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GEOCHEMISTRY OF GROUND WATER AND THE SOURCE OF CONTAMINATION OF FLUORIDE IN THE DRINKING WATER OF THE NARANJI AREA, DISTRICT SWABI, NWFP, PAKISTAN

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Inhabitants of the Naranji village are known for their yellow colouration of teeth throughout the Mardan Division. A general survey of the area shows prevalence of dental and skeletal fluorosis of varied degree in the village. A detailed geochemical analysis of ground water of the village indicates fluoride concentration of 13.5 mg L^{-1} which is about 9 times more than WHO's maximum contaminant level. The source of high fluoride in drinking water is considered to be the alkaline rocks of Koga Complex. Tube well water should be supplied to the area in order to avoid the fluoride contamination.

Key Words: Drinking water, Fluoride, Osteoporosis.

Introduction

Fluoride is an important element of nutrition, because it is present in minute amounts in human bones and teeth and prevents dental caries.The main source of fluoride is usually drinking water. Compared with that in water, the fluoride content in food-stuff is of little importance. The absence of fluoride in drinking water causes a disease called "Osteoporosis" which degenerate bones and teeth [1]. However,extended ingestion of excessive amount of fluoride causes dental and skeletal fluorosis.It is estimated that more than 1.5 mg L^{-1} of fluoride in drinking water causes dental fluorosis (mottling and staining of teeth) [2],where as more than 5 mg L^{-1} causes skeletal fluorosis. According to Steinberg *et al.* [3], x-ray density of bones in lumbar spine, pelvis and elsewhere increases in skeletal fluorosis. In addition to this, there may be an increase in new bone formation as well as in the width and number of osteoids (organic matrix of bone). Crippling fluorosis occurs when the water supply contains 10 mg L^{-1} fluoride [4].

After the report of fluoride toxicity in Kheshki area [5],it was decided to check other areas of NWFP showing indications of fluorosis. The inhabitants of village Naranji are well known throughout Mardan division for the yellow colouration of their teeth which is an indication of dental fluorosis. So a general survey was carried out which showed that nearly 90% of the population of Naranji was suffering from varied degrees of dental and skeletal fluorosis.

Geology of the area. Village Naranji is located 30 kms north of Swabi and is accessible through a road from Gohati (located on main Swabi Mardan road) as shown in Fig. 1. Geologically it is situated at the southwestern boundary of Ambela Granitic Complex (Fig. 2),which comprises of granites, alkali granites, quartz syenites, syenites, feldspathoidal syenites and related rocks and basic dikes [6]. Le Bas *et al.* [7] published Rb/Sr isochron age of 315 ± 15 Ma for the granite and syenites of this area.

Village Naranji is located on an outcrop of alkali granites of the Ambela Granitic Complex. These granites are dominantly composed of alkali feldspar, plagioclase and quartz and minor amounts of muscovite, biotite, epidote, apatite, chlorite, zircon and clay [6]. North of village Naranji lies an oval shape body of syenites, feldspathoidal syenites and associated rocks (Fig. 2) and is named as Koga Complex [8]. Within the Koga Complex lies carbonatites and its related fenites known as Naranji Kandoa Carbonatites [9]. Mian also reported ijolites from this complex [10]. Chaudhry *et al.* [11] and Jabeen [12] presented a detailed petrographic account of the Koga Complex.

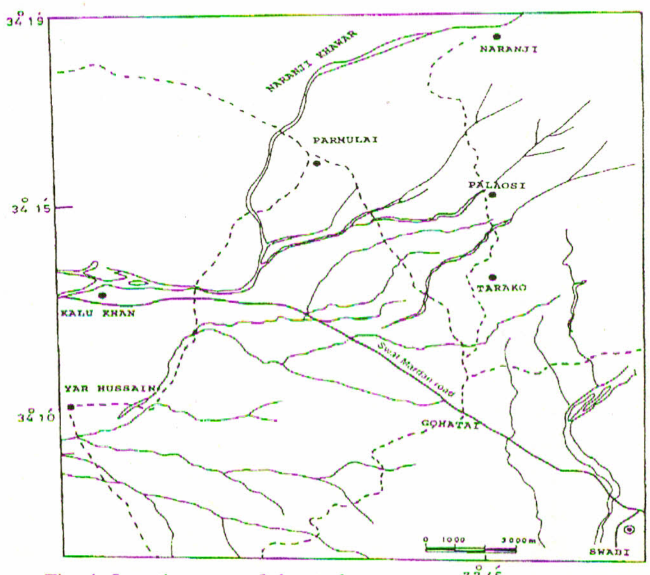

Fig. 1. Location map of the study area.

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Surface and ground water. In Naranji area the principal source of drinking water is a spring which emanates from the alkali granite of Ambela Granitic Complex having a recharge area in north near Naranji Kandao (Fig. 2). Small amount of groundwater is also available in fractured granitic rocks very close to the Naranji Khawar which is a small stream flowing from Naranji Khandao and ending near Kalu Khan (Fig. 1 & 2). This stream,at south of Naranji, has a very small discharge and tends to become dry. However, during rainy seasons it has considerable discharge. Water sample from a dug well was also collected from Kalu Khan to see the effects of this stream on the aquifer of Kalu Khan area. Ground water of Tarako and Gohati was also collected to see the variation in water chemistry with the change of lithology of the aquifer. In Tarako area the aquifer rock is limestone, belonging to Nowshera Formation, whereas, at Gohati volcanic rocks are exposed. Kalu Khan is a plain area having aquifer in the sandy portion of the alluvial and lacustrine deposits.

Geochemistry of water. Out of six ground water samples, three samples were collected from Naranji village (2 from spring and 1 from a dug well) and the remaining three were collected from Tarako, Gohati and Kalu Khan. Both physical and chemical analyses of each sample were carried out. Physical

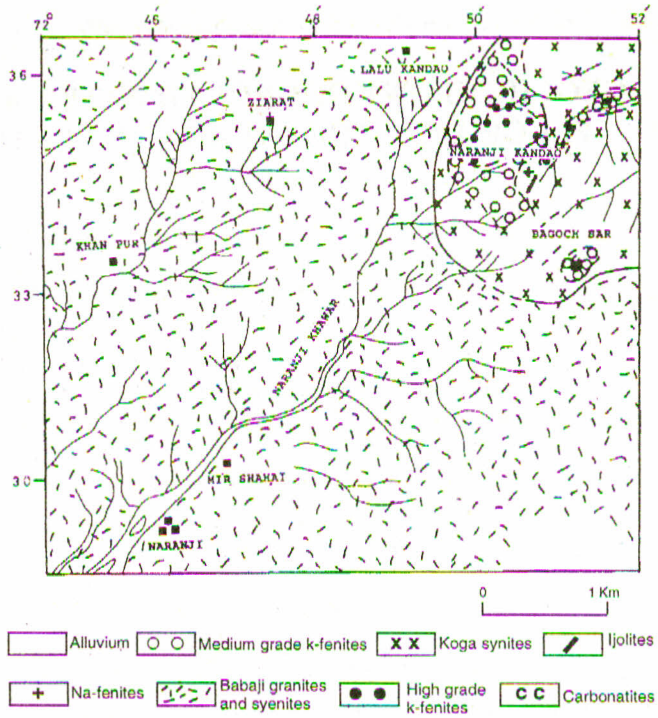

Fig.2. Geological map of the Naranji and surrounding area (modified from Chaudhry *et al.* [11]).

TABLE 1. CHEMICAL ANALYSES OF GROUNDWATER SAMPLES OF NARANJI AND SURROUNDING AREA.

Sample #		1	2	3	4	5	6	WHO
Location		Naranji	Naranji	Naranji	Tarako	Gohati	Kaku Khan	MCL
TDS		203.00	168.00	266.00	350.00	1512.00	616.00	1000.00
pH		7.36	7.10	7.30	7.48	7.08	7.83	6.5-8.5
SiO_2	(mg^{-1}L)	6.09	29.90	20.65	14.17	19.65	15.90	-
SO_4	(mg^{-1}L)	8.00	8.00	11.00	10.00	21.00	46.00	400.00
NO_3	(mg^{-1}L)	4.50	1.90	2.50	1.70	3.00	1.90	45.00
PO_4	(mg^{-1}L)	0.42	0.56	0.38	0.28	0.20	0.27	-
HCO_3	(mg^{-1}L)	35.00	74.00	46.00	140.00	159.20	246.00	-
CO_3	(mg^{-1}L)	0.00	0.00	0.00	0.00	0.00	0.00	-
Cl	(mg^{-1}L)	1.45	1.38	1.62	3.46	10.85	5.25	250.00
F	(mg^{-1}L)	13.52	13.51	13.50	1.56	1.08	1.80	1.50
Ca	(mg^{-1}L)	10.67	11.17	13.67	35.50	42.17	59.33	-
Mg	(mg^{-1}L)	2.00	4.57	3.17	12.50	14.00	25.33	-
Na	(mg^{-1}L)	1.57	1.61	1.72	2.34	6.75	3.83	200.00
K	(mg^{-1}L)	1.06	1.03	15.58	0.58	1.62	1.13	-
Fe	(mg^{-1}L)	0.04	0.04	0.01	0.02	0.01	0.03	0.30
Mn	(mg^{-1}L)	0.03	0.03	0.04	0.06	0.05	0.05	0.10
pb	(μg^{-1}L)	16	40	42	7	22	6	50
Cd	(μg^{-1}L)	1	0	10	6	12	4	5
Cr	(μg^{-1}L)	0	2	13	41	6	3	50
Cu	(μg^{-1}L)	0	0	61	0	27	19	1000
Ni	(μg^{-1}L)	6	0	10	6	12	4	5000
Zn	(μg^{-1}L)	1	4	6	4	3	43	5000

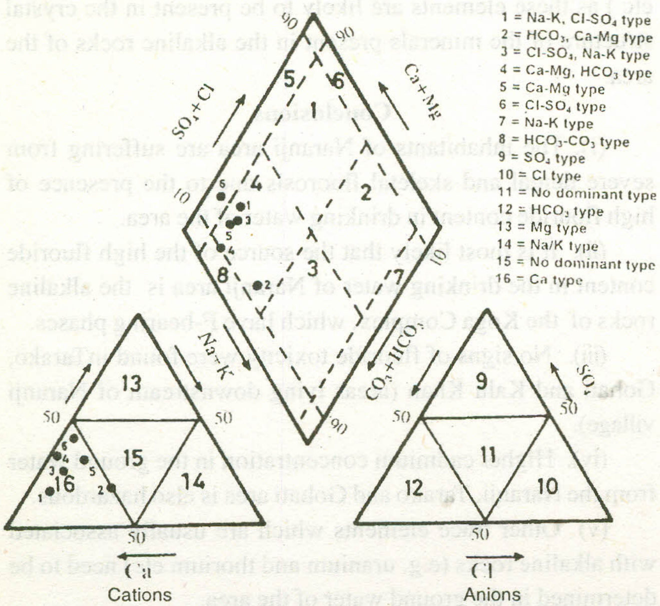

Fig. 3. Geochemical classification of groundwater of the study area on the basis of Piper Scheme [16].

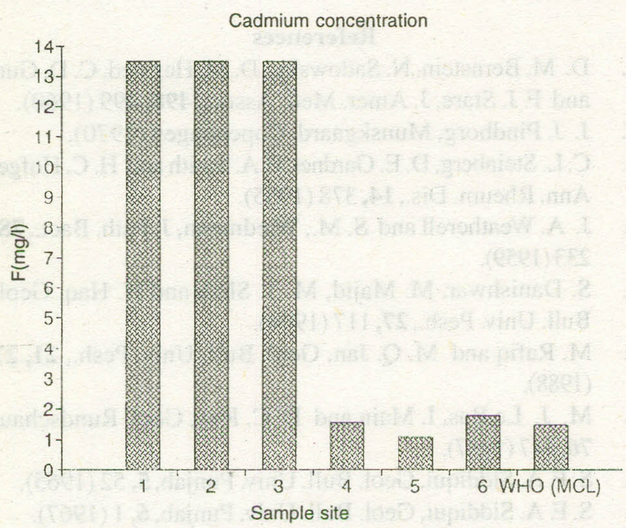

Fig.4. Comparison of fluoride concentration in the groundwater of the study area with MCL of WHO (1-3 = Naranji, 4 = Tarako, 5 = Gohati, 6 = Kalu Khan)

analysis included determination of temperature, pH and conductivity, whereas, chemical analysis included determination of SO_4, NO_3, Cl, CO_3, HCO_3, Ca, Na, K, Mg, Fe, Mn, Pb, Ni, Cr, Cu and Cd. Anions were determined at the sampling site using DR-2000 Hach photometer. The remaining metals and non-metals were determined by Perkin Elmer-3360 Atomic Absorption Spectrophotometer, equipped with HGA 600 graphite furnace and As-60 autosampler in the National Center of Excellence in Geology, University of Peshawar. Analysis of special concern was, of course, the measurement of fluoride in each sample, which was determined by the method of SPANDS as recommended by USEPA [13]

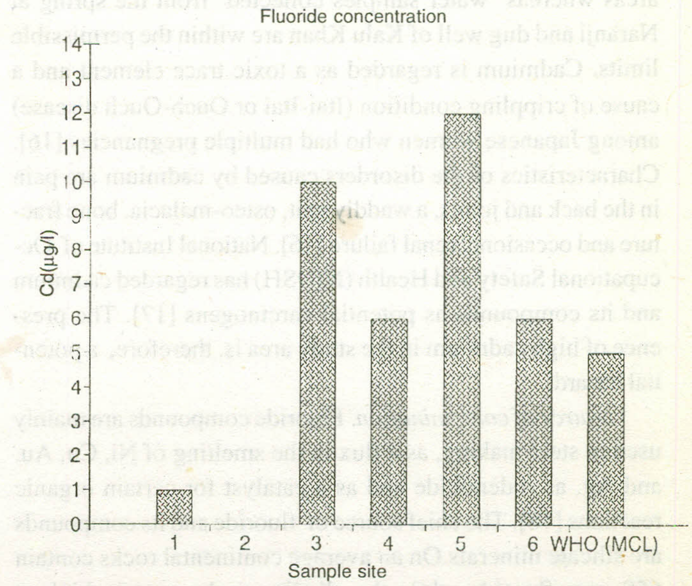

Fig. 5. Comparison of cadmium concentration in the groundwater of the study area with MCL of WHO (1-3 = Naranji, 4 = Tarako, 5 = Gohati, 6 = Kalu Khan).

Results and Discussion

Results of the analyses along with WHO Maximum Contaminant Levels (MCLs) [14] are presented in Table 1. It is clear from the results that all the constituents are within the MCL of WHO except for fluoride, cadmium and Total Dissolve Solids (TDS). The water samples of the areas are classified on the basis of Piper diagram [15] (Fig. 3). The samples from Naranji, Tarako and Kalu Khan area are classified as $Ca+Mg+HCO_3$ type.

A comparison of fluoride concentration with MCL of WHO (Fig.4). clearly indicates that the samples from Naranji area (Nos. 1, 2, 3) have about 9 fold higher concentration of fluoride than that of MCL. However, the samples from Tarako (No. 4), Gohati (No. 5) and Kalu Khan (No. 6) have comparable concentration of fluoride with the MCL.This fluoride toxicity was evident from the survey of the inhabitants of the area which showed that about 95% of the population is suffering from fluorosis. Children of 5-6 years to old men and women, had stained teeth. Most of the elderly people showed signs of skeletal fluorosis and complained about general body aches and pains, easy fracturing of bones and specifically lumbago. Thus the inhabitants of Naranji village are having severe dental and skeletal fluorosis which could be attributed to the high fluoride content in the drinking water of the area.

Cadmium concentration in the samples when compared with MCL of WHO(Fig.5) indicates that the sample from Gohati has the highest cadmium (12 $\mu g\ L^{-1}$) followed by dug well sample of Naranji (10 $\mu g\ L^{-1}$) and the sample of Tarako (6 $\mu g\ L^{-1}$). The three samples surpass the maximum contaminant level (5 $\mu g\ L^{-1}$) thus indicating cadmium toxicity in these areas whereas water samples collected from the spring at Naranji and dug well of Kalu Khan are within the permissible limits. Cadmium is regarded as a toxic trace element and a cause of crippling condition (Itai-Itai or Ouch-Ouch disease) among Japanese women who had multiple pregnancies [16]. Characteristics of the disorders caused by cadmium are pain in the back and joints, a waddly gait, osteo-malacia, bone fracture and occasional renal failure [16]. National Institute of Occupational Safety and Health (NIOSH) has regarded cadmium and its compounds as potential carcinogens [17]. The presence of high cadmium in the study area is, therefore, a potential hazard.

Source of contamination. Fluoride compounds are mainly used in steel making, as a flux in the smelting of Ni, Cu, Au, and Ag, as rodenticide and as a catalyst for certain organic reactions [18]. The chief source of fluoride and its compounds are silicate minerals.On an average continental rocks contain 650 ppm fluoride while the alkaline rocks contain highest fluoride content i.e. 1000 ppm [18]. It is an essential element in minerals like, fluorite, apatite, cryolite, topaz, mica, amphiboles etc.

The source of contamination of fluoride in the Naranji area can very easily be deciphered if we consider the rock composition and general geology of the area. The main source of surface and groundwater in the Naranji area lies in the Naranji Kandao where the rocks are mainly syenites, feldspathoidal syenites, carbonatites and other associated rocks (Fig.2), which are the part of Koga complex [9]. The occurrence of fluoride bearing mineral phases (e.g. fluorite, apatite, muscovite, biotite and amphibole including arfedsonite) in the Koga Complex [11] further emphasizes that the fluoride leaching through these minerals, during weathering, is contaminating the ground water of the area. As the Naranji village lies very close to the source of fluoride, the groundwater of the area has high fluoride concentration. The fluoride content of the groundwater of the area away from the source of contamination is low, most likely due to (a) mixing with the water having negligible amount of fluoride (b)adsorption, (c) precipitation of fluoride mineral phases, usually caused by temperature drops and (d) dispersion operating in the ground water system. The causes 1 and 4 seem to be more effective in the area.

Recommendations. Following remedial measures must be taken urgently to protect the inhabitants of the area from this kind of fluoride contamination: (i) The people should stop the use of water from springs and dug wells, especially for drinking purposes and (ii) Village Naranji and the nearby surrounding area should be provided with the drinking water from tube wells, dug in a distant area.

The groundwater of the area should also be tested for radioactive elements (especially uranium, thorium and radon etc.) as these elements are likely to be present in the crystal structure of the minerals present in the alkaline rocks of the area.

Conclusions

(i). The inhabitants of Naranji area are suffering from severe dental and skeletal fluorosis due to the presence of high flouride content in drinking water of the area.

(ii). It is most likely that the source of the high fluoride content in the drinking water of Naranji area is the alkaline rocks of the Koga Complex, which have F-bearing phases.

(iii). No signs of fluoride toxicity were found inTarako, Gohati and Kalu Khan (areas lying downstream of Naranji village).

(iv). Higher cadmium concentration in the ground water from the Naranji, Tarako and Gohati area is also hazardous.

(v) Other trace elements which are usually associated with alkaline rocks (e.g. uranium and thorium etc) need to be determined in the ground water of the area.

(vi) Similar studies should also be extended to the north of Naranji village.

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