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RESEARCH ARTICLE

Heavy Metal Analysis in soil samples of Some Villages Near Uranium Corporation of India Limited Thummalapalle using Wavelength-Dispersive X-ray Fluorescence Spectrometry.

***P. Mamatha [1], K. Aruna[1], T. Mohammad Munawar[1] and A. V. N. Swamy[2].**

1. JNTUACEP, Department of Biotechnology, Pulivendula-516390, Andhra Pradesh, India.
2. JNTUA, Department of Chemical Engineering, Anantapur-515002, Andhra Pradesh, India.

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Corresponding Author

P. Mamatha.

Abstract

The aim of the present study focuses on identify of heavy metal distribution in soils collected from the surrounding areas of Uranium Corporation of India, UCIL, Thummalapalle, Pulivendula, Andhra Pradesh. Soil samples were collected from a depth of 0-30 cm and were analyzed for trace metals such as Ba, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr, V,Y, Zn , Zr and major oxides such as SiO_2, AlO_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, TiO_2 and P_2O_5 by using Philips PW 2440 X-ray fluorescence spectrometer (XRF). Among the 14 heavy metals detected in the soils of the study area, only Ni, Sr, Zn, Zr and Rb are within the permissible limits. The increased levels of Ba, As, Co, Cr, Cu, Mo, Pb. V and Y in the study area are a major concern for the suitability in agricultural and other land management practices. However, systematic and continuous monitoring of the study area for the increased levels of heavy metals are necessary, these elements may enter the food chain and may be hazardous to human health.

Introduction:-

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 activities [1]. Chemical and metallurgical industries are the most important sources of heavy metals in soils [2, 3, 4]. The presence of heavy metals in soil may affect the quality of food, ground water, micro-organisms activity and plant growth [5]. The attraction of non-destructive methods and the ability to do simultaneous multi-elemental determinations has led to an extensive application in industrial and research laboratories of accurate, precise, sensitive atomic and nuclear analytical techniques for the investigation of different types of materials (industrial, geological, archaeological, biological, environmental etc), such as neutron activation analysis (NAA) [1] and X-ray fluorescence (XRF) [3]. For the analysis of environmental samples XRF has the advantage of being a rapid and inexpensive method with a simple sample preparation. Quantitative and qualitative analyses are done without acid digestion processes and many elements will be determined simultaneously in a short time. Ali et al. studied on a geochemical survey of heavy metals in agriculture and background soils of the Isfahan industrial Zone, Iran. To investigate the soil pollution, a total of 105 agriculture soil samples were taken [6]. Yu et al. investigated on the soils associated with different rock types and the concentration of 19 chemical elements (Na, Al, Si, Ti, V, Cr, Mn, Fe, Co, K, Ca, Ni, Cu, Zn, Pb, Rb, Sr, Y and Zr) has been determined using energy dispersive X-ray fluorescence [7]. Baranowski studied on the direct analysis of elements in soil samples by XRF [8]. Vandana et al. investigated on the assessment of heavy metal contamination in soil around hazardous waste disposal sites in Hyderabad city, India [9]. Determination of high Zn and Pb concentrations in polluted soils using energy dispersive X-ray Fluorescence spectrometry [10]. Determination of Cr, Zn, As and Pb in soil by X-ray fluorescence spectrometry based on a partial least Square Regression Model [11]. Ahamad and Goni, Karanhk et al. and Wu et al. have reported the influence of heavy metal contamination in soils of different regions. [12, 13, 14].

The main goal of the present research was to use the XRF technique in order to assess the heavy metals distribution in some areas near the uranium mining site, Thummalapalle, Pulivendula, Andhra Pradesh, India. Hence, assessment of heavy metal contamination in the soils of uranium mining site, Thummalapalle will play a vital role in the sustainable management of groundwater resources in that area.

Study area:-

The uranium mining site, Thummalapalle, has an area of 5 km2. This area contains uranium ore deposits associated with sedimentary formations and uranium mining has been undertaken by UCIL (Uranium Corporation of India Limited), Department of Atomic Energy (DAE), India. The study area is located in semi-arid climate zone. Average annual rainfall in the area is 600 mm while maximum precipitation occurs during July - November with the onset of southwest monsoon. The temperature ranges from 23°C to 45°C. The soil is yellowish to brown reddish sand with varying content of silt. Soil is fairly permeable and the infiltration rate can absorb most of the rain except for more severe rains which can cause considerable surface flow and erosion.

Materials and methods:-

Sample collection and preparation:

Samples indicated as US1 is the sample of water taken from MabbuchintalaPalle 1, US2 (Mabbuchitalapalle 2), US3 (Thummalapalle 1), US4 (Thummalapalle 2), US5 (Rajakuntapalle 1), US6 (Rajakuntapalle2), US7 (Bhomaiahgaripalle), M8 (V.Kota) samples (Fig. 1).

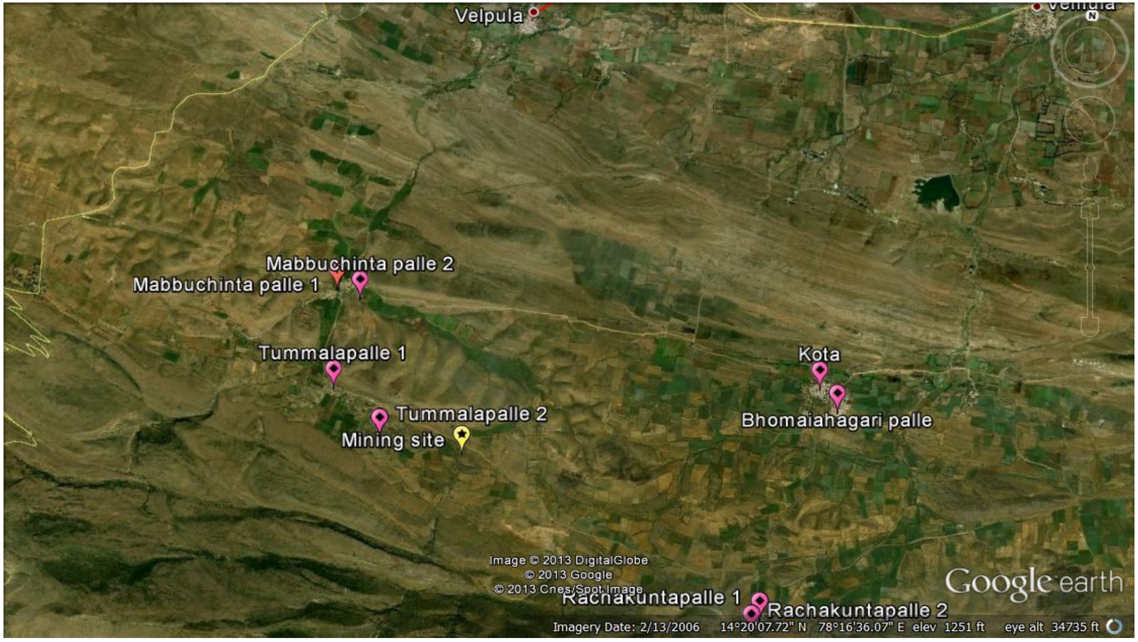

Fig. 1: Location map of the study area for surrounding areas of UCIL, Thummalapalle, Kadapa District, A.P.

Soil samples were collected from 0-10 cm depth. Sampling locations were chosen to provide good area coverage (Fig.1). After sampling, soil samples were dried in a thermostatically controlled oven for two days at 60°C temperature. The dried sediments were then disaggregated in a porcelain mortar with a pestle, and sieved through a 2 mm nylon mesh. The samples were subsequently ground in agate swing grinding mill to a fine powder for the better homogenization of the sample, in order to obtain a representative aliquot for precise analytical results. Two grams of each powdered sample were weighed using an analytical balance with a precision as low as 0.0001g. Pressed pellets were afterwards prepared by using collapsible aluminum cups [15]. These cups are filled at the bottom with ~2.5 g of boric acid, and the 2 g of the fine powdered sample is placed on the top, and then pressed under a hydraulic pressure of 25 tons to obtain the pellet of each sample. These pellets were analyzed by using XRF technique. XRF analyzers were carried out at the National Geophysical Institute, Hyderabad.

Instrumentation:

Elemental composition was determined using an X-ray fluorescence spectrometer, type Philips MagiX PRO model PW2440 XRF with Rh 4KW tube. The MagiX PRO is a sequential instrument with a single goniometer-based measuring channel covering the element range from F to U. The instrument is microprocessor controlled for maximum flexibility. Its high level performance enables, therefore, a sensitive and accurate determination of major and trace elements (Si, Al, Na, Mg, Ca, Fe, P, S, As, Ba, Co, Cd, Cu Mo, Ni, Pb, Rb, Sr, V, Zn and Zr). The accuracy of analytical results was evaluated by comparison with certified values of the analyzed reference materials. Results of certified reference materials were within the quoted confidence limits. International soil reference materials from the US Geological Survey, Canadian Certified reference materials ((SO)-1, 2, 3, 4), International Working Groups (France) and the National Geophysical Research Institute (India) were used for the detection of trace elements, and to check the accuracy of analytical data [15].

Results and discussion:-

Contamination of soil by heavy metals appear to be virtually permanent, as heavy metals can be transformed from one chemical form to another through chemical and biochemical reactions, but are not destroyed. The heavy metals (As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Rb, Sr. V, Y, Zn, Zr) is presented in the Table.1. To access the soil contamination in the study area the concentration of heavy metals and their spatial distribution was compared to the heavy metal concentration in the earth's crust (Table. 2) [16]. Among the 14 heavy metals detected in the soils of the study area, only Ni, Sr, Zn, Zr and Rb are within the permissible limits. The increased levels of Ba, As, Co, Cr, Cu, Mo, Pb. V and Y in the study area are a major concern for the suitability in agricultural and other land management practices. The higher standard deviation observed for heavy metals Ba, Cr, Rb and V in the soil suggest that these metals are not uniformly distributed in the study area. Out of the eight soil samples, three samples of nickel were found to be below detection level. Likewise the statistical summary given in table 2 does not account for nickel samples. Zinc gives the least variation among the heavy metals while copper shows the highest variation in the soil samples.

XRF results for the collected soil samples evidenced the existence of the following major and minor elements.

Table. 1: Summary of the heavy metal concentration (in mg/kg) in soil samples from XRF Data.

Soil Samples	**As**	**Ba**	**Co**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Rb**	**Sr**	**V**	**Y**	**Zn**	**Zr**
US1	2.5	1007.2	22.7	116.5	40.0	2.1	25.4	16.8	92.8	58.9	89.5	30.5	72.7	156.5
US2	2.7	788.5	18.5	102.6	35.9	2.6	16.8	19.9	79.4	43.5	70.5	24.6	76.4	148.8
US3	2.3	314.5	3.6	54.6	13.4	5.7	ND	22.5	30.8	18.6	13.9	15.6	56.9	143.2
US4	5.5	987.1	20.3	96.1	67.6	2.3	11.6	40.2	66.3	45.1	82.1	23.7	75.2	151.5
US5	1.5	464.7	14.5	78.7	17.5	3.3	ND	10.8	38.5	31.6	62.4	18.4	66.4	168.1
US6	1.7	504.0	16.6	80.3	18.1	2.2	ND	14.1	40.1	35.4	72.9	17.6	66.8	134.8
US7	3.1	988.0	23.9	103.0	24.2	0.9	17.4	19.6	60.7	40.3	113.0	25.4	66.8	170.2
US8	3.3	1777.9	24.8	118.2	45.4	1.5	27.3	24.4	61.8	57.6	95.6	23.1	63.3	120.2

Table. 2: Statistical summary of the heavy metal concentration of soil of the study area the reference value in the continental crust.

S. No.	**Elements**	**Minimum**	**Maximum**	**Mean**	**Stand. deviation**	**Coef. Variance %**	**Reference Value**
1	As	1.7	5.5	2.825	1.25	44.12	1.5
2	Ba	314.5	1778.0	854.0	460.17	53.88	550
3	Co	3.6	22.7	18.11	6.86	37.91	10
4	Cr	54.6	116.5	93.75	21.46	18.25	35
5	Cu	13.4	67.6	32.76	18.25	55.70	25
6	Mo	1.0	5.7	2.58	1.43	55.37	1.5
7	Ni	11.6	27.3	19.7	6.51	33.04	20
8	Pb	10.8	40.2	21.03	8.90	42.32	20
9	Rb	30.8	92.8	58.8	21.36	36.33	112
10	Sr	18.6	57.6	41.37	13.30	32.16	350
11	V	13.9	95.6	74.98	29.38	39.19	60
12	Y	15.6	30.5	22.36	4.88	21.83	22
13	Zn	56.9	76.4	68.06	6.49	9.54	71
14	Zr	120.2	170.2	149.16	16.65	11.16	190

Arsenic: The Arsenic varies in the range from 1.5 – 5.5 mg/kg with an average of 2.825 mg/kg. Eighty eight percent of chromium samples are beyond the desirable limit of 1.5 mg/kg. The main source of arsenic may be present in soils due to excess use of fertilizers, pesticides and geogenic in nature. If arsenic contains higher levels in the groundwater causes lung and skin diseases.

Barium: The main source of barium in the study area is predominant siliceous soils. Barium concentration in the soils of the study area ranges from 314.5 – 1778.0 mg/kg with the average of 854.0 mg/Kg. Fifty percent samples exceed the limit of 550 mg/Kg. Source of barium could be both geogenic and anthropogenic. The high standard deviation of barium indicates that it is not distributed uniformly within the area. The high barium concentration can be attributed to feldspar weathering in silicate rocks [17].

Cobalt: The cobalt concentration in the soils of the study area varies from 3.6 – 22.7 mg/kg with an average of 18.11 mg/kg. Ninety percent of cobalt samples exceed the desirable limit of 10 mg/kg. The spatial distribution shows that the concentration of cobalt is high. The main source of cobalt concentration is the application of cobalt salts or cobalt treated phosphate fertilizers [18].

Chromium: The concentration of chromium varies from 54.6 – 116.5 mg/kg with an average of 93.75 mg/kg. Forty percent of chromium samples are beyond the desirable limit of 35 mg/kg. The main source of chromium may be present in soils due to excess use of fertilizers, pesticides and mining activities. If chromium contains higher levels in the groundwater causes cancer.

Copper: Copper concentration varies from 13.4 – 67.6 mg/kg with an average of 32.76 mg/kg. Fifty percent of copper samples exceed the desirable limit of 25 mg/kg. Copper accumulation in the study of the soil area is due to the mining and application of agrochemicals in the agro-based industry. The abundance of copper in igneous rocks is partly controlled by the process of differentiation during crystallization [19].

Molybdenum: The molybdenum concentration ranges from 1.0 – 5.7 mg/kg with an average concentration of 2.58 mg/kg. Seventy five percent of molybdenum samples are beyond the desirable limit 0f 1.5 mg/Kg.

Nickel: The Nickel concentration varies from 11.6 – 27.3 mg/kg with an average of 19.7 mg/kg. Twenty percent of the samples are beyond the desirable limit of 20 mg/kg.

Lead: The Lead concentration varies from 10.8 – 40.2 mg/kg with an average concentration of 21.03 mg/kg. Thirty seven percent of the samples are above the desirable limit of 20 mg/kg. If lead contains higher levels in the groundwater causes renal disease, cardiovascular effects, and may cause irreversible neurologic damage.

Rubidium: Rubidium concentration varies from 30.8 – 92.8 mg/kg with an average concentration of 58.8 mg/kg. All soil samples in the study area are within the desirable limit of 112 mg/kg. The source of rubidium is geogenic.

Vanadium: Vanadium concentration varies from 13.9 – 113.0 mg/kg with an average of 74.98 mg/kg. Eighty eight percent of vanadium samples are above the desirable limit of 60 mg/kg. Therefore the source of this element is directly associated with mining and agricultural activities.

Yttrium: The concentration of yttrium ranges from 15.6 – 30.5 mg/kg with an average of 22.36 mg/kg. Sixty three percent of soil samples are above the desirable limit of 22 mg/kg. The presence of yttrium is geogenic. With water yttrium causes damage to the cell membranes, which have several negative reproductions and on the function of the nervous system.

Zirconium: The concentration of zirconium ranges from 120.2 – 170.2 mg/kg with an average of 149.16 mg/kg. All the soil samples are within the desirable limit of 190 mg/kg.

Zinc: The concentration of zinc varies from 56.9 – 76.4 mg/kg with an average of 68.06 mg/kg. Thirty eight percent of zinc samples are above the desirable limit of 71 mg/kg.

Strontium: The concentration of Strontium varies from 18.6 – 58.9 mg/kg with an average of 41.37 mg/kg. All the soil samples are within the desirable limit of 350 mg/kg.

Major oxides in the soil:-

Soil samples collected throughout the agriculture and surrounding areas of Thummalapalle are analyzed for heavy metals and major oxides. The results of chemical analysis of major oxides (SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, TiO_2 and P_2O_5) were compared with international standards for major oxides in soil by Bhon et al.[20] (Table. 3) and is useful to classify soils on the basis of their chemical composition. The concentration of major oxides was compared with the reference values given by for the major oxide concentration in soil in weight percent.

Table. 3: Summary of major oxide concentration in soil samples of the study area and the reference value [20]

SS	**SiO_2 (%)**	**Al_2O_3 (%)**	**Fe_2O_3 (%)**	**MnO (%)**	**MgO (%)**	**CaO (%)**	**Na_2O (%)**	**K_2O (%)**	**TiO_2 (%)**	**P_2O_5 (%)**
US1	73.19	6.26	3.80	0.10	6.44	2.21	0.44	9.11	1.04	0.11
US2	78.01	5.62	3.38	0.10	8.31	1.55	0.50	10.39	0.90	0.12
US3	ND	3.04	1.28	0.06	0.75	ND	0.36	3.01	0.47	0.07
US4	78.49	5.73	3.31	0.09	4.00	2.90	0.48	10.26	0.96	0.25
US5	84.93	4.81	2.61	0.06	1.91	0.70	0.76	4.68	0.92	0.13
US6	83.79	5.12	2.90	0.06	1.99	0.84	0.80	5.00	1.00	0.13
US7	79.75	6.25	4.21	0.07	4.87	0.88	0.37	4.51	1.31	0.08
US8	77.11	6.47	3.82	0.08	3.84	1.16	0.38	4.90	0.97	0.08
Reference Value	70.29	>13.22	5.77	>0.1	0.99	1.44	0.99	1.2	0.88	0.18

The SiO_2 concentration varies from 73.19 – 84.93%. Hundred percent of SiO_2 is exceeding the permissible limit of 72.64% as recommended Bhon et al.[20].

Al_2O_3 concentration ranges between 3.04 – 6.47%. Hundred percent of the samples are within the limit of 13.22%. Fe_2O_3 values range from 1.28 – 4.21%. Hundred percent of the samples are within the limit of 5.77%. MnO values range from 0.06 – 0.1%. All the samples of MnO are within the permissible limits of 0.1%. CaO values range from 0.7 – 2.90% and Ninety percent of the samples are above the permissible limit of 0.99%. Na_2O values range from 0.36 –0.8%. Hundred percent of the samples are within the limit of 0.99%. K_2O values range from 3.01 – 10.39%. Hundred percent of the samples are beyond the limit of 1.2%. TiO_2 values range from 0.9 – 1.31%. Hundred percent of the samples crossed the limit of 0.88%. P_2O_5 values range from 0.07 – 0.25%. Thirteen percent of the samples are beyond the limit of 0.18%.

Conclusion:-

The study demonstrates that the study area is facing the problem of soil and water quality deterioration, due to the absence of a perennial source of surface water, inadequate rainfall and over exploitation. Water quality has also deteriorated due to increased human population, rapid urbanization, unscientific disposal of water and improper water management. In the mining area, the rainwater and wind erosion is the main cause of the contaminant spreading over the area. The following preventive measures are proposed to curb soil pollution. Soil testing, water testing and continuous monitoring of the area will prevent the soil pollution. The extent of the contamination by Ba, Co, Cr, Cu, Mo, Ni, Pb, Rb, V, Y and Zr should be treated as sensitive zones for further research. Possible options of remedial measures can be excavated and replanting, stabilization of the soil, Phyto-remediation and bio-remediation. It is recommended to have a periodical monitoring of the environment in this area and necessary and mitigative measures are implemented to avoid further deterioration of the environment for sustainable development.

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