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Elemental Analysis of Ground Water from Different Regions of Punjab State (India) Using EDXRF Technique and the Sources of Water Contamination

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Abstract. Intake of the toxic elements through ingestion of the contaminated water has resulted in phenomenal rise in health hazards in the developing countries. Most of the drinking water schemes in the Punjab state of India are based on the ground water and the canal water. Multielemental analysis of the ground water samples from different locations at the boundary between Hoshiarpur and Nawanshahr districts, and Bathinda district of Punjab state (India) are performed. These regions are known to be contaminated by selenium and uranium, respectively. The water samples are analysed using the Energy-dispersive X-ray fluorescence (EDXRF) technique. The EDXRF spectrometer consisted of an Mo-anode X-ray tube equipped with selective absorbers as an excitation source and an Si(Li) detector. The water samples from surroundings of the coal-fired thermal power plant in the city and the industrial waste water draining into Sutlej river are also analyzed to investigate the possible sources of water contamination in Bathinda. Agrochemical processes in the water-logged agricultural areas with calcareous soils and use of phosphate fertilizers are favoured sources deterioration of ground water quality in Bathinda district. Further, the minimal use of ground water is leading to accumulation of chemicals in the ground water to threatening levels.

Keywords: Ground water contamination, Energy-dispersive X-ray fluorescence, Industrial waste, Coal-fired thermal power plant, Agrochemical processes.

1. Introduction

Punjab state is situated in the north-eastern region of India, covering area of about 50 thousands square kilometers and has a population of around 28 millions. Ropar, Hoshiarpur, Nawanshahr and Gurdaspur districts are mainly covered in sub-Shivalik plain whereas the remaining districts of Punjab are lying in the Sutlej-Ghaggar river plain (Fig. 1). Punjab state is one of the most productive agricultural region, where the agricultural area is cultivated with the help of extensive irrigation using the ground water and the canal water from Beas and Sutlej rivers. Various anthropogenic and natural activities are polluting the terrestrial and aquatic ecosystem with chemicals. The ground water in the region at the boundary between Hoshiarpur and Nawanshahr districts (Fig. 2) is contaminated with soluble selenium oxy-anions [1]. Selenium came into scientific focus in north-east Punjab since the last two decades. Its toxicity to farm animals and considerably reduced yield of agriculture product in the fields irrigated with selenium contaminated water has been mainly reported in the region. Recently, the south-west Punjab region received media attention due to reported high levels of uranium concentrations in the ground water [2]. The studies were mainly uranium specific. Concerns are being raised about the possible carcinogenicity and neurological disorders due to the ingested uranium through drinking water in south-west Punjab. The contemplated sources of ground water contamination are in the form of fly ash from thermal power

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plants in Bathinda and the industrial drain Budha Nullah draining into Sutlej in Ludhiana, existence of Tethys sea at nascent stage of earth, weathering of exposed granite rocks at Tosham hills, pesticides and depleted uranium [2,3]. Our studies mainly deliberate on multi-elemental analysis of samples of ground water collected from the villages at the boundary between Hoshiarpur and Nawanshahr districts [1], and Bathinda district [2] in the south-west Punjab state. Also, water samples from surroundings of the coal-fired thermal power plant in Bathinda city and that of the industrial drain Budha Nullah were analysed to assess their role in ground water contamination in the south-west Punjab. The energy dispersive x-ray fluorescence (EDXRF) technique due to its multielement analytical capability, lower detection limit, capability to analyze metals and non-metals alike and easy sample preparation has been utilized in the present study.

2. Experimental and evaluation procedure

The water samples were collected from (a) villages of Bathinda district and (b) villages at the boundary of Nawanshahr and Hoshiarpur districts, (c) surrounding regions of the Guru Nanak Dev Thermal Power Plant (GNDTPP) in Bathinda city and (d) different locations of industrial waste water drain Budha Nullah draining into Sutlej river near Ludhiana (Figs. 1 and 2). The water samples were filtered using normal filter paper and dried in disposable glass containers at ~70^{o}C in an electric oven. More than 500 ml of each of the water samples was used to obtain at least 200 mg of the residue and pressed into pellets. The elemental analysis of the samples was performed using the EDXRF spectrometer shown in Fig. 3. The exciter source consisted of a 3 kW long-fine-focus Mo-anode X-ray diffraction tube along with a 4 kW X-ray generator procured from PanAnalytic, the Netherlands. An Si(Li) detector (100 mm^2 x 5 mm, 8-μm Be

Fig. 1. Map of Punjab state, India.

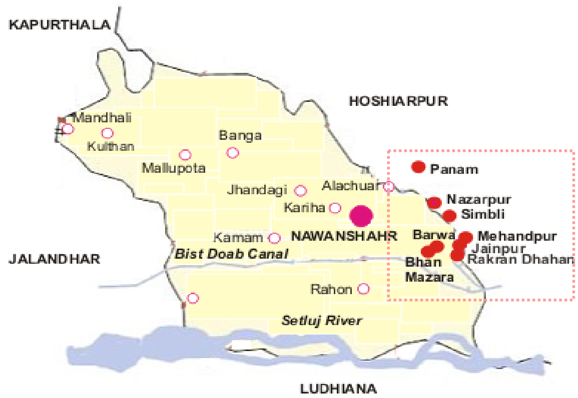

Fig. 2. Se affected region at boundary between Hoshiarpur and Nawanshahr.

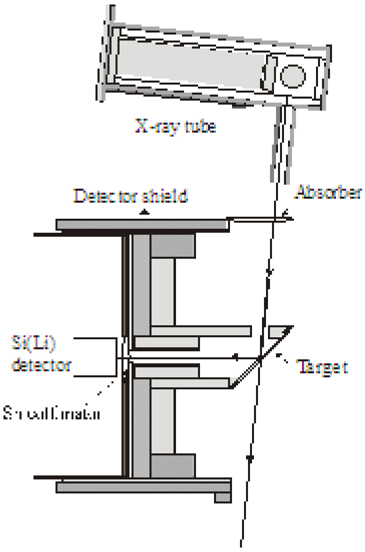

Fig. 3. The EDXRF set up used in the present work.

window, FWHM = 180 eV at Mn $K\alpha$ X rays) in the horizontal configuration coupled with a PC based multichannel analyzer was used to collect the fluorescent X-ray spectra. The spectra were taken using the X-ray tube operating voltages of 28 kV. The incident beam was passed through a combination of selective absorbers consisting of the Ti, Zn and As elements having *K*-shell binding energies (B_K) 4.966, 9.659 and 11.867 keV, respectively, and the K-shell jump ratios ~7. The spectra were taken using the X-ray tube operating voltages of 38 kV and selective absorbers of Zn, Br and Sr. It improved the detection limit in the energy region of the Se-K and U-L X-rays by reducing the background in the spectrum. Typical spectra of residue of water samples collected from different regions are shown in Figs. 4 (a) and (b). The fundamental parameter approach has been used to deduce elemental concentrations in the residue samples from the observed count rate (N_i) for the characteristic X-ray of i*th* element. The procedure is detailed elsewhere [4].

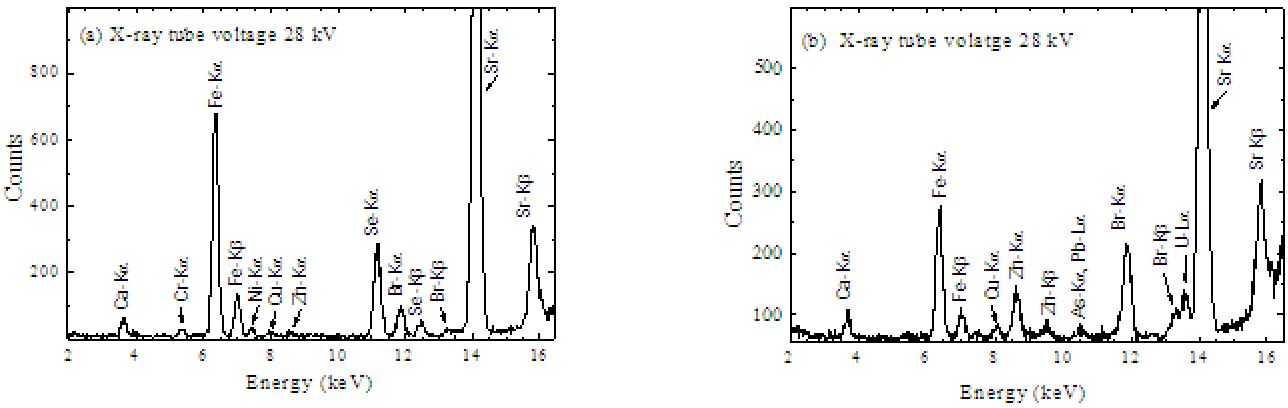

Fig. 4. Typical spectra of the residues of water sample collected from (a) the Nawanshahr-Hoshiarpur boundary region and (b) Bathinda district. Br content in the residue sample from Bathinda is reduced by treating with nitric acid.

3. Results and Discussion

The concentrations of various elements of interest in the samples collected from different locations at the Nawanshahr-Hoshiarpur boundary region, Bathinda district and Budha Nullah (Ludhiana) (Figs. 1 and 2) are given in Tables 1-3, respectively. The overall errors in the measured concentration values for various elements have been estimated to be in the range of 8-15%. The errors are attributed to uncertainties in the photopeak areas, self-absorption corrections, x-ray fluorescence cross sections, incident photon intensity and geometrical factors. The total dissolved salt (TDS) values in the water samples collected from the villages in the Nawanshahr-Hoshiarpur boundary region are in the range ~ 300-400 mg/L (Table 1), which indicates it to be fresh water. The selenium concentrations in the ground water samples from Simbli, Jainpur, Barwa, Mehandpur and Rakran villages by far exceeded the current WHO guideline value of 10 μg/L for drinking water or 20 μg/L for irrigation water [1] and the acceptable Environmental Protection Agency (EPA) limit of 50 μg/L [5]. The Fe concentrations in the ground water are also found to be high with a range of 1.7 – 8.1 mg/L. The present observations are contrary to the earlier reported [1] low concentration of Fe ~ 2 μg/L in the ground water in the region. Interestingly, Zn is observed mainly in the shallow ground water collected from handpumps. The measured Cr concentrations at some places are also found to be above the EPA limit of 100 μg/L. The farmers in the region are aware of the fact that the use of Se-burdened ground water for irrigation leads to contamination of top soil in the agriculture field and decreases the product yield considerably. The crop yield rejuvenates after few cycles of irrigation using the Se-free water. Major part of the selenium is soluble in water and mobile. The concentrations of Br and Sr, and the TDS values in this region are considerably lower than those observed in the ground water of Bathinda (Table 2). The uranium concentration is below the EPA permissible limit of 30 μg/L [5]. Excessive consumption of Se is responsible for selenosis, nail brittleness and neurological abnormalities in humans. It has been recommended by the government that the Se-rich agriculture products from this area should be mixed with the normal ones before supply for human consumption. The selenium affected areas are limited to more than 1000 hectares spread in patches over few villages at the boundary between Hoshiarpur and Nawanshahr districts (Fig. 2). In the Nawanshahr-Hoshiapur region, the soils have largely developed on material laid by the rain water bearing erosion of natural deposits from sub-Shivalik hills. It is likely that the Se in soluble form from the natural deposits was also brought to the region by the flowing rain water. Further, anthropogenic activities mainly related to irrigation of the agriculture land using ground water led to spreading of the element. The deposited soil layer is thick enough that there is no mining history in the region and there is no volcanic eruption activity. The absence of high concentrations of metals like copper does not favour some manmade metallurgical activities in the old times in the region.

Various shallow ground water samples collected from the villages of Bathinda district show high TDS with a maximum value ~ 5 g/L observed in Baluana village. In general, the ground water is brackish and the presence of high levels (above ~1200 mg/L) of TDS in drinking water is generally taste wise objectionable to consumers. The results of water samples from villages that are included in Table 2 are few of the most contaminated samples from the handpumps. In general, high TDS in the ground water in this region is indicative of high concentrations of Br, Sr and U elements. Strontium constitutes ~ 0.1 % of the TDS of the ground water. In a separate study by us, the drinking water schemes based on canal water showed Sr concentrations in the range of 20-200 μg/L and U concentrations below 5 μg/L. The uranium concentration is below ~1 μg/L in case of the water samples collected from the RO based water supply scheme. The U concentrations observed in the ground water are in general above the WHO (World Health Organization) recommended limit of 15 μg/L [2,3] and EPA limit of 30 μg/L [5]. Ingested Sr is not known to have harmful effects. The Mo concentrations observed in the ground water are in general lower than the WHO recommended level of 70 μg/L [3]. The presence of significantly high Br concentration in the ground water samples is a matter of concern in case it is present in the form of bromate anions. These oxy-anions are highly toxic for humans and the WHO maximum permissible limit for bromate (BrO_3^-) anions in the drinking water is 25 μg/L [6]. The bromide anions normally present in water can generate bromate anions during its treatments like chlorination and ozonation, and exposure to UV light [6]. Therefore, the chemical speciation of Br present in the ground water is required and water treatment methods need to be monitored. It is important to mention that the As concentrations in the water samples studied in the present work is below the WHO permissible limit of 10 μg/L [7]. It does not support significantly high concentrations of As reported over whole of the region [7]. It is likely that As is present only at certain localized spots in Punjab.

One of the much talked sources of uranium contamination in the region is the flyash from Guru Nanak Thermal Power Plant (GNTPP) situated in Bathinda city. The observed $_{92}$U concentration values in the water samples collected from the flyash dykes of GNTPP is below the detection limit ~ 2 μg/L. The concentrations of U and Sr in the water samples from the flyash dykes and surroundings of thermal power plant are below those observed at the far off villages (Table 2). Molybdenum concentration in the water collected from the fly ash dykes is significantly high ~ 200 μg/L. However, Mo concentrations in the ground water samples collected from surroundings of GNTPP are below the WHO limit of 70 μg/L [3]. It is concluded that flyash is not the potential source contributing to metal contamination of the ground water. The other potential source of uranium contamination which appeared in print and electronic media is industrial water drain Budha Nullah draining to Sutlej River in Ludhiana district and the river water is further carried through canals to south-west Punjab. It is clear from Table 2 that the Budha Nullah shows discharge of Cr, Fe and Pb, but does not contain significant amounts of U. However, the concentrations of Cr, Fe and Pb are also not that significant that contamination reaches Bathinda through the canal water. Also, the analysis of the canal water shows low TDS and concentrations of toxic elements are below detection limit. The observations favour Budha Nullah is not to be a potential source of the U and other heavy metals contamination in Bathinda. It is likely that the growth of fungus and bacteria has led to processes of bioremediation and phytodegradation of toxic elements in the Budha Nullah water.

South-west Punjab consists of Sutlej-Ghaggar plain, where the soil had largely developed by the material laid by rivers (alluvium) upto a depth of thousands feet. Alluvial deposits have completely shrouded the old land-surface to a depth of thousands of feet. As expected, the region is deprived of any uranium deposits. Tethyan deposits are not observed in geological surveys in the present subsoil system in the south-west Punjab. Sediments which form the aquifer system in south-west Punjab belong to Quaternary period during which alluvium was deposited by rivers draining the area. This rules out the possibility of any Tethyan deposits to be the source of ground water pollution. The uranium content in the soils is ~3 μg/g [8]. Extensive irrigation of rich agricultural area and drinking water supply schemes in the region are mainly based on the available network of canals. Most of the region is water-logged and the soil is calcareous. Solid pieces of calcium carbonate (kankars) are frequently observed in Baluana village (Fig. 5), where maximum uranium concentrations of few hundred microgram/litre, and total dissolved salts (TDS) of 5 gram/litre have been observed. Irrigation water percolating through soil dissolves carbon dioxide gas produced at high pressures from the plant root respiration and the microbial oxidation of the agricultural matter. The resulting carbonic acid reacts with the insoluble calcium carbonate to produce soluble bicarbonate, which is an efficient agent for leaching of uranium from soil [9,10]. Percolating bicarbonate solution adds uranium to the ground water. Phosphate fertilizers (uranium content more than 50 μg/g [9]) used in the cotton cultivation belt further add to the contamination. The concentration of chemicals produced due to decay of agricultural matter in calcareous soil and use of phosphate fertilizers, and dissolved salts in irrigation water are continuously increasing to threatening levels in the ground water due to the minimal use of the ground water. Similar high concentrations of bicarbonates do exist in ground water at many places, but the ground water level is low and there is continuous excessive use of ground water. These features prolong the period before the ground water quality deteriorates. Dr. Jurgens and collaborators from U.S. Geological Survey have reported strong correlations between uranium and bicarbonate in the ground water in Central Valley, California [11], where at least 23 public-supply wells have to be retrieved from service within the last 20 years due to increased concentration of uranium.

Fig. 5. Calcium carbonate kankars in agriculture fields in Baluana village of Bathinda district.

Many health hazards like autism, cerebral palsy, sub normal physical growth of special children of South-west Punjab, and growing incidences of cancer, all are surprisingly blamed on uranium and other metal toxicity in ground water [12]. Carin's group [12] tried DMSA, a known metal-chelating agent for Pb, on the children for removing U without any scientific basis and found it to be ineffective. Some of the commonly used chelators for removal of U are bicarbonate, citric acid, diehylenetriamine pentaacetic acid (DTPA), ethidronate and inositol hexaphosphate (phytic acid) [13]. Simple discontinuing the consumption of contaminated water automatically leads to detoxification [14]. Several studies focusing on health effects have been carried out in Finland among large study population who use their drilled wells as sources of drinking water with broad range of U daily intake, 0.03-2,775 μg/day. These include case-cohort studies of risks of leukemia, stomach, and urinary tract cancers as well as chemical toxicity studies of U intake and renal and bone effects [15]. Nevertheless, none of the studies of human reported so far have shown a clear association between chronic uranium exposure and cancer risk or clinical symptoms of toxicity.

4. Acknowledgements

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Table 1. Concentration for the elements of interest in the water samples collected from villages at the boundary between Hoshiarpur and Nawanshahr districts of Punjab state.

Sample location †	Water residue (mg/L)	Elemental concentration in μg/L												
		Ca††	Cr	Mn	Fe	Co	Cu	Zn	As	Se	Br	Rb	U	Sr
Panam (Distt. Hoshiarpur)														
Davinder Singh - TW	400	127	-	-	1744	-	-	30	-	4	30	4	5	683
Peeran waali Jagah - HP	408	162	-	-	3148	24	-	521	-	-	24	4	8	524
Nazarpur (Distt. Hoshiarpur)														
Kulwinder Singh -TW	295	108	143	-	2043	-		-	-	24	35	4	7	367
Road side-HP	302	125	129	-	1465	55	15	258	-	16	40	5	11	469
Simbli (Distt. Hoshiarpur)														
G.S.S. School - HP	445	192	28	-	4945			534	3	144	39	6	11	261
G.S.S. School - TW1	302	22	427	-	8159	104	50	-	2	85	27	5	11	751
G.S.S. School - TW2	275	14	470	90	5487	51	-	25	-	110	27	3	6	396
Jain pur (Distt. Nawanshahr)														
Jagtar Singh (fields) -TW	412	138			5620	56	-	76		86	22	4	8	626
Jagtar Singh (fields) - HP	405	118	-	-	2797	-	-	-	-	21	41	4		633
Jagtar Singh (home) - HP	388	141	-	-	2473	-	-	31	-		55	7	3	390
Jagtar Singh (home) -TW	302	86	-	-	1668	-	-	148	10	6	19	2	11	125
Barwa (Distt. Nawanshahr)														
Gurmukh Singh-Bolli	398	172	-	-	1469	-	-	-	4	8	42	5	13	416
Saini Jaithere-HP	358	164	-	148	1164			102	-	6	38	6	10	341
Poplar plantation -TW	278	20	534	-	6460	73	52	19	-	175	11	4	4	414
Mehandpur (Distt. Nawanshahr)														
Tarsem Singh - TW	388	7	83	-	2163	-	-	-	-	111	27	4	7	829
Rakran Dhahan (Distt. Nawanshahr)														
Amreek Singh -TW1	412	147	-	-	1970	-	-	-	-	167	49	6	11	901
Amreek Singh - TW2	395	131	-	-	3570	-	-	-	-	84	38	5	14	915
Bhan Mazara (Distt. Nawanshahr)														
Swaran Singh - HP	305	23	478	59	7224	-	49	82	3	18	60	7	4	79

Swaran Singh - TW	375	107	-	-	2134	-	-	-	-	12	50	8	14	476

† HP and TW stand for handpump and tubewell, respectively.

†† Concentration value in mg/L.

Table 2. Concentration for the elements in the water samples collected from various villages in Bathinda district and the surroundings of GNTPP.

Water sample location	Residue (mg/litre)	Elemental concentration in μg/L				
		Fe	Br	Sr	Mo	U
Handpump, Jajjal village†	3467	210	994	1650	27	98
Handpump, Baluana village†	4750	1140	4432	6165	-	212
Handpump, Giana village†	998	140	780	720	40	18
Handpump, Malkana village†	1242	110	1248	970	5	6
Hand pump, Bus stand, Gill Patti village†	3130	<20	1085	2428	27	36
Private Tube well , Gurudwara, Gill Patti village†	1000	<10	198	793	2	22
Hand Pump, Railways crossing, Nehianwala village†	2552	<20	1043	3044	45	78
Bathinda branch canal along Ash dykes of GNTPP††	93	537	3	103	<2	<2
Lake water (GNTPP) ††	289	1425	9	239	23	<3
Ash slurry samples from Ash dykes (GNTPP) ††	324	677	-	281	21	< 2
Ash slurry sample coming out from pipe (GNTPP) ††	350	869	7	341	227	-
Standing water on the Ash dykes (GNTPP) ††	450	537	3	103	1	-
Hand Pump near Ash dykes (GNTPP) ††	602	905	58	1024	9	3
Hand pump opposite GNTPP ††	247	691	16	1210	5	18

† Locations at far off villages from GNTPP.

††Locations surrounding the GNTPP.

Table 3. Concentration for the elements of interest in the water samples collected from Budha Nullah.

Sample location	Water residue (mg/L)	Elemental concentration in μg/L											
		Ca†	Cr	Mn	Fe	Co	Cu	Zn	As	Pb	Rb	U	Sr
Bhamain Kalan	573	126	-	214	3036	-	413	786	3	6	9	2	208
Shamshan Ghat	1033	165	662	-	21888	-	796	1077	7	38	12	12	447
Chand Cinema	1506	232	1534	-	30443	212	908	1075	1	52	18	22	473
Village Wallipur	610	123	421	108	14573	98	524	586	2	21	9	5	171
Upstream river	270	47	202	64	4992	24	168	48	1	4	2	-	36

Downstream river Budha nullah at	237	41	54	99	3381	-	172	36	2	3	1	-	35

† Concentration value in mg/L.