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ASSESSMENT OF SOME HEAVY METALS TOXICITY AND ITS PROBABLE REMEDIATION IN GROUNDWATER AROUND TELWASA AND GHUGUS AREA OF WARDHA VALLEY COALFIELDS, MAHARASHTRA

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Abstract

Present study is about the groundwater quality assessment in terms of heavy metals contamination and deducing feasible remediation around Telwasa and Ghugus area of Wardha Valley Coalfields, Maharashtra. Among analysed heavy metals, Cd, Fe, Pb and Ni were found to be in contamination level for both seasons. Pre-monsoon samples are more contaminated than post-monsoon. These contaminations make water unsuitable for drinking purpose. Sampling locations and corresponding contaminations signifies mining region as a prime source. On correlation analysis, pH of samples was found to be in negative relationship with corresponding metals value, signifying lower pH value favours contamination. Field observation revealed that the sulphur leaching produces acid mine drainage (AMD) in turn lowering the pH of mine discharge. To overcome, pH of mine discharge should be checked to regulate the groundwater acidity. An artificially prepared vertical flow system with anaerobic wetland and limestone bed can be used to precipitate dissolved metals and improve alkalinity of the mine discharge.

Keywords – Heavy metals, Acid mine drainage, Wardha valley coalfields, Vertical flow system.

Introduction

The natural quality of groundwater is controlled by the geochemistry of the lithosphere, the solid portion of the earth, and the hydrochemistry of the hydrosphere, the aqueous portion of the earth (Satapathy et al., 2009). Suitability of groundwater/surface water for a particular purpose depends upon the acceptable water quality standards for which it is being used (WHO, 1984; USPHA, 1993). The usual quality of groundwater is hampered by the anthropogenic activity such as coal mining. Coal fields are the economy boosters for any nation but groundwater quality in and around them have become one of the most fragile issue. Mismanaged and intense mining has troubled the groundwater regime in many settings, especially in terms of heavy metals. Several studies have shown that most of the contaminations in coalmines can be released into the surrounding environment by leaching, and more attention should be paid to this kind of contamination (Filcheva and Noustorova 2000; Haigh 1995; Krothe et al. 1980; Li 1988). Heavy metals are the persistent environmental contaminants because they cannot be degraded or destroyed and can stay for a long period of time in the surrounding. Slowly they bio-accumulates in vegetation through contaminated water used for irrigation and then to other living beings. The heavy metal exists in different chemical compounds and tends to occur in associations, such as sulphides of lead and cadmium naturally occur together with sulphides of iron (FeS_2) and copper ($CuFeS_2$) as minors. Otherwise being recessive, on exposure to certain chemical situation, they became dominant and are released out by every possible means. Although most of the major and trace metals are generally considered to be relatively immobile in the short term and their mobility under certain chemical conditions may exceed the ordinary rates leading to cause a major threat (Scokart et al., 1983). In the present study, groundwater quality for heavy metal toxicity is assessed in Telwasa and Ghugus area of Wardha valley coalfields. The present work will not only untangle the contamination issues but also performs correlation studies to understand the dissolution as well as migration process. The data generated from the present work could provide a feasible remediation policy.

Study area and Geology

The study area is partially divided into Yavatmal (Yeotmal) and Chandrapur districts by the Wardha River with Latitude 19^0 55’ 00’’ N to 20^0 02’ 00’’ N, and Longitude 79^0 02’ 00” E to 79^0 10’ 00” E, covering approximately 14 km^2 area traceable on toposheet no 55P/4 and 56 M/1(Figure 1). The continuous mining in the area since many decades has cost a lot to water quality (Singh and Chandra, 1983). The study area is a part of the Godavari Valley Gondwana basin, located on the western limb of anticline plunging towards NNW. The study area consists of the basement rock of Archean which includes quartzites, granite gneisses, etc (Table 1). The Kamthi Formation of the Gondwana Supergroup is mainly comprised of rocks like red-brown sandstone and variegated

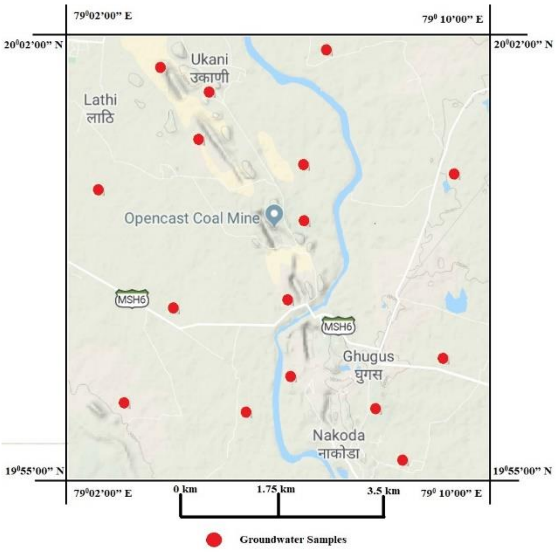

Figure 1: Map of study area showing groundwater sampling locations.

Age	Group/Formation	Lithology
Recent	-	Alluvial gravel bed, black cotton soil
Eocene	Deccan Trap	Basalts
-------------Unconformity------------		
Cretaceous	Lameta Formation	Limestone, charts and silicified sandstone
-------------Unconformity------------		
Late Triassic	Maleri Formation(To SE)	Fine to med. grained sandstone and red shale
Late Permian-Early Triassic	Kamthi Formation	Red, brown sandstone, reddish siltstone and variegated shale & sandstone
-------------Unconformity------------		
Early Permian	Barakar Formation	Light grey to white sandstone, shale & coal seam
Late Carboniferous-Early Permian	Talchir Formation	Tillites, turbidites, varves, needles shale & sandstone
-------------Unconformity------------		
Precambrian	Sullavai Sandstone	White and light brown quartzitic sandstone
-------------Overlap-----------		
	Pakhal Limestone	Grey, bluish or pinkish limestone and chert
-------------Unconformity------------		
Archean		Quartzite, Granite Gneisses, etc.

Table 1: General Geological succession from Wardha Valley Coalfield, Maharashtra, (after, Raja Rao 1982.)

shales, which are underlain by the grey to white sandstone belonging to the Barakar Formation. One persistent coal seam of the Wardha valley is confined to the Barakar Formation. The rocks of the Barakar Formation are underlain by the shale and sandstone of the Talchir Formation (Table 1).

Methodology

16 representative groundwater samples (*09 deep and 07 shallow*) for each pre- and post-monsoon were collected in May 2019 and October-November, 2019 respectively (Fig. 1). The samples were collected in 500 ml of pre-washed narrow mouth high density polyethylene bottles rinsed with the sample water. The turbid samples were first filtered on sampling sites. In order to prevent or minimize any physical, chemical or biochemical change in the sample, they were treated with HNO_3 and put in an ice bath and kept approximately at 4°C until analysis in the laboratory (APHA, 1998).The bottles were air tightened and labelled systematically. The pH was measured on the spot using digital pH meter. After the preliminary treatment, samples were digested by HNO_3 and Aluminium (Al), Cadmium (Cd), Chromium (Cr), Copper (Cu), Iron (Fe), Nickel (Ni), Lead (Pb), and Zinc (Zn) using AAS (GBC SavantAA, Australia). For the

metals having very low concentration, ultrapure water was used to prepare the blank and standards with great precision. The standard solutions of 05 µg/l, 10 µg/l and 20 µg/l were used for each Cd, Ni and Pb. For Al, Cr and Fe standard solution set of 50 µg/l, 150 µg/l and 300 µg/l were used. The standards of 500 µg/l and 1000 µg/l were used for Cu, whereas for Zn 0.5 mg/l and 1 mg/l were used. ICP-MS was also outsourced for those samples where few radicles were below detection limit. The statistical tools were applied on the generated data to deduce relevant inferences.

Result and Discussion

The values obtained for the heavy metals in groundwater samples for both the seasons were compared with the values of maximum permissible limit (in absence of alternate source) suggested by Bureau of Indian Standards for drinking water (BIS 2012).

Sample	pH	Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn
		***(200)**	**(3)**	**(50)**	**(1500)**	**(300)**	**(20)**	**(10)**	**(15000)**
GW1	4.9	180	*8*	44	620	*360*	*34*	*14*	186
GW2	4.8	144	*26*	38	455	*450*	*43*	*22*	1620
GW3	4.9	150	*14*	40	330	*424*	*38*	*21*	515
GW4	5.6	48	ND	ND	100	120	12	ND	300
GW5	6.1	33	ND	14	165	145	11	2	159
GW6	5.5	89	ND	ND	55	160	8	ND	400
GW7	4.2	120	*12*	49	710	*340*	*36*	*16*	320
GW8	4.4	168	*27*	41	540	*624*	*54*	*22*	1050
GW9	4.4	177	*22*	32	440	*540*	*48*	*28*	830
GW10	5.9	40	ND	22	200	50	19	3	128
GW11	5.7	49	ND	18	178	98	ND	2	465
GW12	4.0	108	*3*	38	332	280	*22*	*16*	893
GW13	4.8	160	*7*	41	530	*330*	*27*	*20*	665
GW14	6.0	20	ND	10	ND	66	ND	2	328
GW15	5.0	160	*9*	30	210	*373*	*33*	*24*	123
GW16	4.7	149	*26*	28	334	*460*	*27*	*18*	220
Min.	**4**	**20**	**ND**	**ND**	**ND**	**50**	**ND**	**ND**	**123**
Max.	**6.1**	**180**	**27**	**49**	**710**	**624**	**54**	**28**	**1620**
Arithmetic Mean	**5.05**	**112.18**	**15.4**	**31.78**	**346.60**	**301.25**	**29.42**	**15**	**512.6**
Std. Deviation	**0.66**	**57.15**	**9.04**	**11.94**	**197.55**	**133.37**	**14.03**	**9.08**	**410.86**

**Maximum permissible limit by BIS (2012). ND – Not Determined*

Table 2: Results obtained from groundwater analysis in µg/l for pre-monsoon

Pre-monsoon

On analysing 16 groundwater samples for the pre-monsoon season, 10 samples were found to be contaminated in terms of Cd, Fe, Ni and Pb whereas Al, Cr, Cu, and Zn, were under maximum permissible limit (Table 2). The high value of Cd were observed at 10 sampling locations, like GW1 (08 µg/l), GW2 (26 µg/l), GW3 (14 µg/l), GW7 (12 µg/l), GW8 (27 µg/l), GW9 (22 µg/l), GW12 (03 µg/l), GW13 (07 µg/l), GW15 (09 µg/l) and GW16 (26 µg/l) with maximum permissible limit of 3 µg/l (Table 2). The Fe content was above maximum permissible limit in 09 samples GW1 (360 µg/l), GW2 (450 µg/l), GW3 (424 µg/l), GW7 (340 µg/l), GW8 (624 µg/l), GW9 (540 µg/l), GW13 (330 µg/l), GW15 (373 µg/l) and GW16 (460 µg/l) with maximum permissible limit of 300 µg/l (Table 2). The Ni content was above the permissible limit of 20 µg/l for GW1 (34 µg/l), GW2 (43 µg/l), GW3 (38 µg/l), GW7 (36 µg/l), GW8 (54 µg/l), GW9 (48 µg/l), GW12 (22 µg/l), GW13 (27 µg/l), GW15 (33 µg/l) and GW16 (27 µg/l) (Table 2). The values obtained for Pb at GW1 (14 µg/l), GW2 (22 µg/l), GW3 (21 µg/l), GW7 (16 µg/l), GW8 (22 µg/l), GW9 (28 µg/l), GW12 (16 µg/l), GW13 (20 µg/l), GW15 (24 µg/l) and GW16 (18 µg/l) were above maximum permissible limit of 10 µg/l (Table 2).

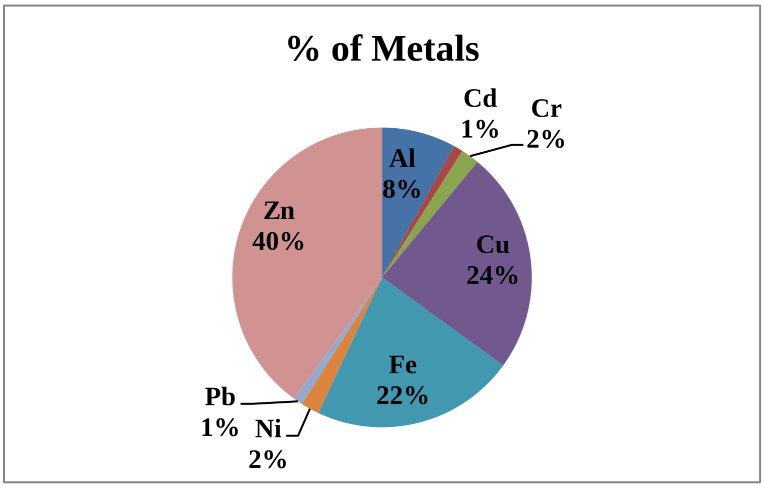

Figure 2: Percentage contribution of each metal in groundwater sample for pre-monsoon.

The percentage contribution of each metal in groundwater samples in pre-monsoon is observed as Al (08 %), Cd (01 %), Cr (02 %), Cu (24 %), Fe (22 %), Pb (02 %), Ni (01 %), and Zn (40 %) (Figure 2). The correlation studies have revealed negative relationship of pH values of samples with their corresponding metals

Parameters	pH	Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn
pH	1								
Al	-0.79	1							
Cd	-0.64	0.74	1						
Cr	-0.78	0.74	0.58	1					
Cu	-0.76	0.74	0.59	0.90	1				
Fe	-0.79	0.90	0.91	0.70	0.69	1			
Ni	-0.75	0.85	0.83	0.77	0.77	0.92	1		
Pb	-0.80	0.89	0.79	0.79	0.68	0.91	0.88	1	
Zn	-0.49	0.37	0.56	0.36	0.34	0.52	0.50	0.48	1

Table 3: Correlation coefficient matrix for pre-monsoon groundwater parameters.

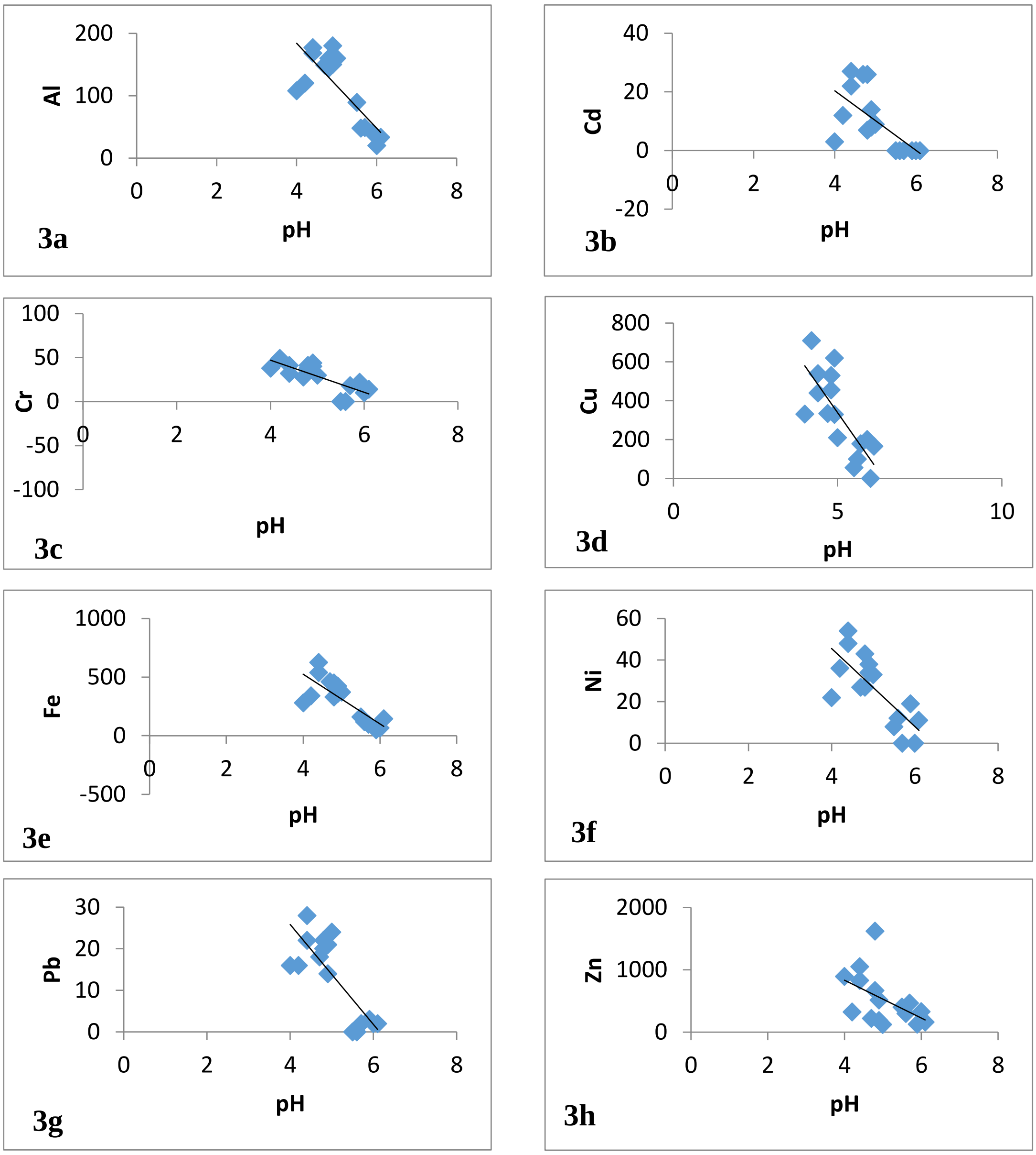

Figure 3: Correlation coefficient of pH for groundwater with; a. Aluminium, b. Cadmium, c. Chromium, d. Copper, e. Iron, f. Nickel, g. Lead and h. Zinc for pre-monsoon.

concentration (Figure 3). The correlation coefficient analysis of Al, Cr, Cu, Fe, Ni and Pb are above – 0.75 indicating their close affinity. All metals are in strong positive relationship among them (Table 3).

Post-monsoon

For the post-monsoon season, Cd, Fe, Ni and Pb were found to be in contamination. The concentration of Cd with the maximum permissible limit of 3 µg/l, indicated the contamination of 08 samples like GW1 (03 µg/l), GW2 (12 µg/l), GW3 (08 µg/l), GW7 (06 µg/l), GW8 (12 µg/l), GW9 (10 µg/l), GW13 (10 µg/l), and GW16 (21 µg/l) (Table 4). The 09 samples for Fe were above maximum permissible limit of 300 µg/l; GW1 (298 µg/l), GW2 (360 µg/l), GW3 (332 µg/l), GW7 (322 µg/l), GW8 (498 µg/l), GW9 (367 µg/l), GW12 (305 µg/l), GW15 (324 µg/l) and GW16 (400 µg/l) (Table 4). The values for Ni at GW1 (25 µg/l), GW2 (31 µg/l), GW3 (28 µg/l), GW7 (20 µg/l), GW8 (32 µg/l), GW9 (40 µg/l), GW13 (20 µg/l), and GW16 (33 µg/l) were above the permissible limit of 20 µg/l (Table 4). The Pb content at GW1 (12 µg/l), GW2 (16 µg/l), GW3 (20 µg/l), GW7 (14 µg/l), GW8 (10 µg/l), GW9 (23 µg/l), GW12 (11 µg/l), GW13 (20 µg/l), GW15 (17 µg/l) and GW16 (17 µg/l) were above maximum permissible limit of 10 µg/l (Table 4).

Sample	**pH**	**Al**	**Cd**	**Cr**	**Cu**	**Fe**	**Ni**	**Pb**	**Zn**
		***(200)**	**(3)**	**(50)**	**(1500)**	**(300)**	**(20)**	**(10)**	**(15000)**
GW1	5.6	98	*3*	40	480	*298*	*25*	*12*	144
GW2	6.2	123	*12*	22	444	*360*	*31*	*16*	870
GW3	6.0	134	*8*	39	279	*332*	*28*	*20*	415
GW4	6.9	56	ND	ND	221	47	ND	ND	302
GW5	7.4	20	ND	ND	118	130	ND	2	168
GW6	6.2	89	2	12	16	98	16	ND	325
GW7	5.4	126	*6*	25	661	*322*	*20*	*14*	300
GW8	5.7	102	*12*	32	364	*498*	*32*	*10*	680
GW9	5.9	75	*10*	41	167	*367*	*40*	*23*	490
GW10	7.2	62	ND	12	241	24	12	3	55
GW11	6.3	81	ND	26	ND	168	ND	2	60
GW12	5.4	44	ND	19	229	*305*	19	*11*	210
GW13	5.8	112	*10*	42	460	247	*20*	*20*	441
GW14	6.2	38	ND	ND	ND	48	ND	2	400
GW15	6.1	10	ND	24	321	*324*	ND	*17*	120
GW16	5.9	70	*21*	32	122	*400*	*33*	*17*	40
Min.	**5.4**	**10**	**ND**	**ND**	**ND**	**24**	**ND**	**ND**	**40**
Max.	**7.4**	**134**	**21**	**42**	**661**	**498**	**40**	**23**	**870**
Arithmetic Mean	**6.16**	**77.5**	**9.33**	**28.15**	**294.5**	**248**	**25**	**12**	**313.75**
Std. Deviation	**0.58**	**37.66**	**5.67**	**10.48**	**173.54**	**143.7**	**8.47**	**7.36**	**232.89**

**Maximum permissible limit by BIS (2012). ND – Not Determined*

Table 4: Results obtained from groundwater analysis in µg/l for post-monsoon.

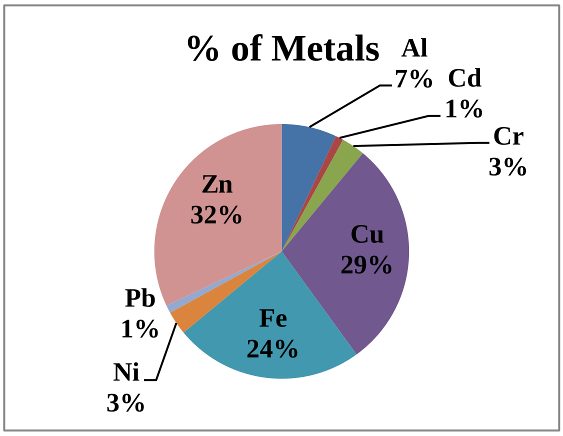

Figure 4: Percentage contribution of each metal in groundwater sample for post-monsoon

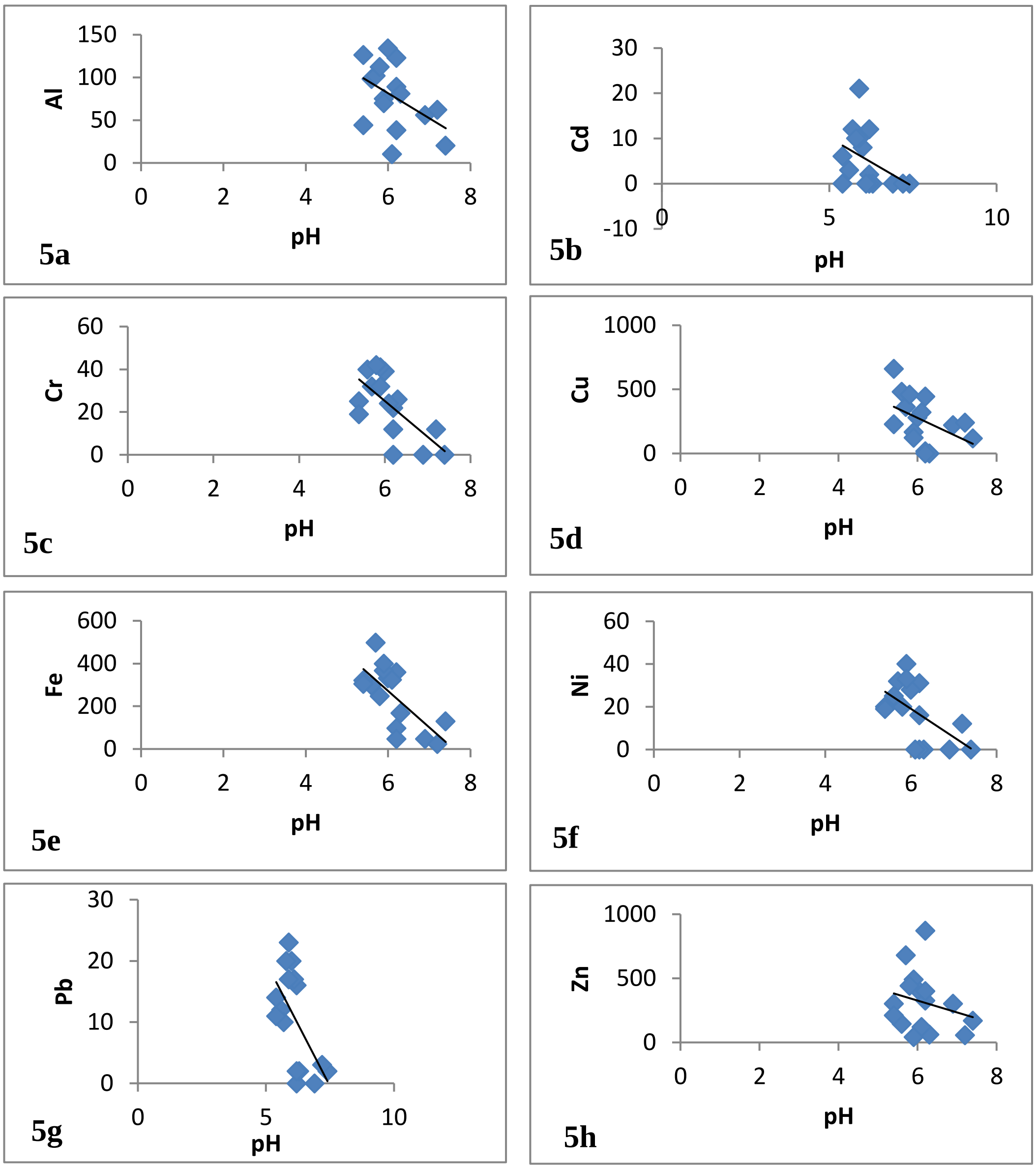

Figure 5: Correlation coefficient of pH for groundwater with; a. Aluminium, b. Cadmium, c. Chromium, d. Copper, e. Iron, f. Nickel, g. Lead and h. Zinc for post-monsoon.

The percentage contribution of each metal in groundwater samples in the post-monsoon was observed as Al (07 %), Cd (01 %), Cr (03 %), Cu (29 %), Fe (24 %), Pb (03 %), Ni (01 %), and Zn (32 %) (Figure 4). The pH of the samples is again in negative relationship with metals concentration in them, but with the mild strength when compared to the pre-monsoon season (Figure 5). Only Cr, Fe, Ni and Pb are the radicals showing correlation coefficient above – 0.50. All metals show the moderate positive relationship among them (Table 5).

Parameters	pH	Al	Cd	Cr	Cu	Fe	Ni	Pb	Zn
pH	1								
Al	-0.45	1							
Cd	-0.39	0.51	1						

Cr	-0.66	0.59	0.59	1					
Cu	-0.44	0.52	0.25	0.45	1				
Fe	-0.69	0.40	0.70	0.74	0.48	1			
Ni	-0.56	0.63	0.79	0.72	0.37	0.74	1		
Pb	-0.59	0.39	0.64	0.81	0.51	0.77	0.70	1	
Zn	-0.23	0.50	0.38	0.16	0.30	0.37	0.47	0.30	1

Table 5: Correlation coefficient matrix for post-monsoon groundwater parameters.

Probable curative measures

The correlation coefficient analysis has disclosed the strong negative relationship between acidic nature of groundwater and metal contaminations. Most of the heavy metals are acid soluble hence, lower pH favours the metal solubility. The sulphur leaching was very distinctly observed during the mine visit (Figure 6). The high Fe concentration indicates the oxidation of pyrite within coal measures and associated strata and removal of oxidation product by in-flowing ground water (Frost, 1979).

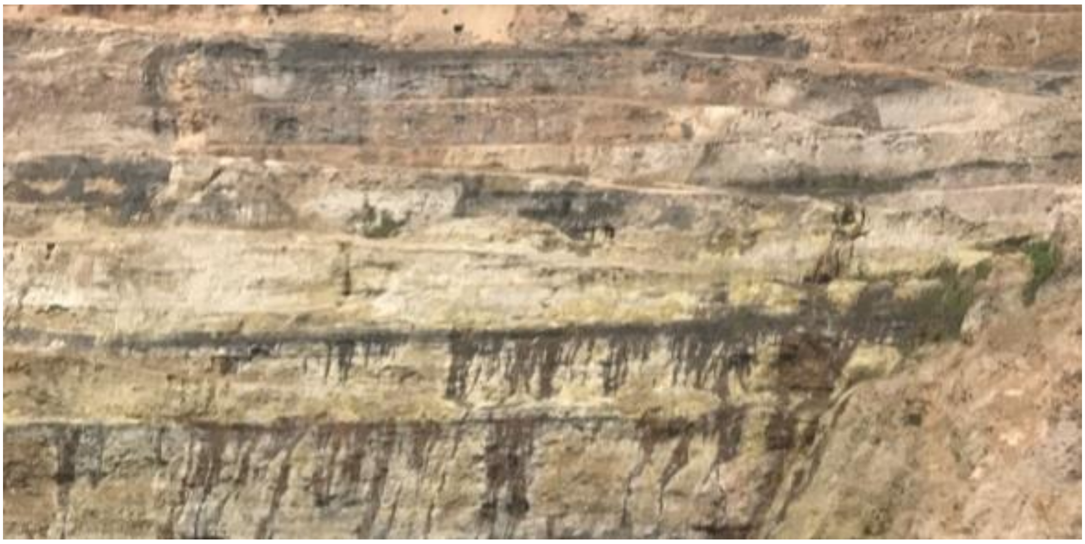

Figure 6: Photograph showing the sulphur leaching in mining region of study area on contact with atmosphere and water.

This sulphur on contact with water and atmosphere creates sulphuric acid (H_2SO_4) which is responsible for the acid mine drainage (AMD) in mine area. The lower pH of samples and respective contaminations could be attributed to the AMD. The AMD is an environmental pollutant that impairs water resources in mining region throughout the world (Zipper et al., 2014; Singh, 1987).To overcome, pH of the drainage water from mine should be checked before discharging into nearby water regime. A vertical flow system of wetland and limestone bed is the cheap and eco-friendly mechanism to treat the AMD. An artificial anaerobic wetland which will turn dissolved metals in drain into sulphides by natural reducing environment and will precipitated accordingly (eq. 1). The resultant bicarbonate (HCO_3^-) will enhance the alkalinity by reducing H^+ ions (eq. 2).

M (Metal) + SO_4^{-2} + $CH_2O \rightarrow MS + HCO_3^-$ (eq.1)

$HCO_3^- + H^+ \rightarrow H_2O + CO_2$ (aq) (eq. 2)

The limestone bed beneath the anaerobic wetland will again boost the alkalinity by limestone dissolution (eq. 3). Ultimately the treated water can now be discharged to the nearby water bodies.

$CaCO3 + H^+ \rightarrow Ca^{2+} + HCO_3^-$ (eq. 3)

Conclusion

On assessing the groundwater samples, majority of them were above maximum permissible limit as per BIS with respect to Cd, Fe, Ni and Pb. Pre-monsoon samples are more contaminated than post-monsoon. The contaminations and corresponding location manifest the mining region as a prime source of these contaminations. The toxicity of these heavy metals makes groundwater unsuitable for drinking purpose at certain sites. The correlation analysis disclosed the inverse relation between pH and metals values of samples. Thus, the lower pH of water enhances the dissolution of heavy metals. The sampling locations, field observation and pH values suggest the role of acid mine drainage in dissolution and migration of heavy metals. High Fe percentage infers oxidation of Pyrite (FeS_2) which on contact with water produces acidic drainage. For the remediation of the enhanced acidic nature of water, a vertical flow system consisting of artificial anaerobic wetland underlain by limestone bed is suggested. This suggested system not only will improve alkalinity but also hold dissolved metals in solid phase by natural reducing environment.

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