# **Sources of Fluoride Contamination in Singrauli with Special Reference to Rihand Reservoir and its Surrounding**

A. L. Usham<sup>1\*</sup>, C. S. Dubey<sup>1</sup>, D. P. Shukla<sup>2</sup>, B. K. Mishra<sup>3</sup>, G. P. Bhartiya<sup>1</sup>

<sup>1</sup>Department of Geology, Center for Advanced Studies, University of Delhi, Delhi - 110 007, India

<sup>2</sup>School of Engineering, Indian Institute of Technology Mandi, Mandi - 175 001, India

<sup>3</sup>Department of Mining, AKS University, Satna - 485001, India

\**E-mail:* arnoldluwang@gmail.com, csdubey@gmail.com

## ABSTRACT

The Singrauli region is known for fluoride contamination and its effect on human population. In this work the possible sources of fluoride contamination in Rihand reservoir water is constrained. They include slurry water, fly ash and coal samples of various thermal power plants, coal seams and granites of the region. Petrographic study depicted the presence of fluoride bearing minerals - flour apatite in pink granite. Preliminary scanning electron microscope studies revealed presence of fluorine peak in coal samples. The chemical analysis confirmed the presence of fluoride in fly ash (12.6 mg/kg), drain water (5.34 mg/l), soil (6.1 mg/kg), coal (3.1 mg/kg). They confirmed the source of fluoride from coal of thermal power plant which utilized coal from Singrauli coal seam (1.6 mg/kg). Further the Rihand reservoir water is also enriched by fluoride contaminant (upto 4.7 mg/l). This contaminates groundwater of the area as well. The contaminated water used for drinking and agriculture affects health of inhabitants in the area. It is concluded that the main source of fluoride contamination in the study area is due to coal burnt in thermal power plant and pink granite formation of the area, both anthropogenic and geogenic sources are implied.

## **INTRODUCTION**

The elevated level of fluoride (F-) in water is the widespread contaminant in India. It is widely prevalent in different parts of India, particularly in the states of Andhra Pradesh, Tamil Nadu, West Bengal, Odissa, Uttar Pradesh, Gujarat, Maharashtra and Rajasthan, where 50-100% of the districts have drinking water sources containing excess level of fluoride and causes fluorosis (Gupta et al., 1998; Muralidharan et al., 2011 and Chakraborti et al., 2011, Susheela, 2007; Duraiswami and Patankar, 2011, Chakrabarti and Bhattacharya 2013, Routroy et al., 2013, Saha et al., 2014, Rao et al., 2016, 2014). It was estimated that 62 million people from 17 states are affected with dental, skeletal and/or non-skeletal fluorosis (Susheela, 2007). Increase in demand and lack of availability of potable water has led the population of these states to consume degraded quality water. The degradation of groundwater may be due to natural or anthropogenic processes. Natural source for fluoride, arsenic and other heavy metals etc. are inherent mineralization and deposits of toxic element bearing ore/minerals (Raju et al., 2009; Shukla et al., 2010; Usham et al., 2012; Rao et al., 2016, 2014) while anthropogenic sources include flushing of wastewater from sewage treatment plants (Schroder 1993; Schroder and Fytianos 1999), discharge from industries (Churchill et al., 1948; Alloway et al., 1997), burning of coal in thermal power plants (Li and Cao, 1994; Ando et al., 1998; Watanabe et al., 2000; Prasad and Mondal, 2006; Aggrawal et al 2011; Dubey et al., 2012; Mishra et al., 2014), from blast furnace/ brick kilns (Jha et al., 2008), in houses (Finkelman et al., 1999); mining activities (Dhar et al., 1986; Beg et al., 2011), etc. The area of study - Singrauli is in the mining hub of about 9.1 billion tonnes coal reserves spreading over an area of approx. 220 km<sup>2</sup> and it has 6 superthermal power plants producing 12 GW of power i.e. 10% of total installed capacity of India (NIC, 2010). Due to remote location of the study area, very few researchers have worked in this area. A few studies that have been carried out indicate fluoride contamination in groundwater in distant parts of this region (Gautam and Tripathy 2005; Raju et al., 2009; CSE, 2011). Fluoride contamination is reported in the eastern portion of study area i.e. Dudhi area, where about 80% of water samples have F contamination (CSE, 2011) and 50% of children (out of total 1796) are affected by fluorosis (Gautam and Tripathy, 2005). CSE 2011 also reported some village ponds of Singrauli region of being fluoride contamination up to 3.14 mg/l and considered due to burning of coal in power plants. Since the source of fluoride contamination in the vicinity of thermal power plants (TPPs) has not vet been studied, the present study concentrates on the possible geologic and anthropogenic sources of fluoride contamination in the region. Therefore rock, coal, fly ash, soil and water samples were collected from the various sites, TPPs, coal mines, ash ponds, and in the vicinity of Rihand reservoir. The samples were analyzed by petrography, SEM and ICP-MS, and the results are presented in this paper.

# **STUDY AREA**

The study area is situated between 24°03' N to 24°33' N and 82°33' E to 83°03' E at the boundary of three states viz. Uttar Pradesh in north, Madhya Pradesh in west and south and Chhattisgarh in the east. Geologically, sedimentary rock formations belonging to Vindhyan (Kaimur and Semri Groups) and Gondwana Supergroups; volcanosedimentary rock formations of Precambrian Mahakoshal Group and Precambrian Chhotanagpur Granite Gneiss Complex (CGGC) (Singh and Srivastava, 2011; Srivastava and Srivastava, 2012) occur in the area. CGGC is represented by the Dudhi Group of rocks in the study area, comprising mainly of migmatitic granitic gneisses and porphyritic granite, besides numerous metasedimentary enclaves (Mazumdar, 1988; Banerji, 1991; Kumar and Ahmad, 2007). The rocks have evolved predominantly under amphibolite facies metamorphism (Mahadevan, 2002) and are present in the eastern portion of the study area. The area is structurally very complex (Srivastava and Gairola, 1997) and tectonically active (Mohan et al. 2007). The Permo-Carboniferous Gondwana Supergroup is known for coal bearing formations. They occur in the western portion of study area. Most of coal belongs to the Barakar Formation, while some areas have Talchir, and Raniganj series coals (Hussain, 2012; Singh et al., 2014). Around 98% of coal reserves of India belong to Gondwana Supergroup (Singh, 1995; Larry, 2002). There is a 91m high concrete dam across river Rihand, a tributary of River Son, which has created a very large reservoir known as Gobind Ballabh Pant Sagar or Rihand reservoir



LEGEND: SW: SLURRY WATER; FA: FLY ASH POND \* GPS CO-ORDINATE

**Fig.1. (a)** Map showing concentration of Fluoride in mg/l in various water samples collected from the study Western portion of the area is dominated by coal mining and TPP while eastern portion lies on CGGC (Srivastava and Srivastava 2012; Banerji 1991; Kumar and Ahmad 2007; Singh et.al. 2014) (For details see text). **(b)** Spatial analysis with contour lines is prepared with the help of software ArcGIS 9.2 IDW method]. **(c)** Google Earth images showing waste materials contaminated into the Reservoir

covering an area of 130 sq. km. (466 sq km when full) and collects 10,608 m cu m of water. The Rihand reservoir supplies potable water to 500,000 inhabitants and provides for irrigation in approx. 65,000 ha and provides water facilities to the STPPs for generation of approx. 10,654 MW of thermal power (Christopher et al., 2002). Six large coal based super thermal power plants (STPP)are located at the periphery of this reservoir, while most of the mining activities are confined to the western side of the reservoir. The host rocks (sandstones and shales) near the Fly ash pond of Vindhyachal STPP, Singrauli STPP belongs to Barakar Formation. The stratigraphic succession of the study area is presented in Table 1 and eastern portion is mostly covered by Dudhi granites (Fig.1). Most of the places in India, where high fluoride contamination is observed, are situated on hard rock terrain mostly granitic and gneissic complexes (Raju et al., 2009) Some towns of Uttar Pradesh, lying on Quaternay-Upper Tertiary deposits of Ganga alluvial plain, are also affected (Raju et al., 2009). Studies on fluoride contamination in parts of Chopan, Dudhi and Myorpur blocks of Sonbhadra district, UP has been carried out by some researchers and NGO (Gautam and Tripathi, 2004; GSS, 2004 and Raju et al., 2009). Fluoride contamination in water due to coal ash is studied in Andhra Pradesh and Jharkhand and is related to anthropogenic activities (Prasad and Mondal, 2006).

# Hydro-Geological Settings of the Area

Due to the construction of the Rihand dam, the groundwater regime in the surrounding area has changed. The water seeps into the subsurface and water table often rises when the reservoir is filled. Hydrological studies conducted by the Central Ground Water Board reported that the water table was between 5 and 10m in the vicinity of the dam/reservoir (Christopher et al., 2002). The high water table indicates that the reservoir water recharges the local groundwater system. However, groundwater discharge for the local drainage basin around the reservoir has been estimated to be 17,100 m<sup>3</sup>/h (NTPC 1995), less than 4% of the average annual inflow to the reservoir. Rainfall is the main source for groundwater recharging, apart from seepage from the surface water bodies. The general hydraulic gradient prevailing in the area is towards river Son or locally towards the subsidiary surface water bodies. More or less, the flow of groundwater is in conformity with the surface topography.

# MATERIALS AND METHODOLOGY

Coal, pink granite, fly ash, soil, and water samples were collected from the study area. A total of 47 samples including. 6 coal samples, 3 pink granite samples, 6 fly ash samples, 17 soil samples were collected. 15 water samples were collected and Ph, Ec, ORP and TDS were measured at the sampling site itself. Then the water samples were acidified by adding 2 ml of concentrated HNO<sub>3</sub> (Keith 1991; Hasan et al., 2007) for preservation and further analysis. The sampling was done in and around two mining blocks, six super thermal power plants and their respective fly ash ponds as shown in Fig.1. The collected samples were analysed using inductively coupled plasma mass spectroscope (ICP-MS) for fluoride concentration and titration method for anion cation analysis (shown in Table 2, & Fig.3). The ICP-MS and titration methods were carried out at Anacon Laboratories, Nagpur, recognized by the Ministry of Environment & Forests (MOEF) vide Notification No. D.L-33004/99 dt.24.10.2007- under EPA. Act. The pink granite samples and coal samples were studied by advanced petrological/ore microscopy. The selected spot are analysed by Scanning Electron Microscope (SEM-EDS) facility using Leica Orthoplan microscope fitted with Image Analyzer and M.A 15 Zeiss at the Department of Geology, University of Delhi.

# **RESULTS AND DISCUSSION**

All the samples analyzed are alkaline in nature, except mine drainage water from Kakri coal mine. Drain water sample from Kakri coal mine has sulphate concentration of 304.1 mg/l which is beyond the permissible limit of 250 mg/l given by USEPA while rest of the samples varied between 3.2 to 90.1 mg/l. Drain water sample of Kakri and treated water sample of Bina coal mine have ORP value of 36.2 mv and 8.2 mv indicating oxidized nature. All other water samples collected in the vicinity of 6 TPP have ORP values ranging from - 30.03 mv to -160 mv which reflects reducing nature. Maximum TDS of 831 mg/l is recorded in the slurry water of Lanco super thermal

Table 1. Stratigraphic succession of study area (after Hota et al, 20	012; Srivastava and Srivastava 2012; Singh et.al., 2014)
---	--

Supergroup	Group/Formation	Formation/Lithology	Age			
Unner	Mahadeva	Conglomerates, shale bands and ferruginous sandstones (medium to coarse grained)	Upper Triassic			
Gondwana	Unconformity					
	Panchet	Siltstones, shale beds, conglomerates and ferruginous sandstones (coarse to medium grained)	Lower Triassic			
	Unconformity					
	Raniganj	Coal seams, clays, carbonaceous shale and coarse to fine grained sandstones	Upper Permian			
Lower	Barren Measures	Ferruginous sandstones (coarse to medium grained), clays and shale beds	Middle Permian			
Gondwana	Brakar Formation	Thick coal seams, sandstones (coarse grained), shale beds	Lower Permian			
	Talchir Formation	Boulder conglomerates, sandstones, siltstones, shales etc.	Lower Permian			
	Unconformity					
Vindhyan	Bhander, Rewa, Kaimur, Semri	Jahander, Rewa, Sandstone and shale, limestone and conglomerate Neoproterozo   Kaimur, Semri Meso proterozo Meso proterozo				
	Unconformity					
Mahakoshal	- Intrusive granite, dyke, quartzite, phyllite and dolomitic limestone Palaeoproteroz		Palaeoproterozoic			
	Unconformity					
	Basement (CGGC) Granite Gneisses Complex and schists		Archean			

S. No.	Location	Туре	Latitute, Longitude	F (Fluoride)	рН	EC (mS/cm)	TEMP. (C)	ORP (mv)	TDS (ppm)
			Water	(mg/l)					
1	KCF	DW	N 24.174533°, E 82.760006°	1.03	5.9	0.7	31.8	36.2	586
2	BCM	TW	N 24.148138°, E 82.762415°	0.538	6.49	0.8	31.3	8.3	641
3	R.R	RD	N 24.107165°, E 82.757737°	4.7	7.25	0.2	30.6	-30.3	218
4	S.T.T.P	DW	N 24.112335°, E 82.756335°	5.34	7.6	0.2	31.5	-58.4	132
5	S.T.T.P	SW	N 24.107931°, E 82.742519°	6.54	7.44	0.2	31.5	-33.9	145
6	V.T.T.P	SW	N 24.086132°, E 82.679253°	8.78	7.33	0.2	31.3	-43.5	149
7	V.T.T.P	CW	N 24.076083°, E 82.673278°	1.14	7.1	0.1	31.8	-38.8	115
8	V.T.T.P	HP	N 24.076098°, E 82.672966°	1.5	6.95	0.5	31.2	-24.2	464
9	V.T.T.P	SW	N 24.077432°, E 82.634715°	5.98	7.2	0.3	31.2	-32.5	271
10	A.T.T.P	SW	N 24.202252°, E 82.897444°	4.08	7.22	0.1	31.2	-33.6	131
11	L.T.T.P	SW	N 24.192815°, E 82.889285°	2.94	9.29	0.9	31.5	-160	831
12	H.T.T.P	SW	N 24.186378°, E 82.785321°	9.94	9.21	0.5	31	-150	465
13	O.T.T.P	DW	N 24.450137°, E 82.966971°	1.97	8.35	0.1	32.5	-104.5	109
14	O.T.T.P	SW	N 24.448253°, E 82.977376°	1.78	8.11	0.1	32.6	-84.7	125
15	O.T.T.P	HP	N 24.448222°, E 82.967808°	1.3	8.4	0.3	32.3	-79.8	290
			Coal (m	ng/kg)					
16	KCF	Coal	N 24.173012°, E 82.758826°	1.6	-	-	-	-	-
17	BCM	Coal	N 24.150917°, E 82.756278°	0.64	-	-	-	-	-
28	S.T.T.P	Coal	N 24.101811°, E 82.704088°	0.32	-	-	-	-	-
19	V.T.T.P	coal	N 24.092659°, E 82.674416°	0.78	-	-	-	-	-
20	O.T.T.P	Coal	N 24.449177°, E 82.976705°	3.1	-	-	-	-	-
			Fly Ash (	mg/kg)					
21	S.T.T.P	Fly Ash	N 24.110181° E 82.742719°	5.43	-	-	-	-	-
22	V.T.T.P	Fly Ash	N 24.070475°, E 82.683192°	5.54	-	-	-	-	-
23	A.T.T.P	Fly Ash	N 24.202511°, E 82.885833°	2.72	-	-	-	-	-
24	L.T.T.P	Fly Ash	N 24.191268°, E 82.889220°	4.3	-	-	-	-	-
25	H.T.T.P	Fly Ash	N 24.186860°, E 82.785404°	12.6	-	-	-	-	-
26	O.T.T.P	Fly Ash	N 24.449250°, E 82.976889°	7.6	-	-	-	-	-
			Soil (m	ıg/kg)					
27	KCF	Soil	N 24.174588° E 82.760121°	3.6	-	-	-	-	-
28	BCM	Soil	N 24.150866°, E 82.756573°	4.87	-	-		-	-
29	BCM	Soil	N 24.148083°, E 82.762107°	5.32	-	-	-	-	-
30	R.R	Soil	N 24.107377°, E 82.757868°	2.84	-	-	-	-	-
31	S.T.T.P	Soil	N 24.112618°, E 82.756357°	6.1	-	-	-	-	-
32	V.T.T.P	Soil	N 24.070282°, E 82.682756°	3.9	-	-	-	-	-
33	A.T.T.P	Soil	N 24.202660°, E 82.885832°	1.4	-	-	-	-	-
34	L.T.T.P	Soil	N 24.192509°, E 82.889281°	0.83	-	-	-	-	-
35	H.T.T.P	Soil	N 24.186419°, E 82.785131°	2.03	-	-	-	-	-
36	O.T.T.P	Soil	N 24.449071°, E 82.977069°	3.8	-	-	-	-	-

Table 2. Fluoride concentration in W	er, Coal, Fl	v Ash and Soil samples	collected from the study area
--------------------------------------	--------------	------------------------	-------------------------------

DW- Drain Water, TW- Treated Water, RD- Reservoir Water, SW- Slurry Water, CW- Canal Water, HP- Ground Water (K.C.F- Kakri Coal Mine; B.C.F- Bina Coal Mine; RD-Reservoir, S.T.P.P- Singrauli Thermal Power Plant, V.T.P.P- Vindhyachal Thermal Power Plant, A.T.P.P- Anpara Thermal Power Plant; L.T.P.P- Lanco Thermal Power Plant; H.T.P.P- Hindalco Thermal Power Plant; O.T.P.P- Obra Thermal Power Plant) (For description see text)

power plant. TDS value found from drain water of Kakri coal mine, treated water of Bina coal mine, and slurry water samples of super thermal power plants are beyond permissible limit of 500 mg/l given by the USEPA. The results of the water samples analyzed by titration method for major cation and anion concentrations along with F were used to create various water quality plots such as Piper diagram, Durov plot etc. From the Piper diagram (Fig.3) it is evident that no dominant type of water facies is present, but mixed composition of water is present among these samples. It shows that the chemical composition of slurry water collected from all the respective thermal power plants are almost similar to domestic water such as hand pump, drain water, canal water and reservoir water. It indicates the slurry water are leached out into groundwater and contaminated it. Four different types of water in the order of dominance found in the study area are Ca-HCO<sub>3</sub>, CaCO<sub>3</sub> Ca-SO<sub>4</sub>, and Na-HCO<sub>3</sub> The CaCO<sub>3</sub> dominant water is found only in slurry water of Lanco STPP. It shows high salinity

as well as highest TDS concentration of 831mg/l. It is not suitable for irrigation purposes. Treated water of Bina coal mine, reservoir water of Rihand, and slurry water of Hindalco power plant belong to the Ca-HCO<sub>3</sub>. The reservoir water shows low concentration of salinity (sodium adsorption ratio=0.23, exchangeable sodium ratio=0.109, magnesium hazard ratio=18.6). The  $Ca-SO_4$  is dominant in drain waters of Kakri coal mine, Singrauli thermal power plant, Anpara thermal power plant, and Vindhyachal thermal power plant. Kakri drain water has high salinity value (sodium adsorption ratio=0.58, exchangeable sodium ratio=0.155, magnesium hazard ratio=31.5) and high TDS value of 586 mg/l, hence it is not suitable for irrigation, while rest of the samples have low salinity value. The Na-HCO<sub>2</sub> dominant type of water is observed in canal water of Vindhyachal STPP (sodium adsorption ratio=0.99, exchangeable sodium ratio=0.774, magnesium hazard ratio=27) and both drain and slurry waters of Obra STPP. These samples have low salinity hazard [(sodium adsorption ratio=0.85,



**Fig.2.** Graphs showing the concentration of Fluoride in [a] Water in mg/l [b] Coal, Fly Ash, and Soil in mg/kg collected from the vicinity of various TPPs.

exchangeable sodium ratio=0.715, magnesium hazard ratio=56.2), (sodium adsorption ratio=1.15, exchangeable sodium ratio=1.064, and magnesium hazard ratio=41.4)]. This physio chemical analysis suggests that there is a clear indication of the contribution from the mixing of mine drainage and industrial affluents.

#### Fluoride Estimation using ICP-MS Analysis

ICP-MS study revealed that the concentration of fluoride in slurry water is directly proportional to its concentration in fly ash samples. The water samples analyzed by ICP-MS showed very high concentration of fluoride (up to 4.7 mg/l) in water sample of Rihand reservoir. Highest concentration of 12.6 mg/ kg fluoride (shown in Fig.1, Fig.2, Table 2) is observed in fly ash sample of Hindalco TPP. The slurry water of same TPP has highest concentration of fluoride (9.94 mg/l). Concentration of fluoride in slurry water of Vindhyachal TPP and Singrauli TPP is found to be 8.87 mg/l and 6.54 mg/l (Fig. 2a) respectively and concentration in fly ash of these plants is observed to be 5.54 mg/kg respectively. Ground water sample near fly ash pond of Vindhyachal TPP has fluoride concentration of 1.5 mg/l. Sample from Obra STPP has high concentration of 7.6 mg/kg in fly ash; 3.1 mg/kg in coal samples (Fig.2b) and 1.78 mg/l in slurry water. As observed from the analysis, it can be suggested that slurry waters are not being properly treated before draining it into the environment. The contaminated slurry and drain water are drained and mixed into Rihand reservoir (as visible in Google Earth image in Fig.1). Hence rapid industrialization in the study area- increased coal mining activities and installation of super thermal power plants to meet the increasing demands for power has led to fluoride contamination in the study area. Untreated waste byproducts of the industries are drained into the Rihand reservoir, increasing the pollution in reservoir. The formation around the fly ash pond sites of respective TPPs are Barakar Formation where low concentration of fluoride is observed in groundwater near Vindhyachal TPP. It is also shown that about 85%- 90% of the fluorine present in coal is emitted as HF when the temperature rises above 850° C<sup>,</sup> (Liu et al., 2006, 2007). During combustion, fluorine is emitted as HF,  $SiF_4$ , and  $CF_4$  (Yan et al., 1999 and Liu et al., 2007). Very little literature on fluoride contamination and its source is available in the study area of Singrauli region; hence water samples (surface, ground, drain, slurry water samples) were collected and analyzed in this work. Unfortunately very less work has been carried out on fluoride in Indian coal, but a lot of literature is present on occurrence of fluoride content in coal, fly ash and soil of China (Swaine 1990; Ren et al., 1999; Liu et al., 2007). Hence the coal samples from various coal mines of the area; fly ash samples from ash ponds of thermal power plants and the soils from the vicinity of these TPPs were collected along with the water samples and analyzed for fluoride content in them by ICP-MS.

#### **SEM Analysis of Coal**

Coal samples were collected and analyzed by scanning electron microscope (SEM-EDS) housed at the Advanced Microscopy Lab, Department of Geology, University of Delhi. Elemental composition was identified through energy dispersive spectroscopy (EDS) embedded onto the SEM. The SEM analysis of coal samples showed the presence of fluorine peak (Fig.4). According to the SEM analysis, coal sample of Kakri coal mine has fluorine concentration of 0.873 weight % and 0.77 atomic % as shown in Figure 4. Coal contains small amounts of fluorine, and coal-fired power plants constitute the largest source of anthropogenic HF emissions (http://www.atsdr. cdc.gov).

### **Petrographical Study of Granite**

The soils developed in the Sonbhadra district are derived from the underlying bedrocks of Archaean to Proterozoic era. They consist of sandstones, limestone, phyllites, shale, slate and granite (Mishra and Mishra, 2013). They are products of weathering, erosion, deposition, and leaching over a long period of time. The study area lies on Dudhi granite which is a part of Precambrian Chotanagpur Granite Gneiss Complex(Mazumdar, 1988; Banerji, 1991; Singh and Srivastava, 2011). Hence sampling was focussed on the granitic terrain. 7 granite



**Fig.3.** Piper diagram showing concentration of various cations and anions in the water samples collected from the study area. (For description see text)



**Fig.4.** Back Scatter SEM image of one spot on the coal sample collected from Kakri mining area showing presence of F and As peak in the graph & Elemental composition as obtained by SEM analysis for coal sample of Kakri mining area.



Fig.5. Petrography of Pink Granite Samples showing presence of Qtz: Quartz, Feldspar: Fel, Apt: Apatite, Bt: Biotite, Hbl: Hornblende, Epd: Epidote.



samples were collected from various areas to the east of Rihand reservoir. The rocks are medium to coarse-grained and composed of pink feldspars, bluish grey or white translucent to opaque quartz, biotite, and hornblende. Thin section studies show presence of apatite in the samples (Fig.5). The minerals apatite, hornblende and biotite are present in the rock samples. These minerals contain fluorine which substitutes for hydroxyl in the crystal lattices (Edmunds and Smedley, 2005). Hence the basement and weathered rocks of the area contain substantial quantities of these F-bearing minerals, especially in the porphyritic pink granites. Fluoride bearing minerals presence in the granite samples are shown by petrography study and XRD analysis (Fig.6).

#### CONCLUSION

The chemical composition of water samples of the area shows dominance of high sulphate and high carbonate water types due to the presence of many thermal power plants and coal mining activities. The discharges (rich in  $H_2SO_4$ ) from TPPs increase the sulphate content in water. High fluoride concentration is observed in ground water, surface water, slurry water, fly ash, soil and coal samples as detected by ICP-MS. Fluorine is observed in coal samples with the help of SEM analysis and fluoride bearing minerals are found in pink granite samples. Coal, fly ash, slurry water of TPPs along with fluorapatite bearing pink granite have contributed towards fluoride contamination in the surface and sub-surface water in the study area. Rapid industrialization in the study area; increased coal mining activities and installation of super thermal power plants to meet the increasing demand power. This led to the contamination of fluoride in study area. So the source of this contamination is both anthropogenic (coal mining, coal used in thermal power plant, improper fly ash disposal) in the western portion of the study area and geogenic (apatite bearing pink granites) in the eastern portion of the area.

Acknowledgements: The authors express sincere and deep sense of gratitude to the University of Delhi for providing financial support to carry out the field work and analysis under R&D project during 2011-2013 sanctioned to Prof. C.S. Dubey. Part of this work was supported by DST- SERB Funded Project No. SR/FTP/ERS-6/2013 sanctioned to Dr. D. P. Shukla, Department of Geology, University of Delhi. The authors would like to acknowledge and highly appreciate to anonymous reviewers for the constructive and suggestive comments which have improved the manuscript.

#### References

- Aggrawal, P., Mittal, A., Prakash R., Kumar M. and Tripathi, S. K. (2011) Contamination of Drinking Water due to Coal-Based Thermal Power Plants in India. Environ. Forensics, v.12(1), pp.92-97.
- Alloway, B.J. And Ayres, D.C. (1997) Chemical principles of environmental pollution, In: Wastes and their disposal (2nd Ed.). Blackie Academy. Professional, London, UK, pp.353-357.
- Ando, M., Tadano, M., Asanuma, S., Tamura, K., Matsushima, S., Watanabe, T., Kondo, T., Sakurai, S., Ji, R., Liang, C. and Cao, S. (1998) Health effects of indoor fluoride pollution from coal burning in China. Environ. Health Perspect, v.106(5), pp.239-244.
- Banerji, A. K. (1991) Geology of the Chhotanagpur region. Indian Jour. Geol, v.63(4), pp.275-282.
- Beg, M., Srivastav, S. and Carranza, J. (2011) High fluoride incidence in groundwater and its potential health effects in parts of Raigarh District, Chhattisgarh. Curr. Sci., v.100(5), pp.750-754.
- Chakrabarti, S. and Bhattacharya, H.N. (2013) Inferring the Hydro-Geochemistry of Fluoride Contamination in Bankura District, West Bengal: A Case Study. Jour. Geol. Soc. India, v.82, pp.379-391.
- Chakraborti, D., Das, B., and Murrill, T.M. (2011) Examining India's Groundwater Quality Management. Environ. Sci. Technol., v.45, pp.27–33.
- Christopher, S., Donald, W.M., Bahadurb, N.P. and Boocock, D.G.B. (2002) A suite of multi-segment fugacity models describing the fate of organic

contaminants in aquatic systems: application to the Rihand Reservoir, India. Water Res., v.36, pp.4341–4355.

- Churchill, H.V., Rowley, R.J. and Martin, L.N. (1948) Fluorine content of certain vegetation in Western Pennsylvania area. Anal. Chem., v.20(1), pp.69-71.
- CSE (2011) Mercury pollution in Sonbhadra district of Uttar Pradesh and its health impacts. (http://www.cseindia.org/userfiles/singrauli\_delhi\_ meeting\_CB.pdf) Centre for Science and Environment.Tughlakabad Institutional Area, New Delhi -110062
- Dhar, B.B., Ratan, S. and Jamal, A. (1986) Impact of opencast coal mining on water environment-a case study. Jour. Mines, Metals and Fuels, v.34, pp.596–601.
- Dubey, C.S., Mishra, B.K., Shukla, D.P., Singh, R.P., Tajbhakh, M. and Sakhare, P. (2012) Anthropogenic arsenic menace in Delhi Yamuna Flood Plains. Environ. Earth Sci., v.65(1), pp.131-139, DOI 10.1007/s12665-011-1072-2 \_ Springer-Verlag.
- Duraiswami, R.A. and Patankar, U. (2011) Occurrence of Fluoride in the Drinking Water Sources from Gad River Basin, Maharashtra Jour. Geol. Soc. India, v.77, pp.167-174
- Edmunds, W.M. and Smedley, P.L. (2005) Fluorine in natural waters occurrence, controls and health aspects. *In:* O. Selnius (Ed.), pp.301-329.
- Finkelman, R.B., Belkin, H.E. and Zheng, B. (1999) Health impacts of domestic coal use in China. Colloquium Paper Proc. Natl. Acad. Sci. USA v.96, pp.3427–3431. Available Online at www.pnas.org. (http://www.pnas.org/ content/96/7/3427.full.pdf)
- Gautam, A. and Tripathi, R.C. (2005) Fluoride testing and fluorosis mitigation in Sonbhadra district. Peoples, Science Institute, Dehradun, pp.1-11. (http:/ /econpapers.repec.org/paper/esswpaper/id\_3a1853.htm; accessed on 26th Aug 2016).
- GSS (2004) Urgent Appeals Programme to Asian Human Rights Commission. Gram Swarajya Samithi (a local human rights organization in Sonbhadra district, UP), pp.1–2; http://www.foodjustice.net/ha/mainfile.php/ha2007/ 87.
- Gupta S.K. and Deshpande, R.D. (1998) Depleting Groundwater Levels and Increasing Fluoride Concentration in Villages of Mehsana District, Gujarat, India: Cost to Economy and Health, report sponsored by Habitat International coalition.
- Hasan, M.A., Ahmed, K.M., Sracek, O., Bhattacharya, P., Von Brömssen, M., Broms, S. Fogelström, J., Mazumder, M.L. and Jacks, G. (2007) Arsenic in shallow groundwater of Bangladesh: investigations from three different physiographic settings. Hydrogeol. Jour., v.15, pp.1507–1522.
- Hota, R.N., Adhikari, P.C., Mohanty, A. and Maejima, W. (2012) Cyclic Sedimentation of the Barakar Formation, Singrauli Coalfield, India. Statistical Assessment from Borehole Logs. Open Jour. Geol., v.2, pp.1-13.
- http://www.atsdr.cdc.gov: Fluorides, hydrogen fluoride, and fluorine; potential for human exposure. pp. 203-242. http://www.atsdr.cdc.gov/toxprofiles/ tp11-c6.pdf.
- Hussain (2012) Geography of India. 3<sup>rd</sup> Ed. Tata Macgraw Hill McGraw-Hill Education India Pvt.Ltd - New Delhi
- Jha, S.K., Nayak, A.K., Sharma, Y.K., Mishra, V.K. and Sharma, D.K. (2008) Fluoride Accumulation in Soil and Vegetation in the Vicinity of Brick Fields. Bull. Environ. Contam. Toxicol., v.80, pp.369-373.
- Keith, L.H. (1991) Environmental Sampling and Guide, Boca Raton, USA. Lewis Publishers, 523p.
- Kumar, A. and Ahmad, T. (2007) Geochemistry of mafic dykes in part of Chotanagpur gneissic complex: Petrogenetic and tectonic implications. Geochem. Jour., v.41, pp.173-186.
- Larry, T. (2002) Coal Geology, John Wiley & Sons, 384p.
- LI, J. and Cao, S. (1994) Recent studies on endemic fluorosis in China. Fluoride, v.27(3), pp.125-128.
- Liu, G., Zheng, L.G., Duzgoren-Aydin Nurdan, S. and Gao, L.F. (2006) Toxic trace elements As, F and Se in Chinese indoor coals combustion and their health implications. Rev. Environ. Contamin. Toxic., v.189, pp.89-106.
- Liu, G., Zheng, L., Qi, Ci. and Zhang, Y. (2007) Environmental geochemistry and health of fluorine in Chinese coals. Environ. Geol., v.52, pp.1307-1313.
- Mahadevan, T.M. (2002) Geology of Bihar and Jharkhand. Jour. Geol. Soc. India, 563p.
- Mazumdar, S.K. (1988) Crustal evolution of the Chhotanagpur Gneissic Complex and the Mica belt of Bihar. In: D. Mukhopadhyay (Ed.),

Precambrian of Eastern Indian shield. Mem. Geol. Soc. India, no.8, pp.49-83.

- Mishra, B.K., Dubey, C.S., Dericks, P.S., Bhattacharya, P. and Usham, A.L. (2014) Concentration of arsenic by selected vegetables cultivated in the Yamuna flood plains (YFP) of Delhi, India. Environ. Earth Sci., v.72(9), pp.3281–3291. DOI 10.1007/s12665-014-3232-7.
- Mishra, S. and Mishra, M. (2013) Role of Biofertilizers in maintaining nutritional status of soil in Sonbhadra and Mirzapur districts of Eastern U.P., India. IJHSSI, v.2(5), pp.23-30.
- Mohan, K., Srivastava, V. and Singh, C.K. (2007) Pattern and genesis of lineament in and across Son-Narmada lineament zone in a part of Central India around Renukoot District Sonbhadra, U.P. Jour. Indian Soc. Remote Sens., v.35(2), pp.193–200.
- Muralidharan, D. (2011) Vicious cycle of fluoride in semi-arid India a health concern. Curr. Sci., v.100 (5), pp.638-640.
- NIC (2010)National Informatics Centre. 2010 (http://singrauli.nic.in/ abtsing.htm)
- NTPC (1995) Environmental study of Singrauli area (study conducted by Electricit!e de France International). National thermal power corporation, India NTPC, Government of India.
- Prasad, B. And Mondal, K. K. (2006) Leaching Characteristics of Fluoride from Coal Ash. Asian Jour. Water, Environ. Pollution, v.4(2), pp.17-21.
- Raju, N.J., Dey, S. and Das, K., (2009) Fluoride contamination in groundwater of Sonbhadra District, Uttar Pradesh, India. Curr. Sci., v.96(7), pp.979-985.
- Rao, N.S., Dinakar, A., Rao, P.S., Rao, P.N., Madhnure, P., Prasad, K.M. and Sudarshan, G. (2016) Geochemical Processes Controlling Fluoride-bearing Groundwater in the Granitic Aquifer of a Semi-arid Region. Jour. Geol. Soc. India, v.88, pp.350-356.
- Rao, P.N., Rao, A.D., Bhargav, J.S., Sankar, K.S. and Sudarshan, G. (2014) Regional Appraisal of the Fluoride Occurrence in Groundwaters of Andhra Pradesh. Jour. Geol. Soc. India, v.84, pp.483-493.
- Ren, D.Y., Zhao, F.H., Wang, Y.Q. and Yang, S.J. (1999) Distributions of minor and trace elements in Chinese coals. Int. Jour. Coal Geol., v.40, pp.109–118.
- Routroy, S., Harichandan, R.S., Mohanty, J.K. and Panda, C.R. (2013) A Statistical Appraisal to Hydrogeochemistry of Fluoride Contaminated Ground Water in Nayagarh District, Odisha Jour. Geol. Soc. India. v81, pp.350-360.
- Saha, D., Singh, B. ., Srivastavai, S.K., Dwivedi, S.N. and Mukherjee, R., (2014) A concept note on geogenic contamination of ground water in India with a special note on nitrate. CGWB report.

- Schroder, H.F. (1993) Pollutants in drinking water and waste water. Jour. Chromatography, v.643(1-2), pp.583-595
- Schroder, H. Fr. and Fytianos, K. (1999) Organic Pollutants in Biological Waste Water Treatment. Results of Mass and Tandem Mass Spectrometry of the Flow Injection Mode Compared with Liquid Chromatographic Examinations: Polar Compounds under Positive Ionization. Chromatographia, v.50(9/10), pp.583-595
- Shukla, D.P., Dubey C.S., Ningthoujam P., Tajbakhsh, M. and Chaudhry, M. (2010) Sources and Controls of Arsenic Contamination in Groundwater of Rajnandgaon and Kanker District, Chattisgarh Central India. Jour. Hydrol., v.395, pp.49-66.
- Singh, B.D. (1995) Lower Gondwana (Permian) coals of Peninsular India: environment of deposition related to organic petrographic types. Proc. Indian National Science. Academy, v.61, (A, No.6), pp.371-394.
- Singh, C.K. and Srivastava, V. (2011) Morphotectonics of the area around Renukoot, district Sonbhadra, U.P. Using Remote Sensing and GIS Techniques, Jour. Indian Soc. Rem. Sens., v.39(2), pp.235-240.
- Singh, P.K., Singh, M.P., Volkmann, N., Naik, A.S. and Borner, K. (2014) Petrological characteristics of lower Gondwana coal from Singrauli coalfield, Madhya Pradesh, India. Int. Jour. Oil Gas Coal T., v.8(2), pp.194-220.
- Srivastava, V. and Srivastava, H.B. (2012) Analysis of folds from the CGGC rocks in Sonbhadra district Uttar Pradesh and their tectonic and geomorphic Implications Journal of Scientific Research Banaras Hindu University, Varanasi. v. 56, pp.1-18.
- Srivastava, V. and Gairola, V.K. (1997) Harmonic classification of multilayered folds: example from central India. Jour. Struct. Geol., v.19(1), pp.107-112.

Susheela A.K. (2007) A treatise on fluorosis. 3rd ed. Delhi: FR & RDF

- Swaine, D.J. (1990) Trace Elements in Coal. Butterworths, London, pp. 109– 386.
- Usham, A.L., Dubey, C.S., Ningthoujam, P.S., Mishra, B.K., Shukla, D.P., Singh, R.P., Naorem S.S., Thoithoi, L. and Singh, N. (2012) Source of Arsenic Contamination in Kakching Area, Manipur. Annual International Conference on Geological &Earth Sciences (GEOS 2012), pp.82-86, DOI:10.5176/2251-3361\_GEOS12.
- Watanabe, T., Kondo, T., Asanuma, S., Ando, M., Tamura, K., Sakuragi, S., Rongdi, J. and Chaoke, L. (2000) Skeletal Fluorosis from Indoor Burning of Coal in Southwestern China. Fluoride, v.33(3), pp.135-139.
- Yan, R., Gautheir, D. and Flamant, G. (1999) Thermodynamic study of the behavior of minor coal elements and their affinities to sulfur during coal combustion. Fuel, v.78, pp.1817–1829.

(Received: 20 March 2017; Revised form accepted: 7 June 2017)