Tap water of AIOU Sahiwal campus, Bilal Colony
SLT9	Tap water of Government High School Nangal-2, mohalla Farid Gonj
SLT10	Tap water of Farid Town

also necessary. Since, ICP gives only the quantity of As_{total} [i.e. As(III) & As(V)], spectrophotometric methods are mostly used to quantify the level of As(III) because of their ease of availability in every lab and ease of operation. Since in all the spectrophotometric methods either toxic reagents are used, or extraction of toxic gas arsine (AsH_3) is required, so a non extracted procedure with leuco crystal violet for As(III) quantification was used. This method encounters less interference of other ions than other methods. It is more sensitive and stable colour formation of oxidized dye occurrence (Agrawal *et al.*, 1999).

Similarly, evaluation of Cr_{total} [Cr(III) and Cr(VI)] was carried out by using ICP-MS (Shraim *et al.*, 2013). Out of a number of procedures for Cr(VI) determination, spectrophotometric methods are preferred because of easiness to approach and friendly to climate (Khan *et al.*, 2013). In the present work the level of Cr(VI) was determined colorimetrically with 1, 5- diphenylcarbazide reagent because all the other reagents used in this method are easily available in every lab and the complexing agent is also cheaper. There was no evolution of toxic gas during the experiment and the procedure completed within very short time, are the additional merits of this method (Mendham *et al.*, 1998). Since, lead is present in very small amount in water so its evaluation was also done by most accurate and precise method ICP-MS (Shraim *et al.*, 2013). Concentration of these heavy metals in drinking water of Sahiwal is showed Table 2.

For arsenic (III). A small amount of sample having 0.004 to 0.04 ppm (4-40 ppb) arsenic was taken in a calibrated tube of 25 mL. 2 mL KIO_3 was added followed with the addition of 1 mL solution of HCl. All the reagents were shaken thoroughly then added 1 mL solution of LCV followed by 4-5 drops of 2 M solution of NaOH. The solution was kept for 5 min in a thermostat at 40 °C. The solution was then diluted with deionized water upto 25 mL and the absorbance was measured against a reagent blank at 592 nm (Agrawal *et al.*, 1999).

For chromium (VI). Method used for Cr(VI) evaluation is reported in Vogel's Textbook (Mendham *et al.*, 1998) is as follows:

15 mL of sample was taken in 25 mL calibrated tube and sufficient 3 M H_2SO_4 was added to make the concentration 0.1 M followed by 1 mL of reagent

Table 2. Concentration of heavy metals in drinking water of Sahiwal district

Locations	As(III) (µg/L)	As_{total} (µg/L)	Cr(VI) (mg/L)	Cr_{total} (mg/L)	Pb (µg/L)
SLF1	4.92	5.60	5.59	5.62	6.81
SLH1	8.93	9.33	4.70	4.72	6.02
SLT1 (I)	6.88	7.14	4.77	4.79	6.14
SLT1 (II)	8.06	8.89	6.37	6.40	3.97
SLF2	17.98	18.43	6.11	6.13	5.04
SLH2	21.04	21.64	5.39	5.42	7.18
SLH3	23.97	25.03	5.68	5.70	9.23
SLT3 (I)	20.02	20.39	5.23	5.25	12.43
SLT3 (II)	19.17	20.70	5.13	5.13	20.69
SLF4	14.31	15.10	5.99	6.01	3.68
SLTW4	14.95	15.08	5.33	5.34	2.31
SLT5	9.12	9.55	5.61	5.62	4.78
SLTW5	7.85	8.63	5.33	5.34	3.98
SLT6	11.78	12.09	5.92	5.97	12.27
SLTW6	9.23	9.97	5.85	5.89	9.91
SLF7	5.64	5.78	5.81	5.83	4.39
SLT8 (I)	nd	nd	6.23	6.24	7.83
SLT8 (II)	nd	nd	5.54	5.57	7.32
SLT9	nd	nd	4.63	4.65	4.73
SLT10	nd	nd	5.53	5.55	2.03

diphenylcarbazide. Deionized water was added upto the mark of 25 mL and the absorbance was measured at 540 nm. The absorbance of 0.0002 M $K_2Cr_2O_7$ (standard stock solution) was measured at 540 nm having known quantity (2.08 mg/L) of Cr(VI). By comparing the absorbance of test solution with standard stock solution the quantity of Cr(VI) in test solution was measured.

For ICP-MS. EPA method 6020A ICP/MS (2007) was used for As and other toxic metals evaluation.

Results and Discussion

The values of As(III) and $\text{arsenic}_{\text{total}}$, are given in (Fig. 2-3) and its ranges in tap, tube well, filter plant and hand pump water are given in Table 3. Arsenic was detected at ppb level, so its values are given in µg/L. It is signified from the Fig. 2-3 that the locations SLT3(I), SLT3(II), SLF2, SLH2 and SLH3 have higher values of As(III) and As_{total} but still they are within the permissible limits of Pakistan Environmental Protection Agency (Pak EPA, 2010). Since, 8 locations had arsenic levels greater than 10µg/L, so 40% drinking water of the studied area was unfit and 60% was fit according to World Health Organization (WHO) limit. All the water samples had arsenic levels lower than 50 µg/L set by Pak EPA, so the water of all the locations was 100% suitable for drinking according to Pak-EPA Standards. Furthermore, the mean level of arsenic 10.668 µg/L was 4.687 times lower than Pak-EPA Standard value and 1.0668 times higher than WHO limit of 10 µg/L also verified that the water of Sahiwal district was fit for drinking purpose related to arsenic. The range of As_{total} (nd-25.03 µg/L) was 0-1.044 times higher than the range of As(III) (nd-23.97 µg/L) indicating that most of the arsenic was present in more toxic As(III) form.

Figures 4-5 illustrate the levels of chromium (VI) and $\text{chromium}_{\text{total}}$ in all types of water samples. These figures show that the concentrations of chromium are very high as compared to Pak EPA, United States Environmental Protection Agency (USEPA, 2011) and World Health Organization (WHO, 2008) recommended values, which is also explained by Table 4-6. The mean level of Cr was 5.559 mg/L which was 111.18 times higher than WHO and local standard of 0.05 mg/L. It was also clear from the ranges of Cr_{total} (4.65-6.40 mg/L) and Cr(VI)

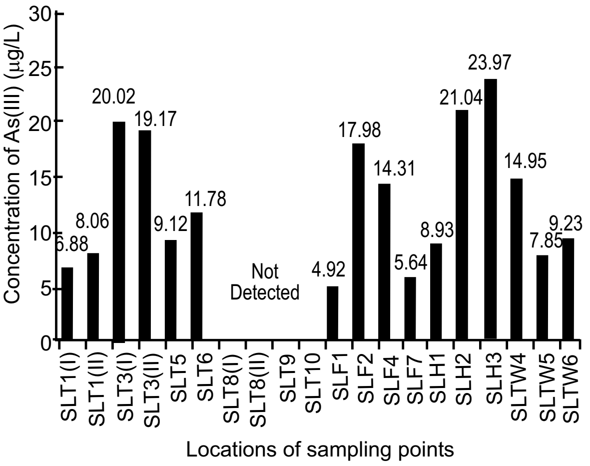

Fig. 2. Comparison of As(III) concentrations.

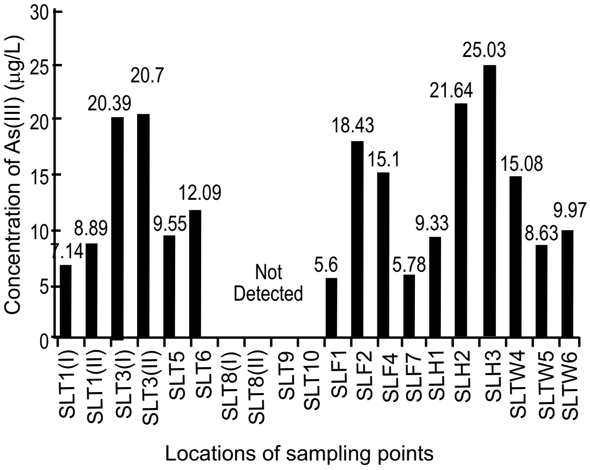

Fig. 3. Comparison of As_{total} concentrations.

Table 3. Ranges of levels As(III), As_{total}, Cr(VI), Cr_{total} and Pb in tap, filter plant, hand pump and tube well water

Metal	Tap water	Filter plant water	Hand pump water	Tube well water
As(III) (µg/L)	nd-20.02	4.92-17.98	8.93-23.97	7.85-14.95
As_{total} (µg/L)	nd-20.70	5.60-18.43	9.33-25.03	8.63-15.10
Cr_{total} (mg/L)	4.65-6.40	5.62-6.13	4.72-5.70	5.34-5.89
Cr(VI) (mg/L)	4.63-6.37	5.59-6.11	4.70-5.68	5.33-5.85
Pb (µg/L)	2.03-20.69	3.68-6.81	6.02-9.23	2.31-9.91

(4.63-6.37 mg/L) that Cr_{total} was 1.0043-1.0047 times greater than Cr(VI) exhibited that Cr(VI) was the major pollutant in drinking water of that region.

Figure 6 shows the concentrations of lead in different types of water samples. The maximum concentrations of lead are found at the sampling points SLT3(I), SLT3(II) and SLT6 but they are lower than the guided values of Pak EPA. Lead was within the range of 2.03-20.69 µg/L. The mean value of Pb was 7.037 µg/L which was 1.421 times smaller than WHO limit of 10 µg/L and 7.1053 times lower than Pak-EPA Standard value of 50 µg/L. It was also observed that 3 (15%) samples had crossed the WHO limit of 10 ppb and no sample had crossed the Pak EPA limit of 50 ppb, so all the samples were suitable according to national standard for Pb.

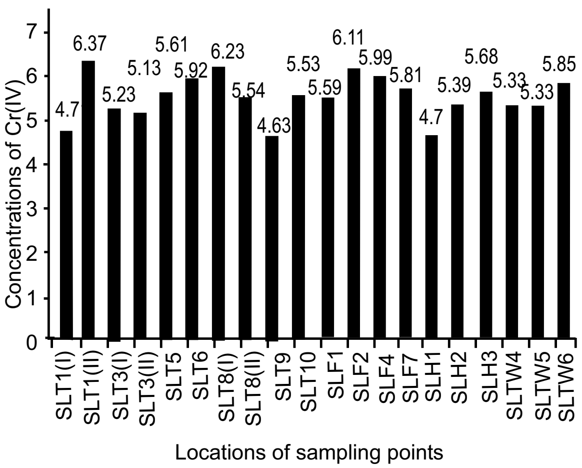

Fig. 4. Comparison of Cr(VI) concentrations.

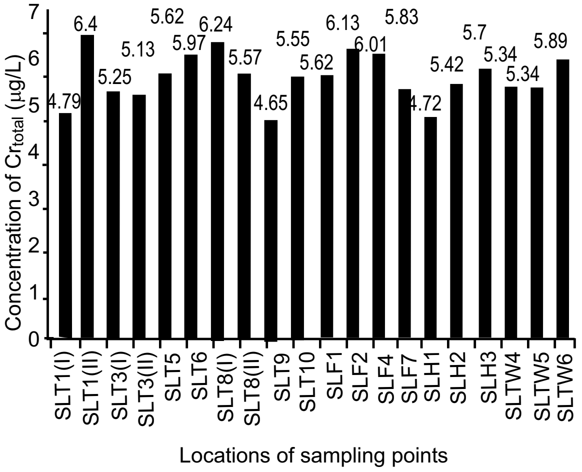

Fig. 5. Comparison of Cr_{total} concentrations.

Table 4. The mean levels of $arsenic_{total}$, $chromium_{total}$ and lead in drinking water of Sahiwal district and its comparison with Pak EPA, EPA and WHO

Metals	Unit	Mean level	Pak EPA	USEPA	WHO
As	µg/L	10.668	≤50	50	10
Cr	mg/L	5.559	≤0.05	0.10	0.05
Pb	µg/L	7.037	≤50	15	10

Table 5. Number of locations with the level of toxic metals >10 µg/L out of total 20 locations

Metal	No. of locations	% of locations greater than 10 µg/L	Locations crossing WHO limits
As_{total}	8	40%	8
Cr_{total}	20	100%	20
Pb	3	15%	3

Table 6. Number of locations with the levels of toxic metals >50 µg/L out of total 20 locations

Metal	No. of locations	% of locations greater than 50 µg/L	Locations crossing WHO limits
As_{total}	0	0%	0
Cr_{total}	20	100%	20
Pb	0	0%	0

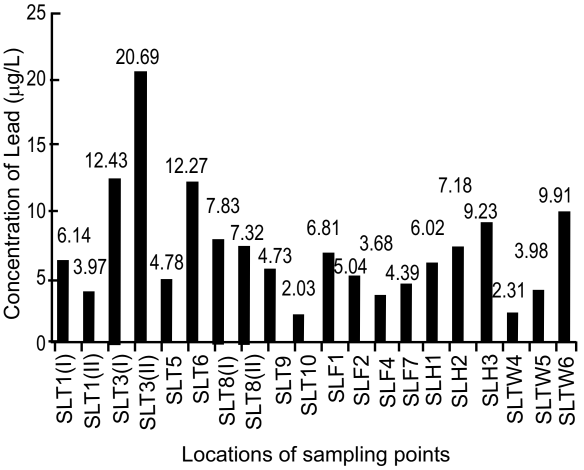

Fig. 6. Comparison of Pb concentrations.

There are few leather factories in district Sahiwal which discharge their effluents containing chromium and arsenic in underground water resources due to which the levels of arsenic and especially chromium (VI) were very high in drinking water. The other sources of arsenic in water were the use of arsenic containing pesticides and manufacturing of preservatives of wood. Chromium was present in all the samples crossing the local and international standards of WHO and USEPA. Hence, a constant monitoring of it is required in this area. Since Cr(VI) is toxic and its toxicity can be reduced by converting it into less toxic Cr(III) which is possible by reduction of Cr(VI). Therefore, reduction of Cr(VI) in drinking water of Sahiwal should be carried out by the government and international cooperation like World Bank, WHO, UNDP and UNICEF. Sources of Pb in drinking water could be anthropogenic as well as natural. Pb from household plumbing system e.g. fittings, solder, pipes dissolves in drinking water and its dissolution depends on various factors like pH, chloride, DO, water standing time and hardness. A comparative study of all studied toxic metals concentrations is depicted in (Fig. 7).

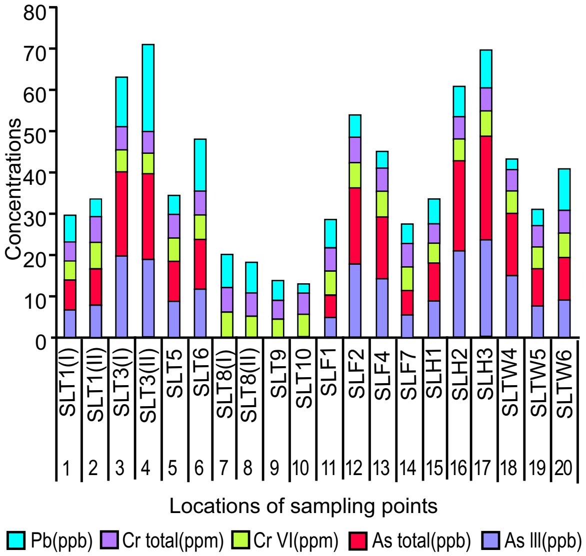

Fig. 7. Comparison of concentrations of all the studied toxic metals.

Conclusion and Recommendations

It is concluded that the concentrations of arsenic and lead were satisfactory in the area of Sahiwal and were lower than the Pak-EPA Standard values with the exception of chromium. Chromium level was greater than Pak EPA and international standards in all the locations hence quick action is required to alleviate the hazardous effects of this metals. To prevent the increased concentration of contaminant in future, it is necessary to monitor the drinking water quality and to follow the following recommendations.

1. The locations having higher level of arsenic, lead and chromium should be confirmed by further assessment and good quality water should be managed alternatively.
2. To overcome the hazardous effects of arsenic and other toxic metals in water, people should be informed immediately by communication and mass media.
3. The procedures for the removal of arsenic and other toxic metals should be developed and used at community and domestic level.
4. WHO, World Bank, UNDP and UNICEF are recommended to support financially for the implementation of above points.

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