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Research Paper

Anthropogenic Influences on the Hydrogeochemistry and Water Quality of Ground Water in Singrauli Power Belt Region, Central India

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This study investigates the groundwater quality of Singrauli power belt region in Central India. Ground water samples were collected from 54 representative sites during pre and post monsoon seasons and analysed for pH, EC, TDS, TH, major ions (Na^{2+}, K^+, Mg^{2+}, Ca^{2+}, SO_4^{2-}, NO_3^-, F^-, Cl^-) and heavy metals (Fe, Cr, Mn). Groundwater samples dominantly belonged to Ca-Mg-HCO_3 water type. Gibbs ratios indicated that rock weathering is the major driving force for controlling the groundwater chemistry. Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} concentrations in the groundwater were well within the permissible limits as recommended by WHO for drinking water. A total of 35% and 44% of the samples during post and pre monsoon season, respectively, had exceeded the F^- concentrations compared to WHO recommended limits of 1.5 mg/L. Likewise, a total of 22% and 26% of the samples had exceeded their regulatory limits of NO_3^- i.e., 45 mg/L during post and pre monsoon seasons, respectively. High fluoride in groundwater near fly ash ponds indicated contamination through leaching from ash ponds. High NO_3^- could be attributed to the formation of nitrogen oxides during coal combustion, their deposition on the surface and subsequently leaching to groundwater. Majority of samples had Fe and Cr concentration exceeding the WHO permissible limits, thus rendering water unfit for drinking purpose. Parameters like percent sodium (%Na), electrical conductivity (EC), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), magnesium hazard (MH) permeability index (PI), chloroalkaline indices (CAI) and Kelly's index suggest that majority of groundwater samples were good for irrigation purpose. The USSL plot suggested that majority of groundwater belonged to C_3S_1 class, representing high salinity hazard and low alkali hazards water, which requires proper drainage otherwise it can adversely affect the soil.

Keywords: Hydrogeochemistry; Major Ions; Heavy Metals; Fluoride; Nitrate

Introduction

Groundwater is a reliable water resource in drought prone Indian subcontinent. Groundwater occurs almost in all the geological formations under the earth's surface (Singh *et al*., 2015). Groundwater supplies are generally free of suspended solids and organic impurities owing to natural filtration process through soils and sediments (Gautam *et al*., 2015). India has the largest user base of groundwater in the world with an estimated consumption of about 230 cubic kilometers per annum (The World Bank, 2010). Nearly 700 million of rural Indians depend on groundwater for their daily needs and nearly 48% of the urban water requirements are met from groundwater (Kulkarni *et al*., 2015). Agricultural sector consumes more than 85% share of groundwater withdrawal in the country (Food and Agricultural Organization, 2013). Anthropogenic activities resulting in its over-exploitation, poor recharge and chemical contamination are major concerns for groundwater sustainability (Shekhar, 2006; Ahada and Suthar, 2018; Chidambaram *et al*., 2018; Kumar *et al*., 2018).

The hydrogeochemical characteristics of groundwater are governed and influenced by groundwater quality and the rock/mineral-water interactions in the sub-surface aquifers and sometimes by intermixing of two different aquifers (Senthilkumar, 2014; Aghazadeh *et al*., 2017; Gan *et al*., 2018).

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Leaching of contaminants of anthropogenic origin does influence the groundwater chemistry (Potapova and Charles 2003; Anshumali *et al*., 2014; Ahada and Suthar, 2017). Once an aquifer contamination occurs due to agricultural, industrial and urban development, it persists for hundreds of years because of very slow movement of water in aquifers (Jerry, 1986; Bikundia and Mohan, 2014).

In this study, we attempt to understand the effects of anthropogenic activities (thermal power plants and coal mining) *vis-a-vis* the rock-water interactions on the groundwater quality in Singrauli industrial region in India.

Study Area

This study was carried out in Singrauli power belt (depicted on the Toposheet No: 63L/12 and 63L/15 of Survey of India) covering the eastern part of Singrauli district of Madhya Pradesh (MP) and southern part of Sonebhadra district of Uttar Pradesh (UP), located in central India (Fig. 1). Singrauli region started emerging as a potential industrial region in the late fifties with the construction of a large-scale dam on the River Rihand, a tributary to River Son which in turn joins River Ganga on its right flank (Anshumali *et al*., 2014). The dam is known as Rihand dam and has an electricity generation capacity of 300 MW. The reservoir named as Govind Ballabh Pant Sagar (GBPS) reservoir is spread over an area of 457 km^2. The capacity of the reservoir is 1,060x10 m^3 and the area of submergence is 46,600 ha (Rai and Tripathi, 2009).

Discovery of coal over an area of 2200 km² in the state of MP (Singrauli District) and UP (Southern part of Sonebhadra District) and availability of water lead to the large scale industrial transformation and development in the entire Singrauli region. Singrauli Coalfields are divided into 11 mining blocks which contributes nearly 13% of India's coal production through mechanized opencast mining. Together, the coal based thermal power plants have an installed electricity generation capacity of nearly 20,000 MW earning the popular name for the region as "Singrauli Power Belt" or 'Energy Capital of India'. Singrauli experiences four seasons, winter, summer/pre monsoon, monsoon/rainy and autumn/post monsoon The normal rainfall of the region is 1132.7 mm and approximately, 89% of the which takes place during monsoon period (CGWB, 2013).

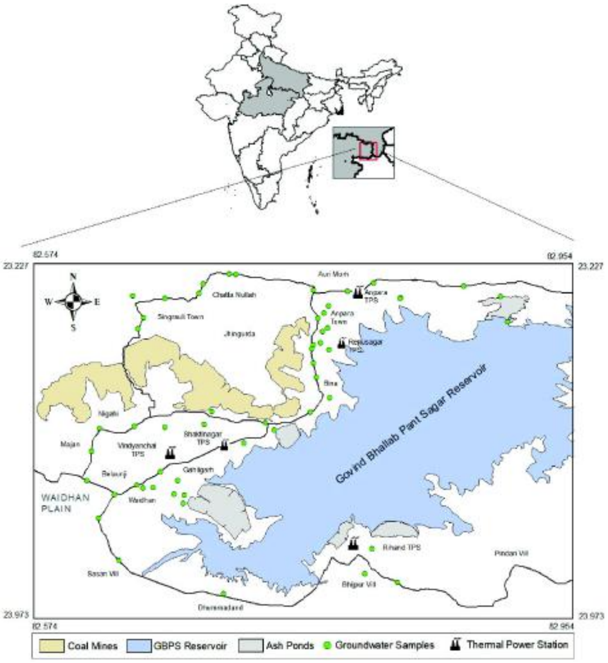


Fig. 1: Map of the study area in Singrauli region in central India showing sampling points for groundwater

Geologically, the sedimentary rock formations in the study area belongs to Vindhyan group (Kaimur and Semri Groups) and Gondwana Supergroups, volcano-sedimentary rock formations of Precambrian Mahakoshal Group and Precambrian Chhotanagpur Granite Gneiss Complex (Srivastava and Srivastava, 2012). The Chhotanagpur Granite Gneiss Complex is represented by the Dudhi Group of rocks comprising mainly of migmatitic granitic gneisses and porphyritic granite, besides numerous metasedimentary enclaves (Kumar and Ahmad, 2007). The study area is structurally very complex and tectonically active (Mohan *et al*., 2007). The coal bearing formations in the area belongs to Permo-Carboniferous Gondwana Supergroup. Predominantly coal belongs to the Barakar Formation, while some areas have Talchir and Raniganj series coals (Usham, 2018). Groundwater regime of the area has undergone significant change due to construction of Rihand dam. Studies carried out by 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). This suggests that the reservoir water recharges the local groundwater system through seepage into the subsurface and water table often rises when the reservoir is filled. Rainfall is the main source for groundwater recharging, apart from seepage from the surface water bodies. The general hydraulic gradient in the area is in conformity with the surface topography and in particular towards river Son and the local subsidiary surface water bodies (Usham, 2018).

Sampling and Analytical Methods

A total of 54 groundwater samples (51 samples from hand pumps and 3 from open wells) were collected during pre and post monsoon seasons in 2015 from different locations in the Singrauli region (Fig. 1). Geographical coordinates of each sampling site were determined using a handheld GPS (Garmin). Prior to the collection, water was pumped out till the in situ parameters were stabilized. The samples were filtered using 0.45 µm pore filters and collected in 250 ml pre cleaned sterilized HDPE bottles. For all collected samples, parameters such as total dissolved solids (TDS), electrical conductivity (EC), oxidation-reduction potential (ORP), temperature (T), salinity and pH were measured in the field using a portable Multi-parameter WTW water analysis kit. The pH-meter was calibrated using standard solution of pH 4, 7 and 10 every day during fieldwork. Each sample was divided in two aliquots, one was stored as it was and the other was acidified using HNO_3 for cation analysis. All sample bottles were sealed properly and brought to the laboratory and stored at 4^{o}C till further analysis.

Groundwater samples were analyzed in our laboratory at School of Environmental Sciences, Jawaharlal Nehru University. Unacidified aliquot of water samples were analyzed for major anions ($F^–$, Cl^-, $NO_3^–$, $SO_4^{2–}$, $PO_4^{2–}$) and acidified aliquot for cations (NH_4^+, Na^+, K^+, Ca^{2+}, and Mg^{2+}) using Metrohm Ion Chromatograph (IC) model882 Compact IC plus1pro1 equipped with conductivity detector. Cations were analyzed using Metrosep C 4-150/4.0 column and dipicolinic acid (0.7 mM) and nitric acid as eluentshaving0.9 ml/min flow rate while anion analysis was done using Metrosep A supp 5-150-4.0 column with bicarbonate 1.0 and 3.2 mM Na_2CO_3 as eluents having 0.7 ml/min flow rate. Field and laboratory blanks were also prepared and analyzed simultaneously with samples. Multi-ion standards procured from E-Merck, Germany were used for calibration of the IC. Concentration of HCO_3 in the groundwater samples was determined by volumetric titration method. The ion concentrations were converted into mill equivalents per liter (meq/L) and the ion balance error (IBE) in the data were calculated. The IBE values were below ±5%, which showed the goodness of analytical procedure.

Metals in the water samples were analyzed on Flame Atomic absorption spectrometer (Model: M-3 Series, Thermo make) installed in our laboratory. Atomic Absorption Spectrometer was calibrated using the standard solutions in the desired range that were prepared by serial dilution method from the single element standard stock solutions of 1000 ppm concentration procured from E-Merck, Germany. The estimated error in the data was less than 10% whereas the precision was well within the limits of 5-7%.

In the primary chemical data based research, it is crucial that the quality of data as represented in their accuracy, precision and blank values were never compromised. Duplicate measurements of pH, EC and TDS were carried out in the collected groundwater samples. The difference of pH values between duplicate analyses were less than 0.03 pH units and in case of EC, a difference of less than 1 ìS/cm was acceptable. Analysis of field and laboratory blanks showed that contamination during the sampling, sample transport and treatment, and analysis was minimal. Analytical uncertainties were estimated by calibrating the IC with freshly prepared working standard solution of 1 ppm, from a 1000 ppm stock solution. The variation in peak area was found to be less than 5%. The detection limit for every ion was calculated as three times the standard deviation of the blank. A standard of 0.5 ppm concentration of soluble ions and the working standards were run after every four samples to check the instrumental stability and precision (the degree of repeatability of the data) of the analysis.

The accuracy of data was monitored by analyzing the standard solutions during sample analysis. Accuracy in terms of percentage error (%) was calculated as:

$$A = Xo – Xa/100$$

Xo and Xa are observed and true values respectively of given ion in solution. To address the possible uncertainty in true value itself, the accuracy has been calculated in terms of relative errors or percentage error (%). Scatter plot made between the milli-equivalent concentrations of anions and cations indicate the goodness of analysis of groundwater samples (see supplementary figure SF1).

Results and Discussions

General Parameters

The statistical summary of the results for physiochemical parameters for groundwater are listed in Table 1. Groundwater temperature ranged between 25.9-32.7°C and 26.5-34.2°C during post and pre-monsoon seasons respectively. The pH values ranged from 6.6-8.2 with an average of 7.3 and from 6.3-7.8 with an average 7.0 during post and pre-monsoon seasons respectively suggesting alkaline nature of groundwater. Total hardness (TH) of groundwater, expressed as $CaCO_3$ equivalents, is calculated as:

$$\text{Total Hardness (as mg/Lof } CaCO_3) = 2.497\,(Ca^{2+}) + 4.115\,(Mg^{2+})$$

Hardness in groundwater is attributed to the presence of alkaline earths metals, dominantly calcium and magnesium. Total hardness ranged from 68.1-528.7 mg/L (avg: 255.7 ± 99.5 mg/L) and 72.8-639.2 mg/L (avg: 290.6 ± 116.2 mg/L) in post and pre monsoon seasons respectively. Whereas, EC ranged from 561-2006 µS/cm (avg: 1067 µS/cm) and 194-2453 µS/cm (avg: 1164 µS/cm) in post and pre monsoon seasons, respectively. Likewise, total dissolved solid (TDS) ranged from 319.8-1143.4 mg/L (avg: 319.8 mg/L and 110.6 -1398.4 mg/L (avg: 663.6 mg/L) in post and pre monsoon seasons, respectively. The large spatial differences in the TDS could be attributed to the variation in geochemical processes and anthropogenic activities in the region (Murkute, 2014; Tiwari *et al.*, 2016). In natural waters, dissolved solids consist mainly of inorganic salts such as sulfates, phosphates, nitrates, carbonates and bicarbonates of Ca, Mg, Na, K, Fe, Mn, Cr, Pb etc. with minor amounts of organic material and dissolved gases (Jain *et al.*, 2010). The lower TDS values in majority of the samples could be attributed to the short residence time of groundwater with the underground rocks or the slow weathering process of existing rocks (Patel *et al.*, 2016).

Soluble Ion and Metal Chemistry

Cation abundances in the groundwater varied in the order of Ca^{2+}> Na^{+}> Mg^{2+}> K^{+} in both sampling seasons (Table 1). The Ca^{2+} and $Mg^{2+}$are major constituents of natural water and dominantly exist as bicarbonates in water and to a lesser extent as sulphate and chloride (Prasanth, 2012). Weathering and dissolution of calcium carbonate, especially calcite ($CaCO_3$), and dolomite ($CaMg(CO_3)_2$), calc-silicate minerals (amphiboles, pyroxenes, olivine, biotite, etc.) and magnesium carbonate (dolomite) in sedimentary rock are the most common source of calcium and magnesium in water (Younger, 2006; Tiwari *et al.*, 2016). The Ca^{2+} concentrations in groundwater samples ranged from 10.3-143.3 mg/L (avg: 65.7 mg/L) and 15.1-199.7 mg/L (avg: 76.4 mg/L) in post and pre-monsoon seasons respectively. Similarly, Mg^{2+} varied from 10.2-48.2 mg/L (avg: 22.3 mg/L) and 8.5-51.4 mg/L (avg: 24.3 mg/L) during post and pre-monsoon seasons respectively. Both Na^{+} and K^{+} are highly soluble in water and neither of them form carbonate minerals (Younger, 2006). In fresh water, Na^{+} concentrations are generally lower than the Ca^{2+} and Mg^{2+} (Prasanth, 2012). Na^{+} concentrations ranged from 6.7-131.4 mg/L (avg: 53.7 mg/L) and 11.3-155.8 mg/L (avg: 58.9 mg/L) in post and pre-monsoon seasons, respectively. Its concentration in the drinking water seldom reached 20 mg/L. The K^{+} concentration in the water samples ranged from 0.3 - 16.3 mg/L (avg: 2.5 mg/L and 0.8-13.5 mg/L (avg: 2.8 mg/L) in post and pre monsoon seasons respectively. Unlike Na^{+} which once released from silicate mineral complex has a tendency to remain persistently in the solution. High Na^{+} concentration in irrigation water are not suitable for irrigational purposes. High intake of Na^{+} by humans from excess salt intake may increase the blood pressure and heart disease. $K^{+}$is released from its minerals with greater difficulty and taken up by plants. The K^{+} concentrations are significantly lower than those reported by Murkute (2014) but close to the values reported by Li *et al.* (2013) in similar studies. In terms of milli-equivalent concentrations, Ca^{2+}, $Na^{+}$and Mg^{2+} did not show any noticeable changes with respect to sampling seasons. The Cl^{-} concentrations ranged from 5.9 to 243.1 mg/L (avg: 64.1 mg/L) and 6.6 to 30.0 mg/L (avg: 70.9) during post and pre monsoon seasons, respectively. The sedimentary rocks significantly contribute chloride (Cl^{-}), especially as evaporates in groundwater (Hem, 1985). Major anthropogenic sources to Cl^- are domestic sewage and municipal effluents and public water supply where it is added as a disinfectant. High Cl^- concentrations in irrigation water may result in leaf necrosis of plants (Sundaray *et al.*, 2009). The large spatial variations in Cl^- concentrations and high values observed in few samples indicate the local recharge, which possibly could be ascribed to the contamination via leaching from ash ponds.

Fluoride (F^-) is a minor constituent in groundwater and comes from common fluoride bearing minerals such as fluorite and apatite. In controlled amounts, F^- is effective in preventing tooth decay and helps maintaining tooth structure but high concentrations could lead to dental and skeletal fluorosis (Raju *et al.*, 2016). Fluoride (F^-) concentrations in groundwater ranged from 0.1-4.4 mg/L (avg: 1.1 mg/L) and 0.3-2.9 mg/L (avg: 1.1 mg/L) during the post and pre monsoon seasons, respectively (Table 1). The F^- concentrations observed here are significantly higher than those reported in groundwater around coal mining area by Tiwari *et al.* (2016) from West Bokaro coalfields, India,Li *et al.* (2013) from Dondsheng coalfields, China, Murkute (2014) from Umrer coal mining area, Nagpur, India.

Sulfate (SO_4^{2-}) in natural water is contributed by weathering of sulfide minerals (e.g. pyrite), gypsum etc. (Younger, 2006). It is generally present as soluble salts of Ca^{2+}, Mg^{2+} and Na^+. Concentration of SO_4^{2-} in the groundwater samples ranged from 7.0-418.9 mg/L (avg: 63.4 mg/L) and 13.7 - 396.5 mg/L (avg: 67.5 mg/L) during post and pre monsoon seasons, respectively. SO_4^{2-} concentrations reported here are significantly higher than those reported by Li *et al.* (2013) from shallow groundwater in Dongsheng coalfield, China. SO_4^{2-}concentrations in groundwater changes periodically due to groundwater recharge from stagnant pools and percolation of rainwater (Jain *et al.*, 2010). Anthropogenic sulfur emissions from fossil fuel combustion may also contribute to the overall SO_4^{2-} concentrations in groundwater. The nitrogenous compounds in natural waters tend to be transformed to nitrate (Kao *et al.*, 2011). A major influx of nitrate in water is attributed to the usage of synthetic fertilizers, sewage disposal and animal residues (Niagolova *et al.*, 2005). Results showed that NO_3^- concentration ranged from 0.9 -105.2 mg/L (avg: 29.4 mg/L) and 1.1-84.2 mg/L (avg: 31.4 mg/L) in post and pre monsoon seasons, respectively. Local human activities such as sewage disposal and irrigation water may introduce additional NO_3^- to the groundwater. Further, NO_3^- contamination from explosives used in the mining cannot be ruled out. In general, NO_3^-concentration observed here are lower than those reported by Murkute (2014) in groundwater around coal mine area in Nagpur, India. In general, soluble ions can be sourced in groundwater through weathering of potash-silicate minerals (feldspar, mica, and other clay minerals) in aquifer zones or via leaching from anthropogenically contaminates surface zones (Hem, 1985; Jain *et al.*, 2010). However, the groundwater chemistry appears to be influenced leaching from ash ponds as all other anthropogenic activities are minimalin Singrauli power belt region.

Many metals are required by the plants and animals in micro amounts whereas metals in high concentrations exhibit toxicity (Singh *et al.*, 2011). In this study, we analyzed three metals (Fe, Mn and Cr) in the groundwater samples (Table 1). Iron in groundwater is usually present as soluble ferrous ions (Fe^{2+}), without causing discoloration or turbidity in water. On exposure to the atmosphere, when pumped out of well, the ferrous iron (Fe^{2+}) in water oxidizes to ferric iron (Fe^{3+}) imparting an objectionable reddish-brown coloration to water (WHO, 2004). At levels above 0.3 mg/L, iron stains laundry and plumbing fixtures. High iron concentration in water is more of a nuisance than an actual health problem. In Singrauli groundwater, iron concentration varied from 0.11 to 23.80 mg/L (avg: 3.27 mg/L) in post monsoon and from 0.07 to 21.46 mg/L (avg: 3.87 mg/L) in the pre monsoon season. Iron values exceeded the regulatory limits of World Health organization (WHO) and Bureau of Indian standards BIS in most of the groundwater samples. The iron could be associated with geogenic sources as the iron on surface remains oxidized which is insoluble in water and restrict leaching.

Manganese (Mn) commonly occurs in many food sources. Higher inhalation exposure to Mn cause neurological health problems, especially in occupational environments. Mn in water supplies at concentration exceeding 0.1 mg/L result in an unpleasant taste in beverages and produces stains in sanitary ware and laundry. Mn concentrations in groundwater samples ranged from 0.01-1.36 mg/L (avg: 0.10 ± 0.20) in post monsoon and 0.02-1.26 mg/L (avg: 0.12±0.21) in the pre monsoon seasons. WHO (2004) has recommended a maximum permissible value of 0.4 mg/L for Mn in drinking water, whereas BIS (2012) recommends 0.1 mg/L as desirable limit and 0.3 mg/L has maximum acceptable limit. Compared to these limits for Mn, groundwater is safe for dinking purposes. Chromium exists in several oxidation states ranging from +2 to +6. Hexavalent chromium (VI), being water-soluble, is highly toxic and a recognized as a carcinogen. Cr concentration in the water ranged from 0.02-0.18 mg/L (avg: 0.070 ± 0.04) during post monsoon and 0.01-1.36 mg/L (avg: 0.10 ± 0.20) in pre monsoon seasons. Both WHO and BIS recommend a maximum permissible limit of 0.5 mg/L for Cr. At certain instances, Cr exceeded the limits but it is difficult to say about the toxicity as total Cr (not in specific oxidation state) is determined in this study. It can be inferred that the metal toxicity exist in groundwater of some pockets in Singrauli region. The metals in ground water could have been contributed by mineral matrix under the reducing condition in sub-surface aquifers or via leaching from ash ponds.

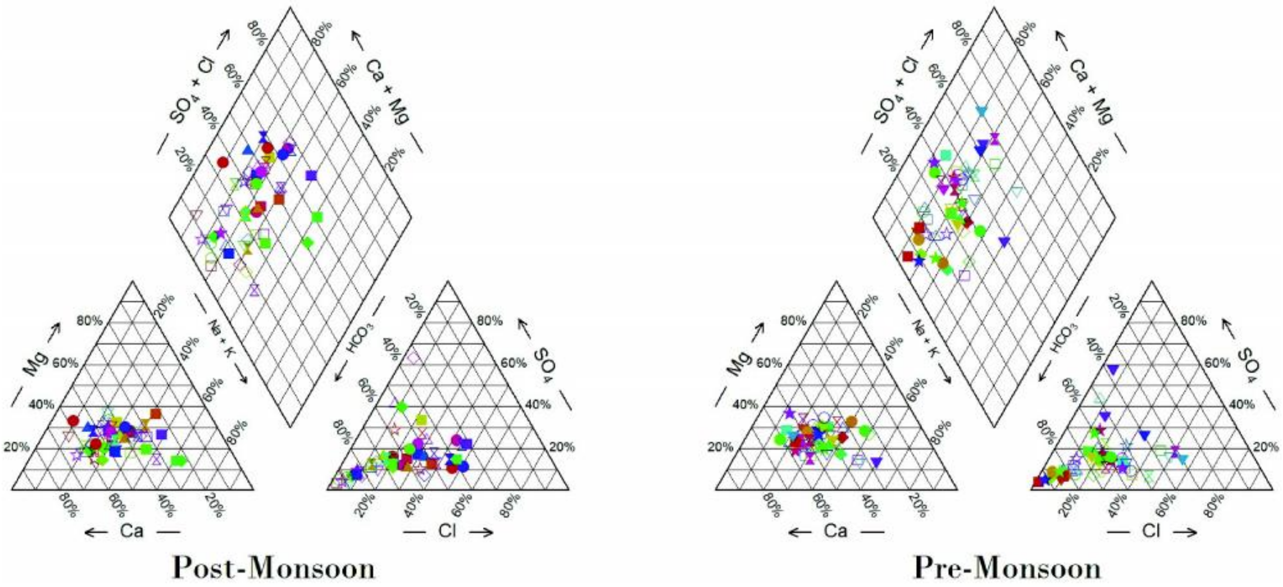
Hydro-geochemical Processes

Hill-Piper diagrams are commonly used to infer the geochemical characteristics and hydrochemical types of groundwater (Raju *et al.*, 2011; Prasanth *et al.*, 2012; Howladar, 2014; Gautam *et al.*, 2015). Hill (1940) first proposed a tri-linear diagram to elucidate the geochemical characteristics of water which was further refined by Piper (1944). In the Piper diagram, percentmilli-equivalent concentrations of major cations and anions are plotted in triangle plots. The concentrations of anions and cations for each sample are projected into the central diamond shaped plot from which interferences are drawn based on hydrochemical facies concept. Hill-Piper plots forpost and pre-monsoon seasons (Fig. 2) indicate that divalent cations (Ca^{2+} and Mg^{2+}) dominate over the monovalent cations (Na^+ and K^+). Among anions, HCO_3 showed dominance over anions of strong acids (SO_4^{2+}, Cl). The plot for the two seasons suggests that Singrauli groundwater is predominantly of Ca-Mg-HCO_3 water type.

Gibbs diagram is other important way for elucidating the mechanisms governing the groundwater composition and aquifer lithological physiognomies (Gibbs, 1970). The Gibbs ratio 1 and ratio 2 are calculated using the following equation:

$$Gibbs\ ratio\ 1\,(anions) = \frac{Cl^-}{(Cl^- + CHO_3^-)}$$

$$Gibbs\ ratio\ 2\,(anions) = \frac{Na^+ + K^+}{(Na^+ + K^+ + Ca^+)}$$



Post-Monsoon

Pre-Monsoon

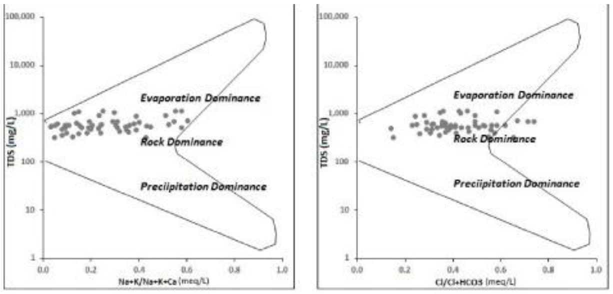
Fig. 2: Piper diagram showing hydro-geochemical characteristics of groundwater collected during post and pre monsoon seasons from Singruali region

Table 1: Statistical description of the physical and chemical parameters analysed in the groundwater samples collected during post and pre monsoon seasons from Singrauli region along with water indices calculated using empirical formulas

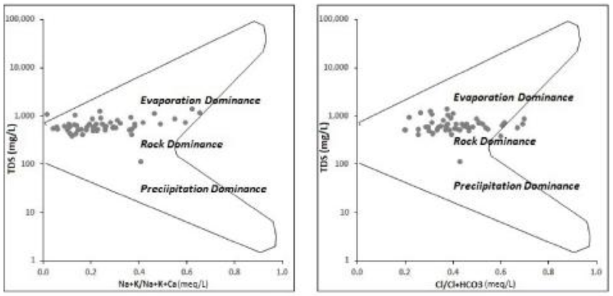
	Post monsoon				Pre monsoon			
	Min	Max	Mean	Std Dev	Min	Max	Mean	Std Dev
pH	6.6	8.2	7.3	0.4	6.3	7.8	7.0	0.3
TDS	319.8	1143.4	608.5	215.9	110.6	1398.4	663.6	236.7
EC	561.0	2006.0	1067.6	378.7	194.0	2453.4	1164.2	415.2
Ca^{2+}	10.3	143.3	66.0	28.1	15.1	199.7	76.4	34.5
Mg^{2+}	10.2	48.2	22.3	9.2	8.5	51.4	24.3	9.3
Na^{+}	6.7	131.4	53.7	28.6	11.3	155.8	58.9	28.9
K^{+}	0.3	16.3	2.5	2.4	0.8	13.5	2.8	2.0
HCO_3^-	132.8	481.8	275.0	77.2	108.3	682.9	314.6	90.6
Cl^-	5.9	243.1	64.1	55.9	6.6	330.0	70.9	67.5
F^-	0.0	4.4	1.1	0.7	0.3	2.9	1.1	0.7
SO_4^{2-}	7.0	418.9	63.4	65.9	13.7	396.5	67.5	64.5
NO_3^-	0.9	105.2	29.4	23.2	1.1	84.2	31.4	23.8
Fe	0.11	23.80	3.27	4.7	0.07	21.46	3.82	4.77
Mn	0.01	1.36	0.10	0.20	0.02	1.26	0.12	0.21
Cr	0.01	0.12	0.06	0.03	0.02	0.18	0.07	0.04
SAR	0.23	4.42	1.49	0.80	0.40	4.50	1.53	0.74
%Na	9.48	63.57	31.64	10.89	12.60	60.13	31.19	9.84
RSC	–4.94	2.74	–0.62	1.80	–7.89	2.41	-0.65	2.08
PI	37.45	107.52	62.03	13.83	33.33	93.61	60.04	12.58
KI	0.09	1.73	0.49	0.31	0.12	1.50	0.47	0.26
CA1	–8.73	0.56	–1.25	1.93	–14.36	0.65	–1.26	2.31
CA2	–0.53	0.40	–0.09	0.19	–0.50	0.73	–0.08	0.21
GR1	0.03	0.60	0.26	0.16	0.02	0.65	0.26	0.15
GR2	0.14	0.74	0.42	0.13	0.20	0.70	0.41	0.12
MH	20.71	62.14	36.61	8.59	21.97	54.96	35.42	7.84
LSI	–1.70	1.10	–0.12	0.50	–1.30	0.92	–0.13	0.43
RSI	6.04	10.01	7.50	0.71	6.26	9.14	7.40	0.62

EC – Electrical Conductivity; SAR - Sodium Adsorption ratio; %Na - Percent sodium; RSC – Residual Sodium Carbonate; PI – Permeability Index; KI – Kelly's Index; CA1 - Chloroalkaline index 1; CA2 - Chloroalkaline index 2; GR1 – Gibbs Ratio 1; GR2 – Gibbs Ratio 2; MH – Magnesium Hazard; LSI - Langelier saturation index; RSI - Ryznar stability index. EC in µS/cm units; all other concentrations in in mg/l units

In Gibb's diagram, ratio for anions (Gibbs ratio 1) and cations (Gibbs ratio 2) of water samples are separately plotted against TDS (Fig. 3). Three types of distinct fields i.e., precipitation dominance, evaporation dominance, and rock dominance are recognized in the Gibb's diagrams. Gibbs ratio 1 and 2 ranged from 0.030-0.604 with an average of 0.264 ± 0.16 and from 0.142-0.740 with an average of 0.419 ± 0.13, respectively. The plotting patterns indicate that rock weathering is the major driving force controlling the groundwater chemistry in Singrauli region with minor influence of atmospheric precipitation. The rock weathering is the result of chemistry between the aquifer material and groundwater (Sarkar and Shekhar, 2013).



Post-Monsoon



Pre-Monsoon

Fig. 3: **Gibbs plots showing different mechanisms which control the groundwater composition in Singrauli region**

Evaluation of Groundwater Quality

Suitability for Drinking and Domestic Purposes : To evaluate the suitability of groundwater quality for drinking, domestic and public health uses, a comparison of the results is made with the drinking water guidelines provided by World Health Organization (WHO, 2004) (Table 2). The pH of groundwater samples was well within the permissible range of 6.5-8.5 (WHO, 2004; BIS, 2012). The TDS values of the samples were also well below the maximum permissible limits recommended by WHO (2004). Similarly, Ca^{2+} and Mg^{2+} concentration in water were well below their maximum permissible limits of 75 mg/L and 200mg/L (WHO, 2004). Likewise, none of the samples exceeded the maximum permissible limits of 600 mg/L for bicarbonates in drinking water.

According to Sawyer and McCarty (1967) classification based on the total hardness (TH), 1.8% and 1.8% of samples were soft, 7.4% and 3.7% were

Table 2: A comparison of physico-chemical parameters of groundwater collected from Singrauli region with World Health Organisation's (WHO) standards for drinking water

Chemical parameter	Post-monsoon		Pre-monsoon		Ranges of standards (Desirable-permissible)	%age of samples exceeding WHO limits	
	Mean	Range	Mean	Range	WHO (2004)	Post	Pre
pH	7.3 ± 0.4	6.6-8.2	7.0 ± 0.3	6.3-7.8	6.5-8.5	—	—
TDS (mg/l)	608.5 ± 215.9	319.8-1143.4	663.6 ± 236.7	110.6-1398.4	500-1500	—	—
TH (mg/l)	255.7 ± 99.5	68.1-528.7	290.6 ± 116.2	72.8-639.2	500	—	—
Ca^{2+} (mg/l)	65.7 ± 28.2	10.3-143.3	76.4 ± 34.5	15.1-199.7	75-200	—	—
Mg^{2+} (mg/l)	22.3 ± 9.2	10.2-48.2	24.3 ± 9.3	8.5-51.4	50-150	—	—
Na^{+} (mg/l)	53.7 ± 28.6	6.7-131.4	58.9 ± 28.9	11.3-155.8	200	—	—
K^{+} (mg/l)	2.5 ± 2.4	0.3-16.3	2.8 ± 2.0	0.8-13.5	12	2	2
HCO_3^- (mg/l)	241.1 ± 51.5	138.4-376.3	271.2 ± 59.1	108.3-476.3	600	—	—
Cl^- (mg/l)	64.1 ± 55.9	5.9-243.1	70.9 ± 67.5	6.6-330.0	200-600	4	4
F^- (mg/l)	1.1 ± 0.7	0.1-4.4	1.1 ± 0.7	0.3-2.9	1.5	35.2	44.4
SO_4^{2-} (mg/l)	63.4 ± 65.9	7.0-418.9	67.5 ± 64.5	13.7-396.5	200-400	2	—
NO_3^- (mg/l)	29.4 ± 23.2	0.9-105.2	31.4 ± 23.8	1.1-84.2	50	22.3	26
Fe (mg/l)	3.27 ± 4.70	0.11-23.80	3.82 ± 4.77	0.07-21.46	0.3	94	96
Mn (mg/l)	0.10 ± 0.20	0.01-1.36	0.12 ± 0.21	0.02-1.26	0.4	24	26
Cr (mg/l)	0.02-0.18	0.70 ± 0.04	0.01-1.36	0.10 ± 0.20	0.05	48	56

TDS – Total Dissolved Solids; TH – Total Hardness; TH as mg/l of $CaCO_3 = 2.497 (Ca^{2+}) + 4.115 (Mg^{2+})$

moderately hard, 68.5% and 62.9% were hard and 22.2% and 37.0% belonged to very hard class in the post and pre monsoon seasons respectively (Table 3). Results suggested that majority of the groundwater samples were hard to very hard in nature. Higher values for hardness in post monsoon may be due to excess leaching of Ca^{2+} and Mg^{2+} ions from the ash ponds during rainy season into the groundwater (Raju *et al.,* 2012). All samples had chloride concentrations well within the desirable limits of 200 mg/L for drinking water (WHO, 2004) except that 4% samples in post and pre monsoon seasons exceeded the maximum permissible limits. A total of 35% and 44% of the samples exceeded the maximum permissible limits of 1.5 mg/L for F^- as recommended by the WHO for drinking water during post and pre monsoon seasons respectively. Only 2% of groundwater samples exceeded the maximum permissible limits of 400 mg/L for SO_4^{2-} concentrations (Table 3). Similarly, 22% and 26% of the samples exceeded the regulatory limits of NO_3^- for drinking water i.e., 45 mg/L (BIS, 2012) and 50 mg/L (WHO, 2004) in post and pre monsoon seasons respectively. Maximum permissible limits recommended by WHO for drinking water are 0.3 mg/L for iron, 0.4 mg/L for manganese and 0.05 mg/L for Cr. For Fe, 94% and 96% of the groundwater samples exceeded maximum permissible limits during post and pre monsoon seasons, respectively. Due to presence of high soluble Fe, water samples showed precipitation after sampling as Fe^{+2} oxidized to Fe^{3+}. This was evident during the sampling. Similarly, a total of 24% and 26% of the samples exceeded permissible limits for Mn and 48% and 56% for Cr, during post and pre monsoon seasons, respectively. The above discussion suggests that F^-, NO_3^-, Fe, Mn and Cr are the major contaminants present in the Singrauli groundwater.

Table 3: Classification of groundwater samples collected from Singrauli region based on selected water quality parameters

Water quality	Parameter	Percentage of samples	
	Salinity EC (Richards 1954)	Post monsoon	Pre monsoon
Excellent	Up to 250	nil	1.80%
Good	250–750	18.50%	7.40%
Fair/medium	750–2,250	81.50%	92.60%
Poor/bad	2,250–5,000	nil	nil
	TDS (Davis and De Wiest, 1966)	Post monsoon	Pre monsoon
Drinking water	<500	27.80%	14.80%
Permissible for drinking	500-1000	42.50%	74.00%
Useful for irrigation	1000-3000	11.10%	11/1%
Very hard	>3000	nil	nil
	% Na (Wilcox. 1955)	Post monsoon	Pre monsoon
Excellent	< 20	9.20%	12.90%
Good	20-40	68.50%	70.30%
Permissible	40-60	18.5	14.80%
Doubtful	60-80	3.70%	1.80%
Unsuitable	>80	nil	nil
	TH (Sawyer and McCarty, 1967)	Post monsoon	Pre monsoon
Soft	<75	1.80%	1.80%
Moderately hard	75-150	7.40%	3.70%
Hard	150-300	68.50%	62.90%
Very hard	>300	22.20%	32.00%

TDS – Total Dissolved Solids; %Na – Percent Sodium; TH – Total Hardness. EC represented in µS/cm; TDS in mg/l; TH as mg/l of $CaCO_3 = 2.497 (Ca^{2+}) + 4.115 (Mg^{2+})$; $\%Na = Na^+ \times 100/ [Ca^{2+} + Mg^{2+} + Na^+ + K^+]$

$_2 + 2OH^-$

Fluoride Spatial Distribution and Contamination : Fluoride is an essential dietary micronutrient required for the healthy growth of bones and teeth but its higher amounts of fluoride can cause joint pain, restriction of mobility and possibly increase the risk of some bone fractures (Susheela, 1999). Drinking water is the main source of fluoride intake in human body. The fluoride bearing minerals in rocks and soil such as fluorite (CaF_2), fluorapatite [$Ca_5(PO_4)_3F$], biotite [$K(Mg, Fe)_3 (AlSi_3O_{10}) (OH,F)$] and phlogopite [$KMg_3 (AlSi_3O_{10}) (F, OH)$] are major sources of fluoride in groundwater (Ali *et al.*, 2016, Singh and Mukherjee, 2015; Dehbandi *et al*., 2017, Raju *et al*., 2017, Ali *et al*., 2018). Granitic rocks contain relatively high abundance of F-rich minerals such as amphibole, biotite and apatite (Naseem *et al.,* 2010; Deshmukh *et al.,* 1995; He *et al.,* 2013).

High precipitation zones have lower fluoride concentration due to the dilution effects on the groundwater. High fluoride concentrations in groundwater are a feature of arid climatic conditions (Smedlety *et al.,* 2001; Jicks *et al.,* 2005, Saha *et al.,* 2016) due to substantial evaporative losses (Singh and Mukherjee, 2015). Fluoride concentration in groundwater depends on factors such as temperature, pH, carbonate and bicarbonate alkalinity, solubility of fluorine-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), and the nature of geological formations (Gupta *et al.,* 2012, Ali *et al.,* 2016). Fluoride minerals such as fluorite and cryolite are sparingly soluble in water under normal pressure and temperature. Under acidic pH conditions, fluoride is absorbed in clay; the alkaline pH is more favorable for fluoride dissolution processes. Saxena and Ahmed (2001) suggested that alkaline conditions with pH ranging between 7.6 and 8.6 are favorable for dissolution of fluorite mineral from the host rocks. The exchange between OH^- and F^- in the fluoride bearing minerals (Illite, mica and amphiboles) at higher pH facilitate its dissolution in groundwater (Gupta *et al.,* 2012). The replacement of F-ion by hydroxyl ions in muscovite can be explained by following reaction:

$$KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \rightarrow$$

$$KAl_2[AlSi_3O_{10}][OH_2] + 2F^-$$

The hydrolysis of alumino-silicate minerals in the sandstone aquifers produces bicarbonate ion, which can enhance fluorite dissolution as below:

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2$$

Fluoride exhibits a positive relationship with sodium and bicarbonate while it extends an inverse relationship with calcium (Kundu *et al.,* 2001). In our samples, insignificant correlations of fluoride with HCO_3^-, pH, Na^+ and Ca^{2+} (Fig. 4) was observed suggesting that in addition to the rock-water interaction, fluoride may have been contributed from other sources too. The spatial distribution maps of fluoride in groundwater samples indicate that high fluoride concentrations were recorded in the samples (GW-19, 20, 47, 38, 10, 3, 42, 17 and 18) collected from the bore holes in the vicinity of the ash ponds (Fig. 5 and Fig. 1). Overall, a total of 35% and 44% of the samples exceeded the WHO recommended limits of 1.5 mg/L during post and pre monsoon season, respectively. Ash settles into the ash ponds while the water drains off, in the present case to the nearby Rihand reservoir. Water leached out of ash ponds is used for irrigation in the surrounding agricultural lands. Ash pond leachates too showed high concentrations of fluoride ranging from 1.3 to 6.0 mg/L (avg: 2.1 mg/L) (Data not presented here).

On the other hand, water from Rihand reservoir has low concentration of 0.5 mg/L fluoride suggesting significant contributions of coal ash to the overall fluoride concentration to the groundwater in addition to parent rocks (Usham *et al.,* 2018). Ando *et al.* (2001) suggested that combustion of coal is a major source of gaseous and aerosol fluoride. In a similar study, high fluoride concentration ranging from 3.10 to 12.6 mg/L, were reported in the ash pond water of thermal power plants in Orissa (Equeeuddin *et al.,*

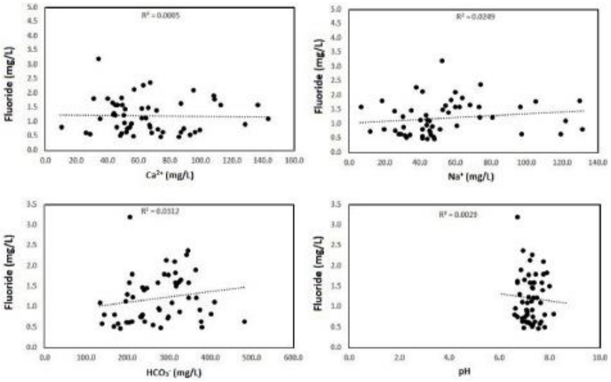
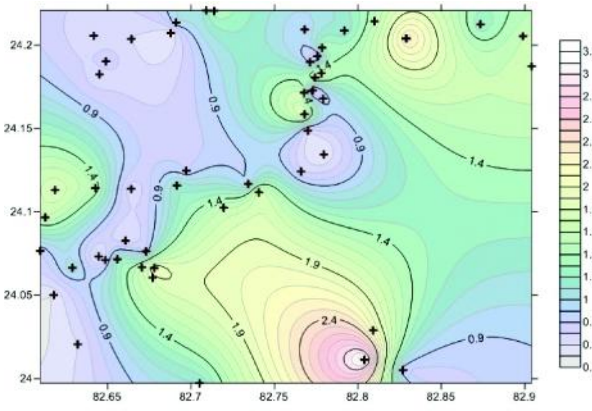
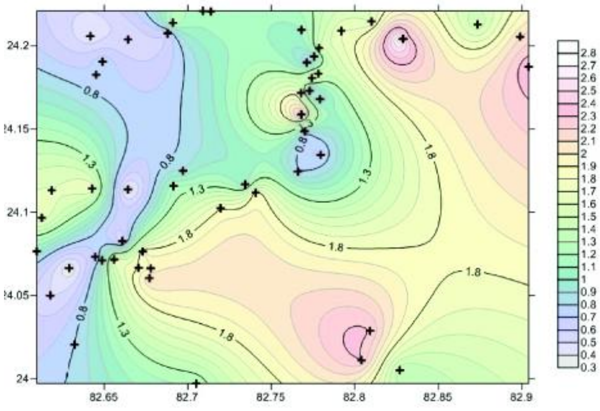


Fig. 4: Scatter plots for fluoride versus calcium, sodium, bicarbonate ion and pH of the ground water samples collected from Singrauli region



Post-monsoon



Pre-monsoon

Fig. 5: Spatial distribution of fluoride in groundwater during post and pre monsoon seasons in Singrauli region (color code bar represent concentration in mg/L units)

2013). Fluoride rich (3.18 mg/L) groundwater is also reported in the vicinity of ash pond in Koradi, Nagpur (Ramya *et al.*, 2012). Patel *et al.* (2016) also observed that groundwater is contaminated with fluoride (2.1 to 12 mg/L) in Korba coal basin (in groundwater).

Nitrate Pollution in Groundwater : In natural waters, the nitrogenous compounds tend to be transformed into nitrate (Kao *et al.*, 2011). Microbial fixation of atmospheric nitrogen and degradation of animal matter are major contributing sources of nitrate in groundwater. A major influx of nitrate in water is attributed to the usage of synthetic fertilizers, livestock operations, sewage disposal and animal residues (Niagolova *et al.*, 2005). High temperature fuel combustion (1210°C to 1763 °C) in coal based thermal power plant and vehicles is main sources of anthropogenic NO_x (NO and NO_2) in the atmosphere (Wang *et al.*, 2006). Among NO_x, NO is the dominant gas produced from the high temperature combustion processes. NO formed by oxidation of atmospheric nitrogen is, known as 'thermal NO' while chemically bound nitrogen within the fuel matrix is known as 'chemical NO'. The concentration of NO_2 is highly dependent upon the rate of oxidation of NO and not on the direct emission. The general reactions for formation of thermal NO are as follow:

$$O + N_2 \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

$$N + OH \rightarrow NO + H$$

$$2NO + O_2 \rightarrow 2\ NO_2$$

During daytime, NO_2 is oxidized by the hydroxyl radical (OH^-) and by Ozone in night time leading to formation of NO_3^- radical, which further reacts with NO_2 to form N_2O_5. In the next step N_2O_5 react homogeneously or heterogeneously with water to form nitric acid (HNO_3) (Seinfeld and Pandis, 2012; Pathak *et al.*, 2009). HNO_3 subsequently reacts with ammonia (NH_3) to form ammonium nitrate (NH_4NO_3) particles (Deshmukh *et al.*, 2011). High nitrate concentrations in groundwater may be attributed to formation of nitrogen oxides during coal combustion, their deposition on the surface and their leaching to groundwater subsequently on account of their solubility in water.

Spatial distribution maps show that sampling points located in the south western part of our study area exhibited higher nitrate contamination (Fig. 6). However, a large contribution of nitrate from the deposition of emissions from thermal power plants (mechanisms explained above) cannot be ruled out in this context as the other sources such as municipal wastes, leakage from septic tank waste, agricultural runoff and animal wastes are limited in the region. Considering the average Cl^-/NO_3^- ratio of major river water as a reference point (Majumder *et al.*, 2008), drawing analogy, majority of the groundwater samples in the study area exhibits Cl^-/NO_3^- ratio <4.9 suggesting NO_3^- buildup in wells or inefficient denitrification, however, a few ratio values indicates efficient denitrification in reducing nitrate from subsurface system.

Suitability for Irrigation : Groundwater suitability for irrigation is contingent upon its mineral constituents. Water parameters such as sodium percentage (%Na), electrical conductivity (EC), sodium adsorption ratio (SAR), residual sodium carbonate (RSC), magnesium hazard (MH), permeability index (PI), chloroalkaline indices (CAI) and Kelly's index have been used here to evaluate the irrigation suitability of the groundwater samples (Table 1).

Electrical Conductivity (EC) and Sodium Percentage *(%Na)* : High concentrations of Na in irrigational water are detrimental to the crops. In water, Na^+ have a tendency to displace Mg^{2+} and Ca^{2+} through base-exchange process which eventually reduces the permeability of soils (Karanth, 1989; Collins and Jenkins, 1996), thus restricting air and water circulation. Sodium when combines with carbonates, results in alkaline soils, while it forms saline soils with chloride (Raju *et al.*, 2011). The %Na in the groundwater samples ranged from 9.48% - 63.57% (avg: 31.64 %) and from 12.60% - 60.13% (avg: 31.19%) during post and pre-monsoon seasons, respectively. Compared to maximum limit of 60% Na allowed for irrigation water (Fipps, 2003), 96% and 98% groundwater samples of post and pre monsoon season were found suitable for irrigation purposes. Wilcox (1948) classified groundwater for irrigational purposes based on %Na and EC. Wilcox plots (Fig. 7) indicate that 3% and 7.5% of the samples belonged to permissible to doubtful category, and 12% and11% belonged to doubtful to unsuitable category while the rest belonged to good to permissible category for irrigation use in the post and pre monsoon seasons, respectively.

Salinity Hazard and Alkali Hazard : Richards (1954) categorized irrigation water based on electrical conductivity (EC) into four groups (Table 3). In accordance to this classification, 18% and 7.4% of the samples were good while the rest 82% and 92.6% had medium salinity in post and pre monsoon seasons, respectively. Sodium or alkali hazard in irrigation water can also be expressed in terms of Sodium Adsorption Ratio (SAR), which represents the relative activity of sodium ion in the exchange reaction with soil and is calculated as follows:

$$SAR = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}/2}} \text{ [meq/L]}$$

The SAR value in the study area ranged from 0.23-4.42 (avg: 1.49) and 0.40-4.50 (avg: 1.53) in post and pre monsoon seasons, respectively (Table 1). All groundwater samples have SAR less than 10, which indicates that samples are good for irrigation purpose.

A more detailed irrigation suitability analysis was made by plotting the US salinity laboratory diagram (USSL, 1954), in which the EC is taken as a salinity hazard and SAR as an alkalinity hazard. The USSL plot indicate that majority of the groundwater (94.4 and 96.4% in post and pre monsoon, respectively) samples in Singrauli belonged to C_3S_1 class (Fig. 8), representing high salinity hazard and low alkali hazards water which require proper drainage otherwise it can adversely affect soil (Karanth, 1989).

Residual Sodium Carbonate (RSC) : The residual sodium carbonate (RSC) determines the hazardous effects of carbonate and bicarbonates on suitability of groundwater for irrigation (Raju *et al*., 2015). When total carbonate levels exceed the total amount of calcium and magnesium, the water quality may be diminished (Sundaray, 2009). If the carbonates are less than alkaline earths, it indicates that the RSC is negligible. Excess carbonates (residual) combine with alkaline earth metals (Ca + Mg) and form scale that settle out in water. Residual sodium carbonate (RSC) is calculated by subtracting the alkaline earths ($Ca^{2+} + Mg^{2+}$) from the carbonates (CO_3^{2-} + HCO_3^-) as follows:

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \text{ [meq/L]}$$

The RSC ranged from –4.94 to 2.74 (avg: –0.62) and –7.89 to 2.41 (avg: -0.65) in post and pre monsoon seasons, respectively (Table 1). A high value of RSC in water leads to an increase in the adsorption of sodium in soil (Eaton, 1950). USSL (1954) classified water into safe (<1.25 meq/L), marginally suitable (1.25-2.5 meq/L), and unsuitable (>2.5 meq/L) categories based on RSC. It is observed that in post monsoon season, 89% samples were safe, 9% were marginally suitable, and 2% sample was unsuitable for irrigation use. In the pre monsoon season, 85% samples were safe, while the rest were marginally suitable based on RSC values.

Permeability Index (PI) : Donnen (1964) diagrams used permeability index as a criterion to

Table 4: Coefficient of correlation between different soluble ions and metals in groundwater

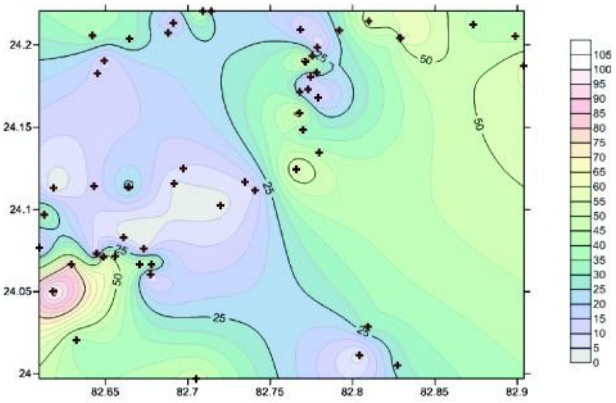
	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	F^-	SO_4^{2-}	NO_3^-	Fe	Mn	Cr
Post-monsoon												
Ca^{2+}	1.00											
Mg^{2+}	**0.65**	1.00										
Na^+	0.26	0.40	1.00									
K^+	0.05	-0.06	0.07	1.00								
HCO_3-	**0.48**	0.30	0.29	0.22	1.00							
Cl^-	**0.56**	**0.60**	**0.56**	-0.05	-0.03	1.00						
F^-	-0.03	0.13	0.16	-0.10	0.17	-0.08	1.00					
SO_4^2	**0.45**	**0.59**	**0.56**	0.00	0.04	0.28	0.10	1.00				
NO_3^-	**0.49**	0.33	-0.02	0.04	0.02	0.36	-0.02	0.00	1.00			
Fe	-0.28	-0.15	-0.14	0.09	-0.19	-0.08	-0.10	-0.12	-0.09	1.00		
Mn	-0.08	0.03	-0.09	-0.06	-0.22	0.05	-0.14	0.03	-0.01	0.07	1.00	
Cr	0.06	-0.06	-0.06	-0.16	-0.07	0.09	-0.21	-0.07	0.07	-0.07	-0.08	1.00
Pre-monsoon												
Ca^{2+}	1.00											
Mg^{2+}	**0.71**	1.00										
Na^+	0.38	0.31	1.00									
K^+	-0.17	-0.11	-0.20	1.00								
HCO_3-	**0.47**	0.40	0.30	-0.20	1.00							
Cl^-	**0.68**	**0.53**	**0.53**	-0.16	-0.06	1.00						
F^-	-0.11	0.07	0.08	-0.07	0.22	-0.24	1.00					
SO_4^2	**0.48**	**0.52**	**0.53**	-0.06	0.06	0.29	0.01	1.00				
NO_3^-	**0.35**	0.31	0.07	0.17	0.06	0.30	0.13	-0.10	1.00			
Fe	-0.32	-0.18	-0.22	0.01	-0.36	-0.13	-0.15	-0.06	-0.10	1.00		
Mn	-0.05	0.03	-0.11	-0.04	-0.24	0.09	-0.12	0.04	-0.04	0.18	1.00	
Cr	0.14	0.07	0.25	-0.21	0.02	0.24	-0.19	0.11	-0.07	-0.13	-0.24	1.00

assess the suitability of water for irrigation. Permeability of soil is highly influenced by Na^+, Ca^{2+}, Mg^{2+}, Cl^- and HCO_3^- contents in irrigation water. The PI of groundwater was calculated following the equation:

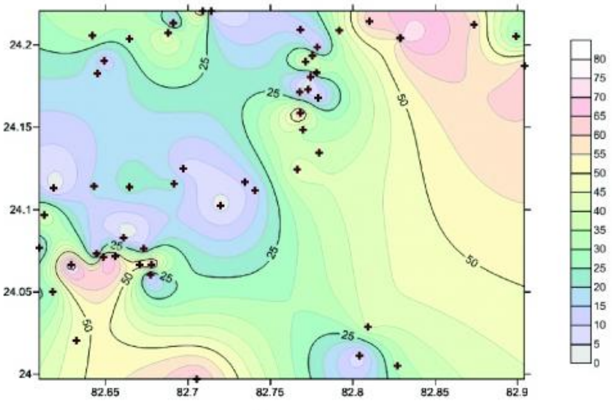
$$PI = \frac{Na^+ + \sqrt{HCO_3^-}}{Ca^{2+} + Mg^{2+} + Na^+} \times 100 \text{ [meq/L]}$$

The PI value of the groundwater samples ranges from 37.45 to 107.52 (avg: 62.03) and from 33.33 to 93.61 (avg: 60.04) in the post and pre monsoon seasons, respectively. Based on Donnen's chart (1964), irrigation water can be categorized into 3 classes. The Class-1 and Class-2 type groundwater, having 75% or more permeability, are appropriate for irrigation purpose while Class-3 is unsuitable for irrigation with 25% maximum permeability (Fig. 9). Nearly all samples of both seasons belonged to Class-I and II of Donnen's chart indicating that the groundwater is good to suitable for irrigation in both seasons without any noticeable variations.

Magnesium Hazard : Calcium and magnesium exist in a state of equilibrium with anions in groundwater. More magnesium in groundwater will adversely affect the soil quality rendering it alkaline (Hem, 1985). Magnesium hazard (MH) ratio for assessing water quality for irrigation (Szabolcs and Darab, 1964) is calculated as:



Post-monsoon



Pre-monsoon

Fig. 6: Spatial distribution of nitrate in groundwater during post and pre monsoon seasons in Singrauli region (color code bar represent concentration in mg/L units)

$$MH = \frac{Mg^{2+}}{(Ca^{2+} + Mg^{2+})} \times 100 \ \text{[meq/L]}$$

The MH ranged from 20.71 to 62.14 (avg: 36.61) and from 21.97 to 54.96 (avg: 35.42) in post and pre monsoon samples, respectively. Magnesium ratios of more than 50% adversely affect the crop yield (Paliwal, 1972). The majority of the groundwater samples (93 and 94% in post and pre monsoon season, respectively) had MH values of less than 50, indicating their suitability for irrigation.

Chloroalkaline Indices : The chloroalkaline indices (CAI-1 and CAI-2) developed by Schoeller (1977) specify the ion exchange mechanisms occurring between the groundwater and the aquifer and are calculated as:

$$CAI - 1 = \frac{Cl^- - (Na^+ + K^+)}{Cl^-} \ \text{[meq/L]}$$

$$CAI - 1 = \frac{Cl^- - (Na^+ + K^+)}{(SO_4^{2-} + CO_3^- + HCO_3^- + NO_3^-)} \ \text{[meq/L]}$$

Depending upon the exchange between Na^+ and K^+, the CAI values may be positive or negative. Positive CAI values are indicator of direct exchange i.e., the exchange between Na^+ and K^+ in water with Ca^{2+} and Mg^{2+} in the rocks. The negative CAI values are an indication of reverse exchange i.e. there is exchange between Ca^{2+} and Mg^{2+} in water with Na^+ and K^+ in rocks. CAI-1 ranged from –8.73 to 0.56 (avg: –1.25) and –14.36 to 0.65 (avg: –1.26), while CAI-2 ranged from –0.53 to 0.40 (avg: –0.09) and –0.50 to 0.73 (avg: –0.08)in post and pre monsoon season, respectively. The CAI-1 and CAI-2 ratios suggest that 72% of the groundwater samples in each season showed reverse exchange of ions while 28% of samples indicated prevalence of direct exchange process.

Suitability of Groundwater for Industrial Purposes : Industrial use of water is primarily dependent on the scale forming property and corrosive nature. Water is fit for industrial use if it has neither scale-forming nor scale-removing properties. Water is considered corrosive if it tends to dissolve minerals like Ca^{2+} and Mg^{2+} or/also to dissolve harmful metals like Pb and Cu from plumbing utilities. Scaling water deposits a layer of minerals on pipe walls preventing corrosion of metallic surfaces. If the rate of scale deposition is too high, it can damage electrical appliances, such as water heaters, and may clog the water pipes. Water is as essential for thermal power plant operations as the availability of coal. Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI) are used to evaluate industrial suitability of groundwater in Singrauli region

Langelier Saturation Index (LSI) : The LSI (Langelier, 1936) is an approximate indicator of the degree of saturation of calcium carbonate in water and used to control the $CaCO_3$ precipitation in water sources containing a RDS concentration of <10,000 mg/L (Patel *et al*., 2016). The LSI is calculated as the difference between the water's measured pH (pHw) and the calculated pH when water is in equilibrium with $CaCO_3$ (pHs) (Alsaqquar *et al*., 2014).

$$LSI = pH_w - pH_s$$

Table 5: Rotated principal component matrix derived from PCA

ParametersPrincipal Components

	Post-monsoon					Pre-monsoon			
	1	2	3	4	5	1	2	3	4
Ca^{2+}	0.427	0.751	0.295	-0.043	0.039	0.872	0.213	-0.016	0.127
Mg^{2+}	0.657	0.550	0.050	0.154	-0.077	0.834	0.034	0.170	0.104
Na^{+}	0.855	-0.075	0.193	0.028	0.066	0.629	0.224	-0.030	-0.345
K^{+}	-0.007	0.033	0.159	0.044	0.862	-0.205	-0.082	-0.032	0.624
HCO_3^-	0.140	0.220	0.719	0.228	0.276	0.328	0.526	0.521	-0.123
Cl^-	0.643	0.483	-0.149	-0.236	-0.046	0.774	0.005	-0.438	0.120
F^-	0.074	-0.069	0.264	0.706	-0.352	-0.043	0.152	0.762	-0.035
SO_4^{2-}	0.821	0.038	-0.016	0.114	-0.053	0.667	-0.163	0.048	-0.365
NO_3^-	-0.092	0.866	-0.047	-0.046	-0.014	0.337	0.139	0.046	0.762
Fe	-0.076	-0.227	-0.451	-0.043	0.403	-0.236	-0.589	-0.190	-0.088
Mn	0.023	0.122	-0.712	0.122	-0.006	0.136	-0.769	0.021	-0.007
Cr	-0.041	0.019	0.195	-0.789	-0.305	0.120	0.512	-0.582	-0.318

Extraction Method: PCA-Principal Component Analysis
Rotation Method: Varimax with Kaiser Normalization

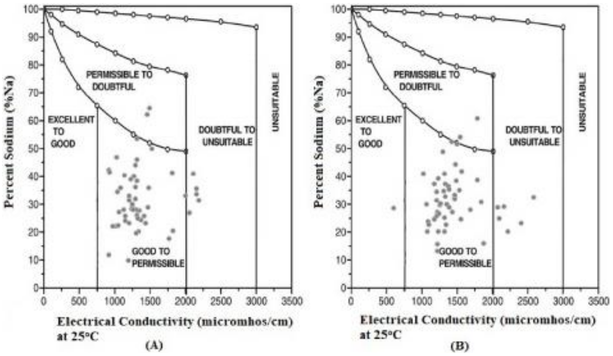


Fig. 7: Classification of water on the basis of EC and %Na in groundwater samples collected during (A) post monsoon and (B) pre monsoon season from Singrauli region. Na% = $Na^+ \times 100 / [Ca^{2+} + Mg^{2+} + Na^+ + K^+]$ (after Wilcox, 1948)

The pHs is calculated as:

pHs = (9.3 + A +B) – (C + D)

The constants A = (Log_{10}[TDS] – 1)/10; B = -13.12 ×log_{10}(ºC + 273 + 34.55; C = Log_{10}[Ca^{2+} as $CaCO_3$] – 0.4, and D = Log_{10}[alkalinity as $CaCO_3$].

A negative LSI value indicates that the solution is under saturated with $CaCO_3$ and has the tendency to remove the existing calcium carbonate protective coating in pipelines and equipments. A positive value suggests that solution is supersaturated with CaCO3 and scaling may take place. A neutral LSI value indicates that solution is at equilibrium with $CaCO_3$ and it is neither scale forming nor scale removing. The LSI values of the ground water samples are plotted in figure 10. The LSI ranged from –1.70 to 1.10 (avg: –0.12) and –1.30 to 0.92 (avg: –0.13) in the post and pre monsoon samples, respectively (Table 1). Results showed that 40% and 37% had positive while 60% and 63% samples were having negative LSI values in post and pre monsoon seasons, respectively. The wide range of the LSI values suggests the differential nature of the groundwater with reference to their scaling properties and therefore, should be used in industrial processes with caution.

Ryznar Stability Index (RSI) : The RSI calculations use the LSI values as a component in a new formula to improve the accuracy in predicting the scaling or corrosion tendencies of water (Ryznar, 1944). The RSI can be calculated as:

RSI = $2(pH_s) - pH_w$

where, pH is the measured pH of ground water samples and pHs is the pH at saturation with calcite or calcium carbonate.

In groundwater with RSI values of << 6, the

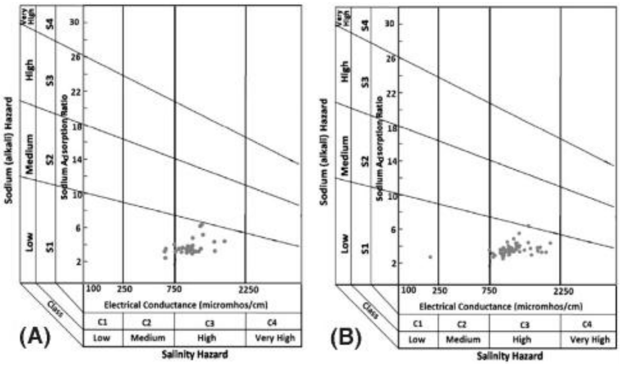


Fig. 8: Classification of groundwater collected during (a) post and (b) pre monsoon season in relation to salinity and sodium hazard (after USSL, 1954)

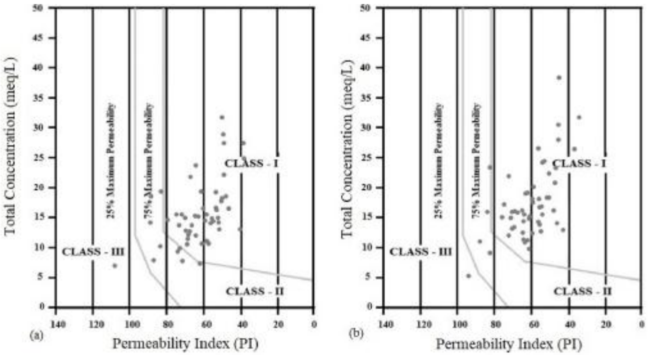


Fig. 9: Classification of groundwater based on Donnen's permeability index plot (Donnen, 1964) for (a) post monsoon and (b) pre monsoon season samples of Singrauli region

scale forming tendency increases as the index decreases. The RSI value of >> 7 indicate that calcium carbonate formation probably does not lead to a protective corrosion inhibitor film, while a value of >> 8 indicates mild steel corrosion which becomes an increasing problem. The RSI ranged from 6.04 to 10.01 (avg: 7.50) and 6.26 to 9.14 (avg: 7.40) in post and pre monsoon seasons, respectively (Table 1 and Fig. 10). The results show that nearly 20.3 % of the samples in each seasons had RSI values in between 6-7 depicting little scaling or corrosion. Similarly 55.6 and 68.5% of the samples had RSI in the range of 7 to 8 could exhibit significant corrosion in post and pre monsoon seasons respectively. The 24.0 and 11.1% of samples were found to be aggressively corrosive in nature with RSI values > 8 in post and pre monsoon seasons, respectively. Results showed the variable nature of groundwater while mild corrosion could result from few samples.

Source Apportionment Using Multivariate Analysis

To discriminate the sources contributing to chemical composition of groundwater, correlation matrix and Principal component analysis (PCA) was performed on the post and pre monsoon groundwater samples. During post monsoon season, significant correlations were observed among the Ca^{2+}-Mg^{2+} (0.65), Mg^{2+}-Cl^- (0.60), Mg^{2+}-SO_4^{2-} (0.59), Ca^{2+}-Cl^- (0.56), Na^{2+}-Cl^- (0.56), Na^{2+}- SO_4^{2-} (0.56), Ca^{2+}-NO_3^- (0.49), Ca^{2+}-HCO_3^- (0.48) and Ca^{2+}- SO_4^{2-} (0.45). Very insignificant correlations were found for F^-, NO_3^- and metals (Fe, Mn and Cr), suggesting their contribution from leaching of these species from ash ponds. Similar trends were observed in the correlation matrix of pre monsoon samples with high correlation among Ca^{2+}-Mg^{2+} (0.71), Mg^{2+}-Cl^- (0.53), Mg^{2+}- SO_4^{2-} (0.52), Ca^{2+}-Cl^- (0.68), Na^{2+}-Cl^- (0.53), Na^{2+}- SO_4^{2-} (0.53), Ca^{2+}-SO_4^{2-} (0.48), Ca^{2+}-HCO_3^- (0.47) and Ca^{2+}-NO_3^- (0.35).

PCA, is a commonly used statistical method to extract a small number of factors based on inter species associations and each factors is assigned a source(s) based on the constituents present in it. The PCA was carried out on the soluble ions and metal data using statistical package for social science (SPSS) version 17 using varimax rotation method. The components with Eigen value greater than unity were only considered following the Kaiser criteria. In post monsoon, five major principal components were identified by PCA (Table 5) Principal component 1, was significantly loaded with Mg^{2+}, Na^+, Cl^-, SO_4^{2-} explaining 27.5% of the variance in the data. These ions are mainly responsible for high EC, TDS and hardness in water and derived from incongruent dissolution of respective feldspar minerals in groundwater indicating rock-water interaction. Component 2 had significantly high loading for Ca^{2+}, Mg^{2+}, Cl^-, and NO_3^- accounting to 13.% of the variance. Cl^- and NO_3^- in groundwater are commonly derived from the anthropogenic sources, leaching of fly ash in present case. This component of PCA possibly indicates to both natural as well as anthropogenic influences. Component 3 explained 11% of the variance and was maximally loaded for F^- and HCO_3^-. The component 4 explained 10% of variance and had higher loading for F^- indicating anthropogenic influences. Component 5 had higher loading for K^+ and Fe and accounted to 8.7% of the

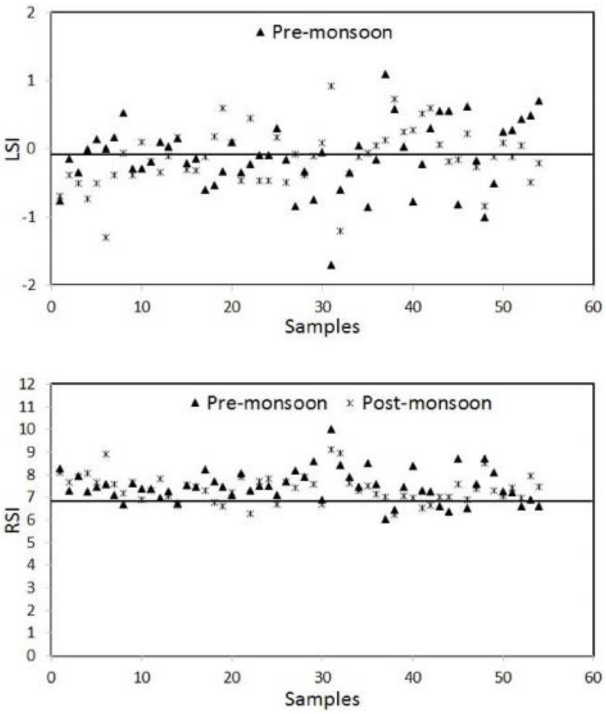


Fig. 10: **The Langelier Saturation Index (LSI) and Ryznar Stability Index (RSI) for assessing calcium carbonate precipitation potential for the groundwater collected during post and pre monsoon seasons from Singrauli region**

variance. Since occurrence of K^+ in the groundwater is mainly from the granitic rocks consisting of feldspars (orthoclase and plagioclase), mica, pyroxene and quartz (Patel *et al.*, 2016), this component can be attributed to the natural rock-water interaction influencing the composition of groundwater.

Similarly, a total of four principal components were identified in the pre monsoon season samples. First principal component accounted for 28.7% of the variance in the data and showed highest loading for Ca^{2+}, Mg^{2+}, Na^+, Cl^- and SO_4^{2-}, the major soluble ions naturally present in water. The component 2 showed maximum loading for HCO_3^-, Cr and accounted to 13.7% of the variance. The component 3 had maximum loading for HCO_3^-, Cl^- and F^- indicating anthropogenic influences. Likewise, the component 4 accounted for 10% of the variance and had maximum loading for NO_3^- and K^+.

Conclusions

The results suggest that the groundwater in Singrauli power belt region dominantly belonged to Ca-Mg-HCO_3water type except that few samples belonged to Ca-Mg-Cl-SO_4 type, which is attributed to anthropogenic interferences. Rock weathering is the major driving force controlling the groundwater chemistry in Singrauli region. Majority of the groundwater samples belonged to hard to very hard categories. Concentrations of Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-} were found to be well within the permissible limits of drinking water prescribed by WHO. A total of 35% and 44% of the samples had F^- concentrations exceeding the WHO recommended limits of 1.5 mg/L during post and pre monsoon season, respectively. Likewise, a total of 22% and 26% of the samples had exceeded their regulatory limits of NO_3^- i.e., 45 mg/L during post and pre monsoon seasons, respectively. High fluoride concentration nearby fly ash ponds indicated contamination from the ash leachates. Elevated nitrate concentrations in groundwater could also be attributed to the formation of nitrogen oxides during coal combustion, their deposition on the surface and subsequently leaching to groundwater. Among the metals analyzed here, majority of the groundwater samples exceeded the maximum WHO permissible limits for Fe and Cr, thus the groundwater in Singrauli is deemed to be unfit for drinking purpose. Based on various parameters such as Sodium adsorption ratio (SAR), residual sodium carbonate (RSC), magnesium hazard (MH), Kelly's index (KI), EC, %Na and Donnen's chart, the groundwater in Singrauli region was found safe for irrigation purpose. CAI-1 and CAI-2 ratios suggest that in each season 72% of the groundwater samples showed the reverse exchange of ions while 28% of samples indicated the prevalence of direct exchange process. The USSL plot for salinity hazard and alkali hazard indicated that majority of the groundwater (94.4 and 96.4% in post and pre monsoon, respectively) samples in Singrauli belonged to C_3S_1 class, representing high salinity hazard and low alkali hazards water, which requires proper drainage otherwise it, can adversely affect the soil. Ryznar Stability Index (RSI) and Langelier Saturation Index (LSI) indicated that scaling and mild corrosion could occur intermittently and therefore, should be used in industrial processes with caution. The effect of leaching from ash ponds appeared to be an important contributor to deterioration of groundwater quality. Therefore, further work is needed to study the leachate composition so that safety and precautionary measures can be suggested for restricting leaching from ash ponds.

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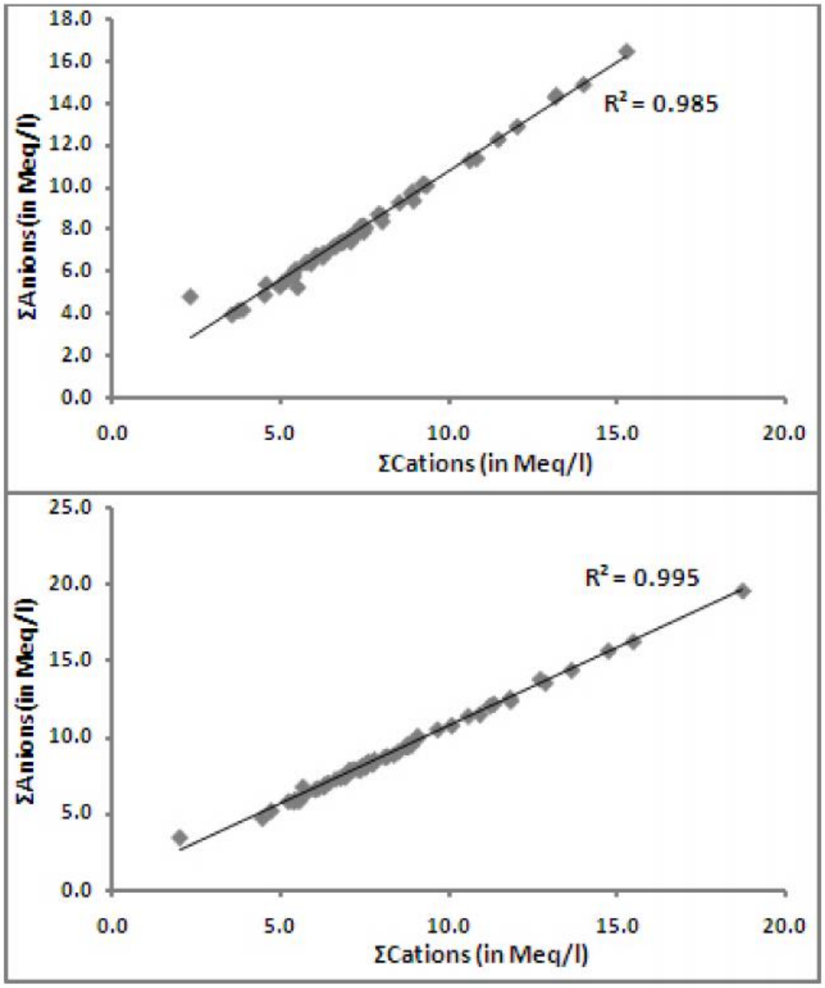

Fig. SF1: Scatter plot among the anion and cation concentrations in groundwater samples during (a) post and (b) pre monsoon seasons