

ORIENTAL JOURNAL OF CHEMISTRY

An International Open Access, Peer Reviewed Research Journal

www.orientjchem.org

ISSN: 0970-020 X CODEN: OJCHEG 2019, Vol. 35, No.(3): Pg. 1045-1053

Wavelength Dispersive XRF Study of Heavy Elements in Soil in Cancer Hit Villages of Malwa region of Punjab, India

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http://dx.doi.org/10.13005/ojc/350317

(Received: May 13, 2019; Accepted: June 01, 2019)

ABSTRACT

Heavy metals in the soil of 13 villages of Bathinda district, Punjab, India, were measured using wavelength dispersion X-ray fluorescence technique (WDXRF). 29 elements for which these samples were analyzed are U, Th , ⁴⁰K, Pb, La, Ba, Cs, Ce,, Sn, Sb, As, Cr, Zn, Cu, Co, Sr, Zr, Sc, V, Ni, Rb, Mo,Ga, Nb, Y, Fe₂O₃, CaO, MnO and TiO₂. Radioactive substances like U and Th are quite low. Alkaline elements like Ca, Ba, Sr are quite high and may be acting as catalysts to low level radioactive elements. As, Fe, Co, Ni, Zr, Cr, Zn too are probably due to proximity of a thermal power plant at Bathinda and use of pesticides and fungicides for plantation.

Keywords: Heavy metals, Soil, Radioactive, Catalysts, WDXRF.

INTRODUCTION

During the last 10-15 years, many reports appeared in the media regarding high radioactivity in the soil and water of Malwa region. Many researchers undertook measurements in water and soil to determine the quantity of uranium, thorium and potassium¹⁻⁴. A good correlation was obtained between uranium concentration in soil and indoor radon in dwellings by Mehra *et al.*,¹. Work on soil samples from Malwa region was also reported by Mehra *et al.*,². Uranium, thorium and K-40 content were found within safety limits. Recently radioactive content in 498 water samples from the region reported by Bajwa *et al.*,³. 338 out of 498 samples had uranium concentration higher than recommended safe limit of 0.03 ppm while 216 samples exceeded the threshold of 0.06 ppm recommended by AERB, DAE, India⁵. Hearing a public interest petition, filed by Brijinder Singh Loomba the Punjab and Haryana High Court Chandigarh assigned the job of measuring radioactivity of Malwa region to BARC, Bombay⁶. The petition was filed after a UKbased clinical toxicologist Carin Smit came out with a startling revelation that traces of uranium and other heavy metals were found in the hair samples

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of children and adults in Faridkot district of Punjab which has no uranium mines. The high concentration of radioactive material was quite baffling for scientists and environmentalists. The BARC report claimed that the high salinity of water in the Malwa region may be acting as a catalyst for uranium toxicity. Otherwise they did not find any higher amounts of uranium or thorium in Malwa region. Still many reports are appearing in the media regarding cases of cancer in the region. In view of all this we have decided to study the metal content in the soils of Talwandi Sabo subdivision of Bathinda District using WDXRF technique to find whether heavy elements or other toxic elements are responsible for any cancer cases.

Soils and sediments have a complex composition and their multi-element chemical composition is of interest in several fields, mostly in geochemical surveys for economical and environmental applications7. Abnormal occurrences of heavy elements in rocks and soils and in monazite sands have been identified in several regions of the world. The most important sources of heavy metals in the environment are the anthropogenic activities such as mining, smelting procedures, steel and iron industry, chemical industry, traffic, agriculture as well as domestic activities⁸⁻¹⁰. The heavy metals from these sources are dispersed in the environment and they contaminate soil, water and air. Directly or indirectly through plants, water and food they get into the human and animal bodies¹¹. The presence of heavy metals in soil can affect the quality of food, groundwater, micro-organism activity and plant growth etc.¹²⁻¹⁴. Evaluation of the threat of accumulation of toxic metals in soils is difficult and depends upon many factors. The availability of these metals to crops can be explained by knowing their distribution in the soil profile and the chemical forms in which they occur. Several metals, such as As, Pb, U, Th, Cd, Cu etc. accumulate in the surface soil horizon due to their low mobility and strong association with organic matter. In this current work the pollutants which found in high amount are Co, CaO, Pb, As, Ni, Y, Rb and Zr. Such elements are generally found in cancerous tissues and responsible for cancer related health issues. The aim of the present study is to find out the concentration of heavy elements in the soils of cancer hit villages of Malwa region of Punjab State.

Geography of selected area

Bathinda district is situated in the northwestern region of India and is a part of the Indo-Gang tic alluvial plains. The exact cartographic co-ordinates of Bathinda are 30.20°N 74.95°E with an average elevation of 660 ft (201 meters). The study area of 13 villages of Talwandi Sabo is 30km from the head quarters of the district towards South East (Fig. 1). Its climate corresponds to high variation between summer and winter temperatures namely 45°C to 15°C. Average annual rainfall of Bathinda is in the range of 20 mm to 40 mm.



Fig. 1. Study area of Bathinda District (Talwandi Sabo)

Soil sample Characteristics

To get the large variations, the soil samples of different soil types were selected. Most of the soils in the study area are dry contain stones and pebbles.

Sample Collection and Methodology

Soil samples were collected from 39 locations from various villages selected with 3 samples from each village on random basis. Each sample was taken from a depth of 70-80 cm at some selected points within the study area. In order to cover a large area and to observe a significant local spatial variation in terrestrial radioactivity, sampling points were at a minimum distance of 2 km from each other. In order to get uniform and representative samples they were dried, sieved to remove stones, pebbles grass roots and straws and then crushed to pass through a 150 micron mesh sieve to homogenize the contents. Then they were packed in plastic bags, which were well sealed. The weight of the soil sample in each bag was kept constant on 20 g. All the 39 samples were analyzed to detect the elements of interest using wavelength dispersion X-ray florescence in SAIF, Panjab University Chandigarh. A diagram of a WD system is shown in Figure 2.



Fig. 2. Schematic diagram of a wavelength-dispersive X-ray spectrometer

This instrument operates according to the principle of Bragg diffraction of a collimated X-ray beam. A detector is angularly scanned relative to the analyzing crystal and registers the spectrum. A great advantage of XRF techniques compared to wet chemical procedures is that the multi-elemental analysis can be directly carried out on solid samples. This avoids the tedious and laborious wet digestion steps and the possible analyte losses and sample contamination as well as a considerable decrease in analysis time. The higher detection limits compared to spectroscopic techniques the precision and accuracy obtained educing XRF methods are good enough for various environmental studies purposes¹⁵. Additionally, it relates to non-destructive analytical techniques, i.e. the techniques which do not damage the samples under study. It enables us for the simultaneous determination of about 40 elements that makes it one of the most universal and appropriate analytic technique. Major and many trace elements can be determined with very good precision and accuracy⁷. In the present study WD-XRF (wavelength dispersive X-ray fluorescence) Model: S8 TIGER, made of Bruker, Germany, has been used for the soil sample analysis. Soil sample and binder were grinded together to make homogenized fine powder so that particle size became less than 50 µm. Sample quantity was taken as 9 g. The binder tablet amount was 2.7 g, which made the total weight equal to 11.7 g. A pellet was made of 10 g of total sample (11.7g) using hydraulic press at pressure of 15 tons. The soil sample pellet with diameter 34mm and thickness 4mm was ready for analyses. Each pellet of different soil sample was processed and analyzed for approximately 37 min and a variable range of 29 elements were detected with different concentration levels as shown in Table 1(a,b).

RESULTS AND DISCUSSION

Table 1(a,b) shows the concentration of 29 elements detected in 39 soil samples that were collected from 13 villages of Talwandi Sabo of Bathinda District. From each village 3 samples were collected. Samples 1,2,3 were from Natt village. Similarly, (4,5,6 (Burj Sema)), (7,8,9 (Chatewala)), (10,11,12 (Kaureana)), (13,14,15 (Mirjeana)), (16,17,18 (Manuana)), (19,20,21 (Gehlewala)), (22, 23, 24 (MaurChart)), (25, 26, 27 (Burj)), (28, 29, 30 (Shekhpura)), (31, 32, 33, (Jogewala)), (34, 35, 36 (Gatwali)), (37, 38, 39 (Ram Nagar)) as shown in Table 1(a,b). Table 2 summarizes their maximum and minimum values. Radioactive elements like U Th and ⁴⁰K have 2-6, 11-18, and 40-785 ppm ranges respectively. Some major elements were also detected like CaO, Fe₂O₃, TiO₂, MnO are having limits 9773-132462, 24300-56700, 4100-7300 and 400-800 ppm respectively. Among the major elements CaO has maximum variation than others. Heavy metals like Pb, Cs, Ce, Ba, Sn, Sb and La are found in variable ranges 25-32, 0-13, 78-116, 349-542, 0-7, 0-6 and 17-41ppm respectively. Toxic elements like As, Cu, Cr, Co, Ni were found in variable ranges 33-64, 11-30, 71-154, 72-291 and 25-95 ppm respectively. Other elements Zn, Sr, Zr, Sc, V, Rb, Ga Nb, Y and Mo were also found in different concentration of 38-310, 125-408, 222-363, 4-14, 41-85, 97-264, 13-22, 10-18, 26-37 and 0-2 ppm respectively.

Although Uranium and Thorium in the measured soil samples were quite low to cause any damage yet elements like CaO, Co, Zr, Rb are found in higher amounts. CaO, Co, Zr were noted much higher than their permissible values (Table 3) in all the villages (except one location of Kaurena village having CaO concentration of 9773 ppm).74% of villages have high value of Rb (Table 3). Among these the elements that cause alkalinity such as Ca, Rb are quite high. These may be due to coal fired TPP (Tharmal Power Plant) at Bathinda which is not very far off from the invested area. When coal or lignite rich in limestone, produce ash having calcium oxide, it (Lime stone (CaO)) easily diffuses in water bodies and make calcium hydroxide Ca(OH)₂ and transformed through rain water to canals or agriculture water systems and ultimately reach into the soils¹⁶. In India, the ash content in the coal utilized in power production is about 30 to 40%, which is rather more than the other developed nations. Higher values of coal fly ash resulting in high damage to the plants as well as machines. All the heavy elements commonly found in the coal fly ash are poisonous in nature¹⁷.

Contaminated locations of metalbearing solids can originate from a wide variety of anthropogenic sources in the form of pesticides, coal combustion residues, metal mine tailings, land application of fertilizer, disposal of high metal wastes in improperly protected landfills, animal manures, sewage sludge, leaded gasoline, lead based paints, compost petrochemicals, and atmospheric deposition¹⁸⁻²⁰. Among these use of fertilizers, pesticides and weedicides are most common in the agriculture.

Table 1(a): Measured values (in ppm) of 16 elements in soil samples of 13 villages Bathinda District using WDXRF

Sample No.	U	Th	К	CaO	As	Pb	Cr	Cu	Cs	Co	Zn	Sr	Ce	Zr	Sc	V
1	3	15	72.5	17818	33	28	121	21	9	76	63	143	88	290	13	82
2	3	15	235	12412	33	27	116	24	13	81	62	146	93	275	14	82
3	4	16	185	12683	40	27	81	21	9	122	64	136	99	292	9	80
4	3	12	90	14558	37	25	124	16	8	108	44	132	87	280	7	58
5	4	15	123	10985	36	28	117	23	9	72	62	155	93	263	11	82
6	2	15	268	24698	36	26	137	24	10	158	63	156	91	292	11	79
7	5	15	180	39515	48	26	124	19	10	206	59	151	105	285	10	72
8	4	14	130	65290	37	25	71	23	11	114	56	183	88	272	11	75
9	3	15	120	24952	41	27	142	18	7	174	53	142	105	300	11	74
10	3	15	123	9773	58	27	119	19	9	249	57	140	116	306	8	67
11	4	16	133	23745	54	27	101	20	6	258	51	195	111	334	5	59
12	4	13	68	132462	46	26	109	20	4	248	47	264	96	268	7	66
13	4	17	130	16924	52	31	106	22	12	233	68	170	111	321	8	72
14	6	14	83	51988	44	25	129	23	8	195	60	198	105	282	11	79
15	3	15	188	14458	52	28	104	18	4	268	57	144	97	300	5	63
16	4	12	85	91888	43	25	99	17	9	194	44	408	96	280	8	60
17	5	18	170	10323	45	32	124	30	8	213	76	153	110	310	11	85
18	2	11	173	16553	57	25	83	11	2	267	38	125	105	276	4	41
19	4	16	68	12493	53	28	114	20	3	242	62	138	113	304	9	77
20	4	16	85	39160	39	27	79	20	8	119	56	164	99	287	10	79
21	3	17	58	19385	41	27	139	23	8	167	59	146	106	318	12	79
22	3	13	40	63789	43	26	139	22	8	193	53	172	98	253	8	76
23	4	16	110	17266	53	29	106	17	8	260	55	185	97	308	7	65
24	4	15	600	101429	48	28	89	24	5	182	55	361	99	238	5	69
25	3	14	63	36366	38	26	154	20	10	147	58	158	90	269	11	79
26	2	13	103	117365	44	25	115	18	1	273	51	238	91	245	9	79
27	2	14	490	16143	54	23	117	15	_	276	39	146	108	314	7	52
28	4	14	50	58223	38	27	79	21	9	119	56	223	89	270	11	79
29	2	15	213	20130	44	26	74	19	4	151	52	164	103	316	9	67
30	3	15	238	42149	50	27	112	27	9	211	66	225	110	270	9	77
31	5	16	245	56111	48	30	109	25	4	224	57	205	103	306	11	75
32	3	18	785	14822	58	30	99	20	4	291	52	151	113	368	8	61
33	2	13	120	59118	50	24	118	18	9	235	47	231	108	286	7	62
34	2	12	428	127048	34	26	135	22	6	109	49	217	78	222	7	73
35	3	11	143	37860	56	26	80	12	3	291	47	218	91	268	5	51
36	4	13	343	94903	43	26	104	19	7	204	45	228	85	285	9	64
37	4	16	255	23361	64	29	88	20	11	222	310	155	115	310	8	75
38	3	15	130	25110	36	25	125	17	10	84	55	142	90	299	10	74
39	4	16	70	12570	34	27	119	20	9	78	61	137	93	289	11	79

$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Sample No.	Ni	Fe ₂ O ₃	Ва	Rb	Sn	Sb	Мо	TiO ₂	MnO	Ga	Nb	La	Y
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	1	46	47000	505	128	2	ND	ND	6900	800	17	15	33	33
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2	48	47800	520	131	4	4	1	6800	800	18	15	29	32
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3	47	46500	489	131	3	4	1	6700	700	17	15	26	33
548468005071304226700800171423316454560049212731167007001715323374340600437116131670060016142629840402004321142325800600151333319384070045911611ND61007001614293210434160048512811161007001614293211343510044511722ND560060014122528134745600483138741630070017153533163533700399105ND2ND4600500141229291758567005421562117300800221830332046435004881231ND16900800171432312146459004861231ND1690080017143233153	4	36	32900	437	107	1	1	ND	5400	500	14	13	24	28
6454560049212731167007001715323374340600437116131610060016142629840402004321142325800600151333319384070045911611ND61007001614293210434160048512811161007001714293211343510044511722ND5600600161341321239357003392641ND1480060014122528134745600483138741630070017153533153941200476133ND115700600181524331635337003919732ND410040013102526194846100482125ND3ND68008001714333120464350045812013ND68008001714333030 <td< td=""><td>5</td><td>48</td><td>46800</td><td>507</td><td>130</td><td>4</td><td>2</td><td>2</td><td>6700</td><td>800</td><td>17</td><td>14</td><td>23</td><td>31</td></td<>	5	48	46800	507	130	4	2	2	6700	800	17	14	23	31
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	6	45	45600	492	127	3	1	1	6700	700	17	15	32	33
840402004321142325800600151333319384070045911611ND61007001614333210434160048512811161007001714293211343510044511722ND6600161341321239357003392641ND1480060014122528134745600483138741630070019153134144845100462120NDND146007001715353315394120476133ND11570060018152433163533700399105ND2ND4800500141229291758567005421562117300800221830371825243003919732ND410040013102526194846100482125ND3ND6100600171432312146	7	43	40600	437	116	1	3	1	6100	600	16	14	26	29
9384070045911611ND61007001614333210434160048512811161007001714293211343510044511722ND5600600161341321239357003392641ND1480060014122528134745600483138741630070017153533153941200476133ND11570060018152433163533700399105ND2ND4800500141229291758567005421562117300800221830371825243003919732ND410040013102526194846100482125ND3ND6100600171432312146435004861231NDND580070018153233224541300433110NDNDND5800700161330302	8	40	40200	432	114	2	3	2	5800	600	15	13	33	31
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	9	38	40700	459	116	1	1	ND	6100	700	16	14	33	32
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	10	43	41600	485	128	1	1	1	6100	700	17	14	29	32
1239357003392641ND1480060014122528134745600483138741630070019153134144845100462120NDND1640070017153533153941200476133ND11570060018152433163533700399105ND2ND4800500141229291758567005421562117300800221830371825243003919732ND410040013102526194846100482125ND3ND61006001714323120464350045812013ND6100600171432332146459004861231NDND580070018152831244040200420122ND21520060017143331244040200420122ND152008001512242727 <td< td=""><td>11</td><td>34</td><td>35100</td><td>445</td><td>117</td><td>2</td><td>2</td><td>ND</td><td>5600</td><td>600</td><td>16</td><td>13</td><td>41</td><td>32</td></td<>	11	34	35100	445	117	2	2	ND	5600	600	16	13	41	32
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	12	39	35700	339	264	1	ND	1	4800	600	14	12	25	28
144845100462120NDND1640070017153533153941200476133ND11570060018152433163533700399105ND2ND4800500141229291758567005421562117300800221830371825243003919732ND410040013102526194846100482125ND3ND68008001815303320464350045812013ND6100600171432312146459004861231ND16900800161330302341412004591281NDND580070018152831244040200420122ND21520060017143331264039900389103NDND1620070017143331264039900451116451620070017142830 <td< td=""><td>13</td><td>47</td><td>45600</td><td>483</td><td>138</td><td>7</td><td>4</td><td>1</td><td>6300</td><td>700</td><td>19</td><td>15</td><td>31</td><td>34</td></td<>	13	47	45600	483	138	7	4	1	6300	700	19	15	31	34
153941200476133ND11570060018152433163533700399105ND2ND4800500141229291758567005421562117300800221830371825243003919732ND410040013102526194846100482125ND3ND68008001815303320464350045812013ND6100600171432312146459004861231NDND5900600161330302341412004591281NDND580070018152831244040200420122ND215200600171422302341412004591281NDND580070018152831244040200420122ND21520060017143331264039900389103NDND1520080015122427<	14	48	45100	462	120	ND	ND	1	6400	700	17	15	35	33
163533700399105ND2ND4800500141229291758567005421562117300800221830371825243003919732ND410040013102526194846100482125ND3ND68008001815303320464350045812013ND6100600171432312146459004861231ND1690080017153233224541300433110NDNDND5900600161330302341412004591281NDND580070018152831244040200420122ND215200600171423312544441004741201ND1640070017143331264039900389103NDND15200800151224272730292004069922ND530050014132628 <t< td=""><td>15</td><td>39</td><td>41200</td><td>476</td><td>133</td><td>ND</td><td>1</td><td>1</td><td>5700</td><td>600</td><td>18</td><td>15</td><td>24</td><td>33</td></t<>	15	39	41200	476	133	ND	1	1	5700	600	18	15	24	33
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	16	35	33700	399	105	ND	2	ND	4800	500	14	12	29	29
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	17	58	56700	542	156	2	1	1	7300	800	22	18	30	37
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	18	25	24300	391	97	3	2	ND	4100	400	13	10	25	26
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	19	48	46100	482	125	ND	3	ND	6800	800	18	15	30	33
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	20	46	43500	458	120	1	3	ND	6100	600	17	14	32	31
22 45 41300 433 110 ND ND ND 5900 600 16 13 30 30 23 41 41200 459 128 1 ND ND 5800 700 18 15 28 31 24 40 40200 420 122 ND 2 1 5200 600 17 14 22 30 25 44 44100 474 120 1 ND 1 6400 700 17 14 33 31 26 40 39900 389 103 ND ND 1 5200 800 15 12 24 27 27 30 29200 406 99 2 2 ND 5300 500 14 13 26 28 28 46 43100 451 116 4 5 1 6200 700 17 14 28 30 29 37 38000 441 <t< td=""><td>21</td><td>46</td><td>45900</td><td>486</td><td>123</td><td>1</td><td>ND</td><td>1</td><td>6900</td><td>800</td><td>17</td><td>15</td><td>32</td><td>33</td></t<>	21	46	45900	486	123	1	ND	1	6900	800	17	15	32	33
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25 44 44100 474 120 1 ND 1 6400 700 17 14 33 31 26 40 39900 389 103 ND ND 1 5200 800 15 12 24 27 27 30 29200 406 99 2 2 ND 5300 500 14 13 26 28 28 46 43100 451 116 4 5 1 6200 700 17 14 28 30 29 37 38000 441 108 2 6 1 6100 600 17 14 33 31 30 45 44800 462 126 3 1 1 6200 700 18 13 29 30 31 45 44900 432 122 1 3 ND 6000 700 17 14 31 33 31 45 44900 432 122	24	40	40200	420	122	ND	2	1	5200	600	17	14	22	30
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27 30 29200 406 99 2 2 ND 5300 500 14 13 26 28 28 46 43100 451 116 4 5 1 6200 700 17 14 28 30 29 37 38000 441 108 2 6 1 6100 600 17 14 33 31 30 45 44800 462 126 3 1 1 6200 700 18 13 29 30 31 45 44900 432 122 1 3 ND 6000 700 17 14 31 33	26	40	39900	389	103	ND	ND	1	5200	800	15	12	24	27
28 46 43100 451 116 4 5 1 6200 700 17 14 28 30 29 37 38000 441 108 2 6 1 6100 600 17 14 33 31 30 45 44800 462 126 3 1 1 6200 700 18 13 29 30 31 45 44900 432 122 1 3 ND 6000 700 17 14 31 33	27	30	29200	406	99	2	2	ND	5300	500	14	13	26	28
29 37 38000 441 108 2 6 1 6100 600 17 14 33 31 30 45 44800 462 126 3 1 1 6200 700 18 13 29 30 31 45 44900 432 122 1 3 ND 6000 700 17 14 31 33 30 45 44900 432 122 1 3 ND 6000 700 17 14 31 33	28	46	43100	451	116	4	5	1	6200	700	17	14	28	30
30 45 44800 462 126 3 1 1 6200 700 18 13 29 30 31 45 44900 432 122 1 3 ND 6000 700 17 14 31 33 45 44900 432 122 1 3 ND 6000 700 17 14 31 33	29	37	38000	441	108	2	6	1	6100	600	17	14	33	31
31 45 44900 432 122 1 3 ND 6000 700 17 14 31 33	30	45	44800	462	126	3	1	1	6200	700	18	13	29	30
	31	45	44900	432	122	1	3	ND	6000	700	17	14	31	33
32 40 38400 439 124 1 4 ND 5700 600 16 15 31 33	32	40	38400	439	124	1	4	ND	5700	600	16	15	31	33
33 35 34200 426 104 1 1 ND 5200 600 14 13 34 29	33	35	34200	426	104	1	1	ND	5200	600	14	13	34	29
34 37 37900 382 106 ND ND 1 5100 800 15 12 31 26	34	37	37900	382	106	ND	ND	1	5100	800	15	12	31	26
35 29 29300 393 106 2 3 ND 4600 500 14 12 17 28	35	29	29300	393	106	2	3	ND	4600	500	14	12	17	28
36 38 34000 359 104 ND 2 ND 4000 600 14 12 26 20	36	28	3/000	350	104		2	ND	1000	600	1/	12	26	30
20 30 37500 305 104 IND 2 IND 4500 000 14 12 20 30	30	05	46700	407	104		~		4300	700	14	16	20	00
37 35 46700 487 127 3 4 1 6700 700 17 15 33 33	37	95	46700	487	127	3	4	1	6200	700	17	15	33	33
30 41 41300 400 110 3 3 1 0300 700 13 13 26 32 30 47 4570 497 135 2 3 ND 6900 900 17 15 27 29	30	41	41300	400	10	3	3		6800	200	17	15	20 27	3∠ 22

Table 1(b): Measured values (in ppm) of 13 elements in soil samples of 13 villages Bathinda District using WDXRF (ND-Not Detected)

Table 2: Minimum and maximum limits (in ppm) of 29 elements detected in 13 villages of Bathinda District

U		Th	ı	к		C	aO	A	S	Pb)	
Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
2	6	11	18	40	785	9773	132462	33	64	25	32	
C	Cr	C	u	С	S	C	ю	Z	า	Sr		
Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
71	154	11	30	0	13	72	291	38	310	125	408	
Ce		Z	r	S	С		V	Ν	li	Fe ² O ₃		
Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
78	116	222	363	4	14	41	85	25	95	24300	56700	
E	Ba	R	b	Sn		5	Sb	Μ	0	Ti	TiO ₂	
Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	
359	542	97	264	0	7	0	6	0	2	4100	7300	
M	nO	G	ia	N	lb	l	_a		Y			
Min	Max	Min	Max	Min	Max	Min	Max	Min	Max			
400	800	13	22	10	18	17	41	26	37			

Fertilizers

For healthy plant growth not only macronutrients, but also some micronutrients (such as Co, Cu, Fe, Mn, Ni, and Zn) are also required in limited amounts. But if the range of theses essential heavy elements crossed the safety limits, then the soil becomes polluted. Large quantities of fertilizers are regularly added to soils in intensive farming systems to provide adequate N, P, and K for crop growth. In the study area generally Urea containing N, Di-ammonium Phosphate (containing N, P), Zinc phosphate (containing Z, P) etc. are used. The compounds used to supply these elements contain trace amounts of heavy metals (e.g., Cd and Pb) as impurities, which after continued fertilizer, application may significantly increase their content in the soil²¹. These toxic elements not only affect the grown plants and crops, but also get transferred to human bodies through food items. In the present study it has been found that micronutrients like Zn in Manuana and Ram Nagar, Co, Ni in all villages and macro nutrient K are quite high in amounts in Maur Chart, Burj, Joge Wala and Gatwali villages, as compared to the permissible values.

Pesticides and weedicides

The chemicals used as insecticides and fungicides are based on compounds which contain Cu, Hg, Mn, Pb, or Zn. Examples of such pesticides are copper-containing fungicidal sprays such as Bordeaux mixture (copper sulphate) and copper oxychloride²². Formulations of Cu, Cr, and As (CCA) derelict sites where soil concentrations of these elements greatly exceed background concentrations. Compared with fertilizers, the usage of these substances is more localized, being restrained to particular locations and plantation²³. In the current work, Zn in Manuana and Ram Nagar, Cu in Gehlawal and Shekhpura and Pb in all villages are far more than their permissible values (Table 3) showing that pesticides and weedicides may influence the quality of soils.

Radio nuclides

Environmental radio nuclides with varying fractions can enter the atmosphere in the form of aerosols or fine dust particles that may be deposited directly on growing vegetation or be inhaled directly by humans and other animals. The human body absorbs these radio nuclides by two routes: inhalation and through food and water. The heavy (or transition) metal elements make up a large part of the periodic table and include some of the most toxic agents known, like mercury and cadmium). In the present case, radio nuclides like U and Th were much below the safety limits as shown in the Table 3. K-40 is quite high in one of the locations in Maur Chart, Burj Jage Wala and Gatwali villages, but overall it is below the permissible values. It shows that radio nuclides are not causing much effect in this region.

Correlation

The Pearson Correlation Program is used to find correlations among the elements found in soil analysis (Table 4). A significant positive correlation has been found for Th-Nb, Th-TiO₂, As-Co, Zn-Ni, Ce-Zr, Zr-La, V-Fe, V-Ba, V-TiO₂, Fe-Ba, Fe-Nb, Ba-Nb, Nb-Y, showing that the presence of one parameter may increase the concentration of the other. Similarly, some negative correlations have been found for K-Cu, K-Cs, As-Cr, Pb-Sc, Cr-Cu, Cs-Co, Zn-Sr, Zr-Mo, V-Rb, Ni-Mo, Ba-MnO, Sn-MnO as shown in Correlation Table 4. These indicate that if one of the element in a given pair is elevated the amount of other decreases.

 Table 3: Permissible values in ppm for some elements found in the study area as below

Element	Permissible values (ppm)	Reference
U (226Ra)	35	[24]
Th	40	[24]
К	400	[24]
CaO	14400	[25]
As	20	[26]
Pb	20	[27]
Cr	35	[27]
Cu	25	[27]
Co	10	[27]
Zn	71	[27]
Sr	350	[27]
Zr	190	[27]
V	60	[27]
Ni	20	[27]
Fe ₂ O ₃	57700	[25]
Ba	550	[27]
Rb	112	[27]
Мо	1.5	[27]
TiO ₂	8800	[25]
MnO	1000	[25]
Y	22	[27]

1	1																												- 1
~																												-	0.617
<u>a</u>																											-	0.417	0.912
qN																										-	0.799	0.36	0.753
Са																									-	-0.096	-0.257	0.317	-0.126
MnO																								-	-0.262	0.491	0.786	0.445	0.631
TiO2																							-	0.085	-0.179	-0.159	-0.141	-0.201	-0.334
Mo																						-	-0.252	0.366	-0.147	0.348	0.433	0.359	0.394
Sb																					-	0.651	0.135	0.32	-0.519	0.427	0.477	0.078	0.422
Sn																				-	0.143	-0.105	-0.19	0.227	-0.055	0.221	0.147	0.483	0.38
Вb																			-	0.186	0.671	0.467	0.008	0.748	-0.521	0.758	0.913	0.297	0.807
Ва																		-	0.944	0.092	0.558	0.534	-0.037	0.832	-0.345	0.802	0.949	0.339	0.798
Fe ₂ O ₃																	-	0.774	0.727	0.104	0.517	0.441	-0.113	0.771	-0.117	0.47	0.787	0.225	0.658
īz																-	0.653	0.908	0.1805	-0.059	0.482	0.54	0.171	0.858	-0.398	0.591	0.758	0.233	0.521
>															-	0.847	0.451	0.711	0.691	-0.204	0.526	0.673	0.217	0.65	-0.457	0.305	0.556	0.289	0.392
Se														-	0.178	0.096	0.341	0.314	0.359	0.435	0.15	0.278	-0.273	0.406	0.191	0.309	0.492	0.875	0.723
Zr													-	0.838	-0.106	-0.082	0.127	0.153	0.165	0.478	-0.115	0.018	-0.261	0.199	0.49	0.4	0.318	0.849	0.552
Ce												-	0.05	-0.331	-0.807	-0.774	-0.599	-0.704	-0.72	-0.084	-0.498	-0.362	-0.272	-0.776	0.49	-0.247	-0.637	-0.303	-0.544
s											-	-0.442	0.035	0.247	0.259	0.395	0.922	0.489	0.445	0.046	0.433	0.349	-0.086	0.555	0.048	0.16	0.524	0.105	0.424
Zn										-	-0.433	0.65	0.505	0.222	-0.758	-0.767	-0.563	-0.646	-0.655	0.156	-0.645	-0.568	-0.043	-0.541	0.684	-0.239	-0.458	0.193	-0.224
Сe									-	-0.806	0.566	-0.68	-0.195	0.042	0.652	0.709	0.677	0.745	0.767	0.123	0.708	0.494	0.011	567	-0.535	0.406	0.671	0.075	0.533
Cu								-	0.4	-0.35	-0.092	-0.215	0.296	0.321	0.405	0.536	0.223	0.648	0.634	0.218	0.427	0.516	-0.325	0.421	-0.358	0.768	0.625	0.407	0.6
స							-	-0.195	-0.299	-0.091	0.044	0.14	-0.218	a-0.166	-0.102	-0.099	0.016	-0.199	-0.115	-0.021	-0.132	-0.138	0.111	0.1	-0.262	-0.319	-0.238	-0.32	-0.361
Pb						-	-0.195	0.62	0.144	0.078	0.141	0.089	0.501	0.517	-0.096	0.076	0.32	0.423	0.407	0.285	0.101	0.269	-0.748	0.185	0.05	0.634	0.597	0.371	0.735
As					-	0.309	-0.097	-0.222	-0.637	0.908	-0.103	0.589	0.683	0.434	-0.735	-0.665	-0.237	-0.462	-0.494	0.313	-0.497	-0.376	-0.273	-0.34	0.77	-0.087	-0.24	0.376	0.014
CaO				-	0.447	-0.362	0.098	-0.577	-0.708	0.606	-0.441	0.764	-0.238	-0.49	-0.702	-0.716	-0.693	-0.86	-0.965	-0.18	-0.689	-0.462	-0.015	-0.703	0.526	-0.649	-0.857	-0.366	-0.803
×			-	0.527	0.227	0.029	0.241	-0.184	-0.402	0.313	-0.215	0.448	-0.246	-0.146	-0.299	-0.428	-0.366	-0.476	-0.54	-0.468	-0.36	-0.024	-0.112	-0.39	0.116	-0.487	-0.361	-0.269	-0.404
片	, I		-0.315	-0.688	0.093	0.589	-0.163	0.612	0.379	-0.161	0.4	-0.511	0.675	0.762	0.452	0.611	0.64	0.767	0.696	0.332	0.202	0.384	-0.232	0.805	0.041	0.674	0.847	0.778	0.86
⊃	0	0.4/0	-0.407	-0.274	0.295	0.661	-0.659	0.29	0.331	0.088	0.32	-0.079	0.496	0.409	-0.09	0.068	0.313	0.349	0.312	0.418	0.004	0.029	-0.601	0.134	0.253	0.48	0.477	0.428	0.674
	⊐≓	= :	¥	CaO	Aa	Pb	ΰ	Cu	ບັ	ů	Zn	S	Ce	Zr	Se	>	ïz	Fe_2O_3	Ва	Rb	Sn	Sb	Мо	TiO ₂	MnO	Ga	qN	La	≻

Table 4: Correlation Matrix of 29 elements using Pearson Correlation Program

CONCLUSION

- Elements U, Th, Sr, Cr, Mo, TiO₂ and MnO are having a lower concentration than permissible values (Table 3).
- Elements like Cu, Ba and Fe are having normal concentration found in such soils.
- Elements such as K-40 in one of the locations in Maur Chart, Burj Joge Wala and Gatwali villages and Zn in Manuana and Ram Nagar are higher in concentrations, but in rest of villages it is below the permissible values (Table 3).
- Co, Cao, Pb, As, Ni and Y are unusually higher in amounts and might be responsible for routine cancer diseases.
- Alkaline elements such as Ca, Rb and Zr are very high, particularly Calcium which has been found in higher content in cancerous tissue usually.
- The basic sources of pollutants (Co, CaO, Pb, As, Ni, Y, Rb and Zr) which are found in extra amount than their permissible limits (Table 3) for this region are may be the coal fired TPP (Tharmal Power Plant) at Bathinda (nearby the
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studied area) and pesticides, weedicides and fungicides used for agricultural purposes.

To sum up radioactive elements like uranium, thorium and potassium (K-40) are low in content to cause any cancers. Excess of alkalinity causing elements, may be acting as a catalyst for such radioactive elements to be harmful⁶. Hence excess of alkalinity might be the main reason for tumor growth and cancer scare.

ACKNOWLEDGMENT

The authors are thankful to the chairman of SBBSIET, Khiala, Jalandhar for providing facilities and encouragement. Ms. Kirandeep Kaur is especially in debt to RIC, IKG PTU, Kapurthala for registration for Ph. D.

Conflict of interest

There is no conflict of interest because this work is drawn from original thesis of corresponding author submitted and accepted under UGC guidelines to Punjab Technical University, Kapurthala.

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