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SUSTAINABLE INDUSTRIAL AND ENVIRONMENTAL BIOPROCESSES

Assessment of water-quality parameters of groundwater contaminated by fly ash leachate near Koradi Thermal Power Plant, Nagpur

Vikas Pandey[1] · **Madhurya Ray**[1] · **Vipin Kumar**[1]

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Abstract

Thermal power generating industries affect the surrounding environment in various ways. Fly ash escapes along with flue gases and can be found in undesirable quantities in soil and water sources in the region. The water quality of an area must be evaluated regularly to ensure the quality of potable water. The present study evaluates the pre-monsoon and post-monsoon concentrations of several important physico-chemical parameters and heavy-metal contents of groundwater samples collected from sites near the Koradi Thermal Power Plant, a major source of power generation in the Nagpur Region. The maximum amount of total dissolved solids observed during the two seasons studied were 1571 mg/l and 1591 mg/l which is within the desirable limit implying that fly ash contamination did not affect this water quality parameter. The total hardness of samples from GW-3, GW-5 and GW-9 were 844 mg/l, 775 mg/l and 675 mg/l during pre-monsoon season, while GW-3 and GW-5 along with GW-4 continued to show high levels of total hardness at 1015 mg/l, 741 mg/l and 650 mg/l, respectively. These values are higher than the permissible limit due to the high levels of ions of bicarbonate, calcium, sodium and sulphate derived from fly ash leachate. Statistical analysis showed that sulphides, total hardness, electrical conductivity and total dissolved solids were the significant water quality parameters of the region. The evaluation of the parameters found that the three water sources (GW-3, GW-5 and GW-9) out of 10 are the most affected groundwater sources of fly ash pollution.

Keywords Groundwater contamination · Thermal power plant · Fly ash · Leachate concentration · Water quality · Leaching

Introduction

The amount of power generated in India has increased greatly over the last decade with the current demand standing at around 300,000 MW. Coal is one of the major sources of power generation in India. More than 70% of the power needs of the country are generated by burning coal. A majority of the coal used is low-grade coal with high ash content. It is required in huge amounts by thermal power generating industries (Khan and Umar 2019). Fly ash (FA) is generated in large quantities near thermal power plants. FA can contain an abundance of heavy metals including mercury, lead, arsenic and chromium depending on the source of the coal used. It poses a threat to human health because if consumed or inhaled in higher quantities, it can cause respiratory disorders, gastrointestinal diseases and act as a carcinogen (Maree et al. 1987; Landrigan et al. 2000; Adamu et al. 2015). It is estimated that 1 in 50 people develop cancer when the source of drinking water contains heavy metal pollution. Fly ash is one of the major wastes generated indirectly from the mining industry. FA is a product of coal combustion and is composed of very fine particles (Carlson and Adriano 1993). FA can be disposed in dry landfills or in ash ponds (Kanchan et al. 2015). Some of the FA is recycled either as building materials, road base or for agricultural uses (Ghosh et al. 2018; Jambhulkar et al. 2018). Low-cost adsorbents have been developed using FA which can be used to adsorb dyes, mercury, organic pollutants, NOx and SO_X. FA can be transformed into zeolites for aiding ion exchange (Ahmaruzzaman 2010). FA can also be used in formulation to immobilize lead (Dermatas and Meng 1995). Ash ponds contain

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✉ Vipin Kumar
vipinmicro1@gmail.com; vipinmicro1@iitism.ac.in

[1] Laboratory of Applied Microbiology, Department of Environmental Science and Engineering, Indian Institute of Technology (Indian School of Mines), Dhanbad, Jharkhand, India

the risk of infiltration of leachate or leaking of slurry to nearby water sources (Du et al. 2018; Demir et al. 2019). Leaching of fly ash happens in the form of dilute slurry from ash ponds; the process depends on the pH of the slurry and the liquid to solid ratio (Lindahl and Bockstaller 2012; Lu et al. 2019). Ninety percent of the potable water supply of the population is sourced from groundwater (Karthika et al. 2018). The groundwater contamination with FA leads to the subsequent addition of metals in the biogeochemical cycle (Mirzabeygi et al. 2017). Water sources can also be polluted via the routes of soil erosion and surface runoffs (Atafar et al. 2010). Devices like electrostatic precipitators are used for capturing FA escaping along with flue gases in thermal power industries. FA can be classified as Class F FA and Class C FA depending upon the composition of elements in it. Class F fly ash is chiefly generated during the burning of aged anthracite and bituminous coal, while Class C is produced by lignite and sub-bituminous coal. Class C contains a major amount of CaO (Jeon et al. 2018). FA contamination increases the amount of toxic heavy metals in the groundwater resources. The groundwater quality can be affected by several factors, including natural and anthropogenic causes (Kumarathilaka et al. 2018). Anthropogenic causes behind the water quality deterioration of groundwater include mining activities, industrial waste generation, sewage and solid waste disposal and urbanization (Gadgil and Guha 2013). The pollutant levels in groundwater sources remain unaltered for a longer period of time than the pollutant levels in surface water because of the slow rate of movement of groundwater (Shrinivasa Rao and Venkateswaralu 2000; Phoungthong et al. 2018; Schomburg et al. 2018). The quality of groundwater is assessed by analyzing the physical, chemical and biological properties of the water (Kaliprasad and Narayana 2018). Apart from harming human life, contamination of groundwater with toxic pollutants can lead to the deterioration of the flora and fauna in the region. The presence of a high amount of toxic elements in the water can also lead to metabolic impairments.

Physico-chemical properties of a water sample provide an in-depth analysis of the groundwater quality of a region apart from highlighting the important pollutants (Patil et al. 2012; Yadav et al. 2012). The evaluation of physico-chemical properties is necessary to determine the potability of a source of water (Kumar et al. 2018; Nzung'a 2018).

The accumulation of trace metals in FA occurs as a result of condensation and evaporation during different production operations (Dandautiya et al. 2018). During the monsoon season, the rate of leaching is enhanced leading to increased concentrations in GW sources. Coal contains traces of fluorine and chlorine. FA generated during combustion contains between 10 and 40% of the F and Cl content of coal (Deng et al. 2016).

The analysis of metals in groundwater is necessary to evaluate its possible impact on the environment and human health. FA is a heterogeneous mixture implying that the elemental composition is not evenly distributed. The distinguished components releasing from FA leachate include Ca and SO_4^{2-}, Cl and Na. The leachability depends on factors like the combustion procedure, class of coal, redox conditions and pH (Izquierdo and Querol 2012). Fluorine condenses in minute proportions in FA, and its leaching level ranges from between 5 and 60 mg/kg (Piekos and Paslawska 1998; Álvarez-Ayuso and Querol 2008). These values are not very significant for consideration of FA leachate contamination. FA leachate can affect the composition of different metals depending on conditions like pH and temperature of coal combustion process and amount of sulphates and phosphates in the coal.

Arsenic (As) condenses on the surface of FA in the form of arsenate (Goodarzi et al. 2008). As has maximum solubility in the pH range of 7–11. This is attributed to the lower affinity of arsenic to metal oxides at higher pH. Arsenic uptake by plants is primarily dependent on the type of plant rather than the concentration of arsenic in groundwater or soil. The arsenic concentration in plants changes with different arsenic bearing phases of the plant life-cycle. The young tissues of the root and stem take up the maximum amount of arsenic during the vegetative phase. A considerable reduction of As concentration is observed during the reproductive phase. This can be attributed to the reduction of use of groundwater during this phase. Methylation by microorganisms present in the field also aids the removal of As. During the ripening phase, a considerable gain in As concentration is again observed due to crystallization of thermodynamically unstable Fe oxyhydroxide and the subsequent release of adsorbed As (Chowdhury et al. 2018). Arsenic is a known carcinogen in humans, and ingestion in even minute countries can be harmful. The groundwater sources of several regions of West Bengal are contaminated by As (Samadder 2011).

Cadmium is highly toxic to the aquatic ecosystem due to its high solubility. However, it is immobile in neutral and alkaline pH and hence does not usually cross its desirable limit.

Chromium (Cr) is found in bituminous coal and is a potential carcinogen in its hexavalent (Cr^{6+}) form in aqueous environment. Cr+ remains in FA as trivalent chromium (Cr(III)) and is less dangerous due to its lower solubility in this form. Leachability of Cr is highly pH dependent with effective leaching occurring only at higher pH values (Dubikova et al. 2006).

Lead (Pb) is associated with sulphides in coal and is highly insoluble and immobile. Earlier studies suggested Pb leaching rates to be generally low and only effective at high alkaline values of pH. The leachability of elements like Zn and Ni varies highly in FA depending on the surrounding conditions. Zn is found in close association with sulphide in coal.

Mercury is a highly toxic metal found in coal in minute quantities. The sorption of g depends on the presence of Cl and S (Meij 1995). The leachability of Hg is very low in FA eliminating it as an environmental concern as FA leachate.

The electrical conductivity of the water can be used to estimate the amount of conductive ions present in it. The presence of ions of inorganic materials and salts in dissolved form results in a high conductivity (Tank and Chandel 2010). The pH measures the hydrogen ion concentration of the water, which in turn, is necessary for determining the alkalinity of the water source. High values of alkalinity suggest the presence of a large amount of carbonates and bicarbonates. Total dissolved solids can affect the taste of the water.

Another important parameter for measuring the water quality is the hardness of water. Excess amount of hardness is undesirable as it can have laxative effects upon drinking. Groundwater contains more calcium than surface water (Sienko and Plane 1974; Spielmeyer et al. 2017). Since fly ash contains a high amount of calcium oxide (CaO), the concentration of calcium is high in the FA polluted groundwater sources. Fluoride is present in water in ionic form and is important for dental health and bone density. However, a large quantity of fluoride is that values exceeding 1.5 mg/l can lead to occurrence of fluorosis. Presence of excess amount of sulphates in water can lead to scaling in boilers and alter the taste of drinking water (Wanganeo et al. 2018; Walaszek et al. 2018).

Koradi thermal power station (KTPS) located in Maharashtra is one of the major power stations of the region, which began its operation during the 1970s. It has a power generation capacity of 2400 MW. The nearby localities of Koradi power plant, Nagpur, were selected as the study area. Presently, the plant operates 8 units with plans of further increasing the power outputs. The present study investigates the role of FA leachate on groundwater contamination near thermal power plants before and after the monsoons and subsequently tries to recognize their possible effects on human health.

Materials and methods

Sampling site

Nearby locality of Koradi Thermal Power Plant, Nagpur, was selected as the study area. Koradi Thermal Power Plant is situated in close proximity to Nagpur City and as the latitude and longitude of 21°14′56″ N and 79°5′56″ E, respectively. The plant had 2 units of 210 MW each at the early stages. Currently, its total capacity has increased to 2400 MW. The regional climate consists of hot summers with less humidity throughout the year except during the south-west monsoon season, i.e., June to September. The peak temperature during the seasons of summer and winter ranges between 45 and 12 °C, respectively, with annual rainfall of about 1200 mm. The three ash ponds in the study area receive ash from the two thermal power stations at Koradi and Khaparkheda. The ash generated in the power plant is eliminated by two different modes. Firstly, it is disposed of as fly ash in the atmosphere from the stacks and secondly the ash slurry containing the bottom ash is cast aside in ash ponds. The ash slurry is a mixture of the bottom ash with water and which is then transported to the pond through pipelines.

Collection of samples

Groundwater samples were collected from 10 different locations near Koradi Thermal Power Plant during pre-monsoon (April 2017) and post-monsoon (Nov 2017) season. The 10 locations were of nearby villages which could possibly be impacted by FA generation, and the details of the sample locations are given in Table 1. The sampling site lies between 21°15′ and 21°12′ in north latitudes and between 79°3′ and 79°11′ in east longitudes (Fig. 1). Each of the water samples was filtered with 0.45 μm membrane filters and collected in sterilized plastic bottles, which were pre-cleaned with concentrated nitric acid and distilled water in the laboratory. The samples were divided into two parts, of which one was acidified with concentrated nitric acid for cation estimation and the remaining was used for the estimation of other physico-chemical properties. The water was stored at 4 °C in the laboratory. The analysis of the water samples was done within 2 h of sampling.

Physico-chemical analysis

Physico-chemical parameters like pH, turbidity and conductivity were measured using a multi-parameter tester. Alkalinity was measured by acid titration, while total hardness, calcium hardness and magnesium hardness were determined by (ethylenediaminetetraacetic) EDTA titration. Chlorine was determined by argentometric titration. Fluoride was measured by colorimetry method. Standard reagents of analytical grade like KCl, $CaCO_3$ EDTA and indicators were obtained from Merck® and were used for analysis, and the instruments were calibrated.

Analysis of heavy-metal compositions

Metals that have higher densities are categorized as heavy metals. They are found to have highly carcinogenic effects on human beings and animals (Alkarkhi et al. 2008). To determine the safety of a source of drinking water, its heavy metal analysis is necessary. The heavy metal composition of elements like arsenic, nickel, chromium, cadmium, zinc and nickel was found using standard methods of APHA (2012). ICP-MS analysis using PerkinElmer SCIEX ELAN DRCe was done for trace metals.

Table 1 Groundwater sample locations

Sample code	Village	Latitude	Longitude	Source	Water level (mbgl)	
					Pre-monsoon	Post-monsoon
GW-1	Mahadula	21°15′13.38″ N	79°4′35.36″ E	HP	4.7	2.9
GW-2	Suradevi	21°14′49.81″ N	79°7′12.63″ E	DW	4.9	3.1
GW-3	Waregaon	21°14′46.29″ N	79°9′10.81″ E	DW	5.4	3.4
GW-4	Khairy	21°13′3.21″ N	79°9′12.23″ E	HP	5.8	3.4
GW-5	Mhasala	21°12′53.47″ N	79°7′41.73″ E	HP	5.1	2.8
GW-6	Kawatha	21°13′28.84″ N	79°8′19.58″ E	DW	4.6	2.7
GW-7	New Khasala	21°12′4.61″ N	79°8′3.34″ E	DW	5.2	3.2
GW-8	Godhni	21°13′16.06″ N	79°3′38.12″ E	HP	5.8	3.8
GW-9	Kamptee	21°13′58.45″ N	79°10′12.38″ E	HP	6.8	4.0
GW-10	Yerkheda	21°12′57.87″ N	79°11′12.24″ E	HP	6.7	3.9

HP handpump, *DW* dugwell, *mbgl* metres below ground level

Statistical analysis and evaluation of source of ionic composition of groundwater

The overall ionic distribution of cations and anions in the samples and analysis of contributing elements was done using the Pipers Trilinear Diagram generated by the software Grapher 13. Statistical analysis was done using Excel 2007 for a detailed comparison of the different physico-chemical properties during the two seasons. The distribution pattern of sulphate ions was analyzed using Arcmap 10.3.

Results

Physico-chemical properties of groundwater

The pH was found to be between 7.1–7.7 during pre-monsoon and 6.8–7.5 during post-monsoon season. The pH of groundwater samples was found to be within the acceptable limit of BIS (2012). Electrical conductivity was found in the range of 540–2652 ms/cm in pre-monsoon season and 708–2618 ms/cm during post-monsoon season (Tables 2 and 4). Higher conductivity of groundwater is due to downward percolation

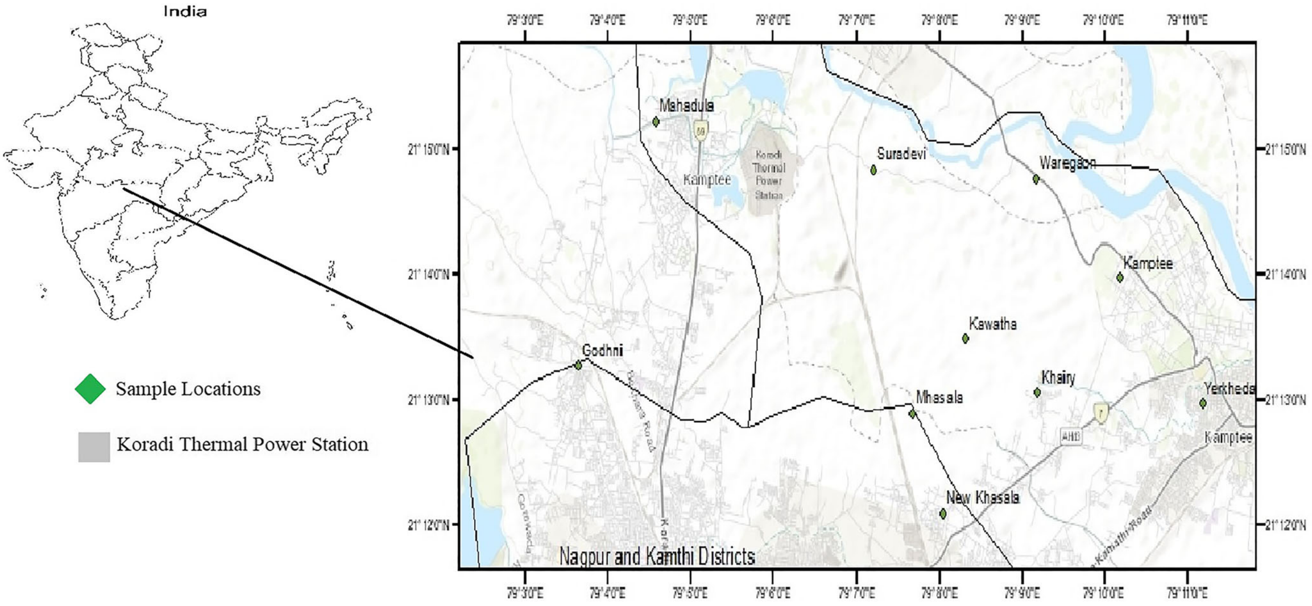


Fig. 1 Groundwater sample locations

Table 2 Physico-chemical properties of water in pre-monsoon period

Sample no.	pH	Turbidity (NTU)	E. cond. (ms/cm)	TDS (mg/l)	Total alkalinity (mg/l)	Total hardness as $CaCO_3$ (mg/l)	Ca^{++} (mg/l)	Mg^{++} (mg/l)	SO^{-}_{4} (mg/l)	Cl^{-} (mg/l)	NO^{-}_{3} (mg/l)	PO^{-}_{4} (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Bicarbonate (mg/l)	Fluoride (mg/l)
GW-1	7.1	2.9	540	324	134.4	246	56	26	130	78	9	1.08	50	3.4	164	0.6
GW-2	7.6	1.2	1192	715	235.2	365	78	41	172	103	19	1.41	86	7.2	287	0.7
GW-3	7.3	1.0	1534	920	303	844	110	138	260	156	43	1.48	68	7.9	370	0.8
GW-4	7.2	1.9	2652	1591	230.1	535	113	61	721	433	35	0.54	356	13.7	281	0.7
GW-5	7.4	3.1	2626	1576	241.8	775	211	60	649	389	54	0.91	286	12.4	295	0.6
GW-6	7.7	1.0	966	580	88.2	212	11	45	251	150	10	0.65	119	7.7	108	0.6
GW-7	7.2	1.6	1086	651	226.8	244	25	44	155	93	23	0.62	140	1.9	277	1.1
GW-8	7.1	1.3	1413	848	218.4	426	129	25	113	68	33	0.44	132	3.8	266	0.6
GW-9	7.1	1.2	2579	1548	217.6	678	217	33	296	177	44	0.60	216	13.4	265	0.7
GW-10	7.7	1.1	1030	618	213.52	258	63	24	209	125	7	0.39	141	6.1	260	0.7

of ions of chloride, sulphide and carbonates from ash ponds through soil strata. The total dissolved solid (TDS) varied between 324 and 1591 mg/l in pre-monsoon season and 425–1571 mg/l in post-monsoon season. Total dissolved solid is a measure of the organic and inorganic contents of substances in a liquid in molecular, ionized and suspended form. TDS value was found to be exceeding most of the time the acceptable limit of 500 mg/l (BIS 2012). Alkalinity of water may be due to either the presence of strong bases like sodium hydroxide or potassium hydroxide in water or the extreme low concentration of them. Maximum alkalinity of 303 mg/l was recorded in GW-3 in pre-monsoon and 420 mg/l in post-monsoon season which exceeds the standard value.

Total hardness is due to the presence of cations of calcium and magnesium and anions of carbonate and bicarbonate, chloride and sulphate in water. Hardness of groundwater in pre-monsoon was 212–844 mg/l and 207–1015 mg/l in post-monsoon season.

The anion chemistry showed that bicarbonate and sulphate were the dominant anions in groundwater with a minor contribution of chlorides. In the samples, the concentration of bicarbonate varies from a 108–370 mg/l in pre-monsoon season and 211–512 mg/l in post-monsoon season. Bicarbonates are derived mainly from the rhizospheric soil zone CO_2 and dissolution of carbonates and reaction of silicates with carbonic acid. The soil in the rhizospheric zone is rich in CO_2 pressure as a result of decay of organic matter and root respiration. This CO_2-rich zone forms bicarbonates when infused with rain water. Bicarbonate may also be derived from the dissolution of carbonates and/or silicate minerals by the carbonic acid. Calcium was observed as 11–217 mg/l in pre-monsoon and 45–147 mg/l in post-monsoon season.

In most of the samples, calcium was found to be exceeding from the desirable range of 75 mg/l (BIS 2012). Magnesium was found to be exceeding the acceptable limit of BIS (2012) i.e. 30 mg/l in all samples except at GW-1, GW-8 and GW-10 in pre-monsoon season, and GW-1 and GW-10 in post-monsoon season. It was observed as 24–138 mg/l in pre-monsoon and 11–161 mg/l in post-monsoon.

Analysis of heavy-metal compositions

Heavy metal compositions were found to be within the permissible limits of WHO guidelines (WHO 2004). The concentration of iron, zinc and nickel reduced during the post-monsoon season to 0.237 mg/l, 0.131 mg/l and 0.012 mg/l, respectively (Tables 3 and 5). The concentration of these metals implied that the drinking water sources of the region did not possess the risk of cancer (Fig. 4).

Table 3 Heavy-metal analysis of water in pre-monsoon period

	Sample no.	Iron (mg/l)	Copper (mg/l)	Manganese (mg/l)	Cadmium (mg/l)	Lead (mg/l)	Total arsenic (mg/l)	Zinc (mg/l)	Total chromium (mg/l)	Nickel (mg/l)
Desirable limit by WHO 2004		0.3	2	0.04	0.0003	0.01	0.01	4	0.05	0.07
Desirable limit by IS 10500:2012		0.3	0.05	0.1	0.0003	0.01	0.01	5	0.05	0.02
	GW-1	0.21	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.29	< 0.03	0.02
	GW-2	0.33	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.18	< 0.03	0.01
	GW-3	0.26	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.17	< 0.03	< 0.01
	GW-4	0.30	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.98	< 0.03	0.01
	GW-5	0.44	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.19	< 0.03	0.04
	GW-6	0.36	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.46	< 0.03	< 0.01
	GW-7	0.25	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.21	< 0.03	< 0.01
	GW-8	0.39	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.36	< 0.03	0.01
	GW-9	0.40	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.17	< 0.03	0.03
	GW-10	0.11	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	< 0.1	< 0.03	0.04

Statistical analysis and evaluation of source of ionic composition of groundwater

The correlation of various water quality parameters showed that the most relevant parameters (> 0.8) were EC, TDS, total hardness, calcium and sulphate concentrations during both pre-monsoon and post-monsoon seasons (Supplementary Tables 1 and 2). The values marked in red highlight the significant parameters. Sulphate is a good indicator of pollution caused by industries. High concentrations of sulphate mark the groundwater source unfit for drinking. Similarly, excessive hardness can cause scaling in boilers, hindrances in industrial operations, and can impart an objectionable taste at higher concentrations. TDS and conductivity indicate the presence of ions of elements like nitrate, arsenic, copper, lead, etc. which can be detrimental for human health.

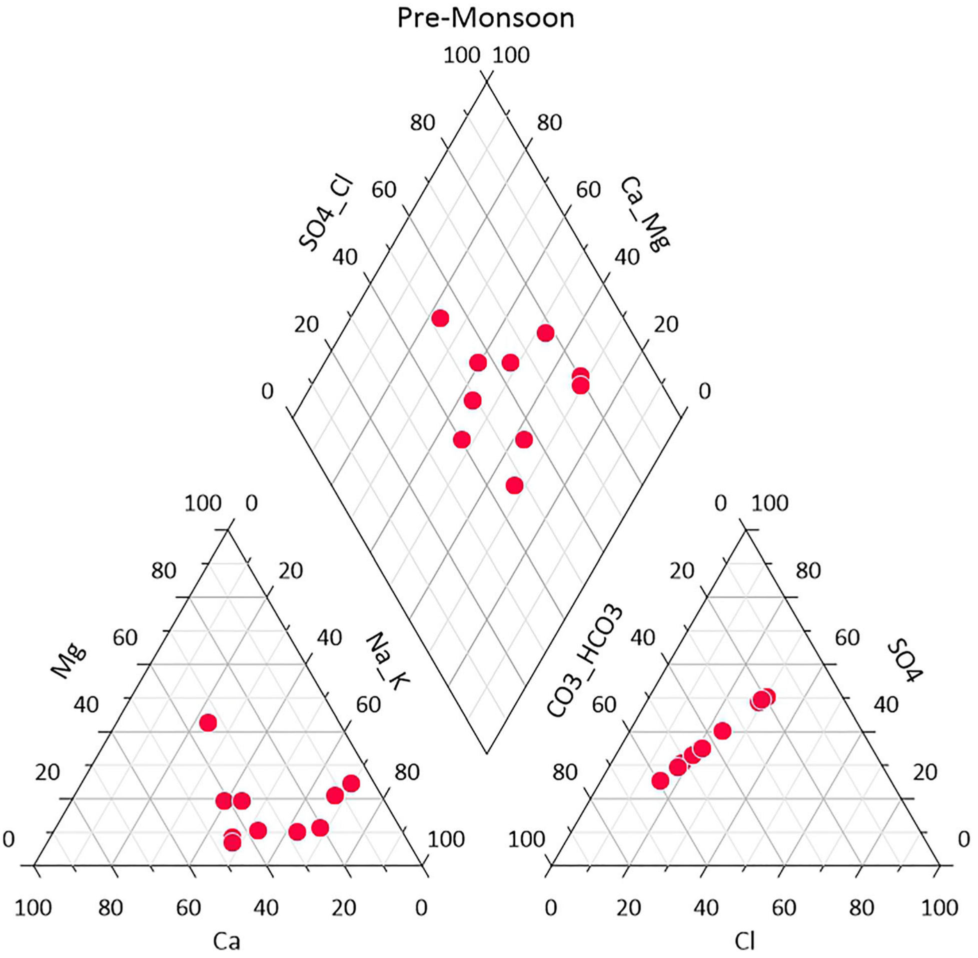
The distribution of anions and cations based on the source of ions is depicted in Figs. 2 and 3. Ca^{2+}, Na+ and K+ were the main contributors of anions, while cations were mainly supplied by Cl^- and HCO_3^-.

Discussion

Groundwater quality assessment based on important parameters

Groundwater is an important source of potable water. The values of physico-chemical parameters of groundwater remained within desirable limits of WHO (2004) and (BIS 2012), and it might be due to the samples not being affected by a source of significant pollution in the region. Much of the groundwater is used for domestic purposes (Karthika et al. 2018). The suitability of groundwater is analyzed by measuring the quantity of several physico-chemical parameters and heavy metal composition of the source. Industries have a significant effect on the groundwater and surface water sources of a region because of which it is necessary to assess the water quality parameters from time to time. Contamination due to fly ash occurs in the Nagpur Region due to the operations of several thermal power plants. Fly ash contains a significant amount of calcium carbonate and metals (Aubert et al. 2006). Excessive deposition fly ash constituents in groundwater via various routes lead to the unwanted increase of certain water quality parameters. The water quality parameters that were assessed in this study include pH, alkalinity, electrical conductivity, total hardness, calcium and magnesium concentration, nitrogen, phosphorus bicarbonate and several metal compositions (Fig. 4). Fly ash if not treated at the site of generation can travel a consequential distance and pollute the air, water and soil surface (Khan and Umar 2019). Fly ash components can percolate into groundwater sources. World Health Organization (WHO) has guidelines for the maximum permissible limits of various water quality parameters beyond which they are considered inconsumable (WHO 2004). pH of water can be altered by the presence of various chemical components. Electrical conductivity, which is a measure of the ionic constituents of water, indicates the presence of minerals in it. The total dissolved solid concentration in this study ranged from 324 to 1591 mg/l during the pre-monsoon period and from 425 to 1571 mg/l during the post-monsoon period. GW-5, GW-4 and GW-9 had greater values of TDS than the maximum permissible limit. The presence of dissolved

Fig. 2 Pre-monsoon ionic distribution of the groundwater sources



solids in water sources can lead to changes in its taste (Vasanthavigar et al. 2012). GW-1 had minimum values for most of the water quality parameters indicating that it was one of the least affected groundwater sources in the region sampled. High TDS concentrations can often have adverse effects if ingested regularly. In the past, high TDS values in water resources have been suggested as a possible source of cardiovascular diseases, gastrointestinal disorders and cancer (Karthika et al. 2018).

The concentration of chloride in groundwater sources can also indicate the prevailing amount of pollution in the region. High chloride concentration is often caused by surface runoff and industrial discharges into water sources. Chloride ion values ranged from 70 to 378 mg/l during post-monsoon season and 78–433 mg/l during the pre-monsoon season. GW-4 showed a high presence of chloride in both cases. The chloride concentration of the groundwater samples was within the permissible limits and showed declines in their concentration during the post-monsoon season while the heavy-metal compositions were also within desired limits in the given period. (Tables 4 and 5).

Sulphates can be present in water sources in various forms, including magnesium sulphate and calcium sulphate. The concentration of sulphate ranged from 67 to 629 mg/l during post-monsoon season and 113 to 721 mg/l during pre-monsoon season. The concentration of sulphates was considerably high in many of the samples. The presence of a high amount of sulphate can be toxic. It can also alter the pH and make it more acidic.

Phosphate values ranged from 0.39 to 1.48 mg/l during the pre-monsoon period and 0.08 to 0.38 mg/l during the post-monsoon period. Phosphate concentration was considerably low in the groundwater sources of the region. The phosphate values also declined during the post-monsoon season. Hardness of water is one of the most important parameters based on which we deem it fit or unfit for drinking. The total hardness varied from 212 to 844 mg/l during pre-monsoon season, while it ranged from 207 to 1015 mg/l during post-monsoon period. The total hardness was also found to be exceeding the permissible values in many samples. GW-3, GW-4 and GW-5 showed maximum values for total hardness during post-monsoon season. It was also observed that the values of total hardness increased during the latter season. While the reduction of some

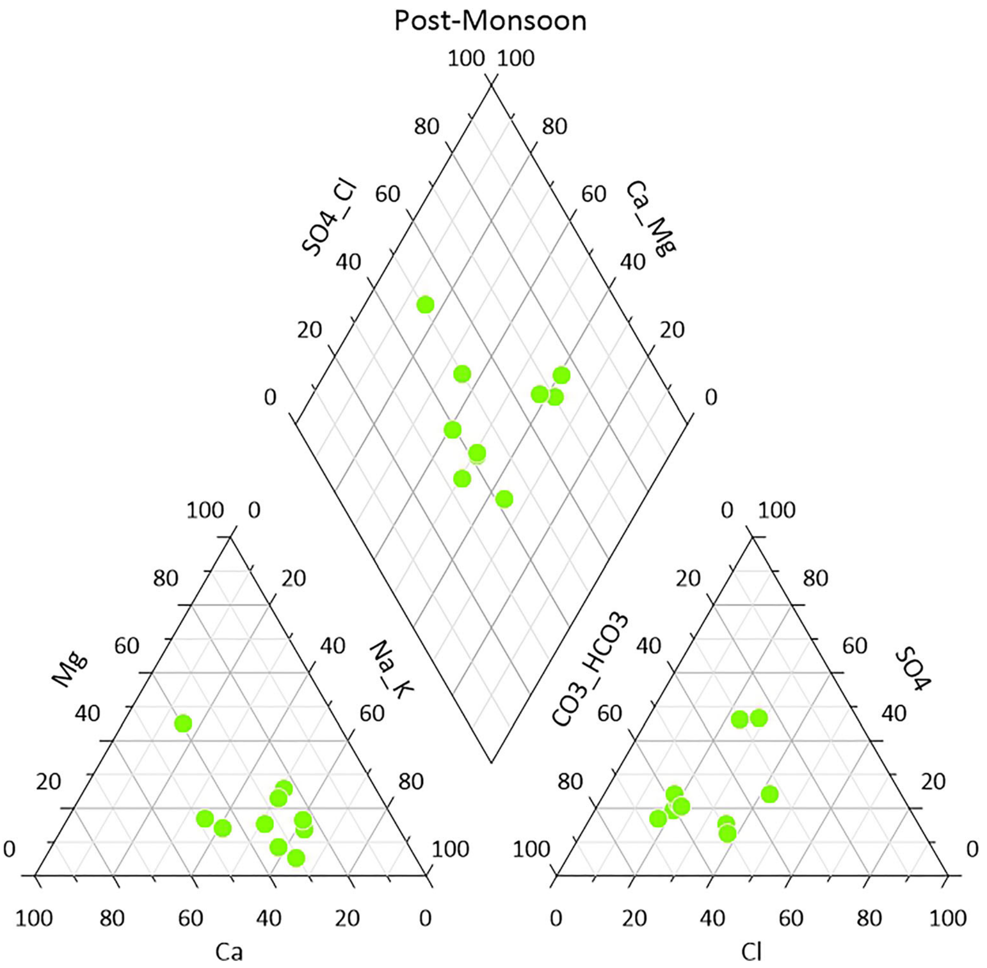


Fig. 3 Post-monsoon ionic distribution of the groundwater sources

parameters during the post-monsoon season could be attributed to the dilution caused by the rainfall, the increase in certain other parameters implies that the percolation of pollutants also increases during monsoon.

The metal compositions of the groundwater samples were found to be in check. Metals in excess quantities can be harmful to the digestive system while heavy metals can be carcinogenic even in small quantities (Covelo et al. 2007).

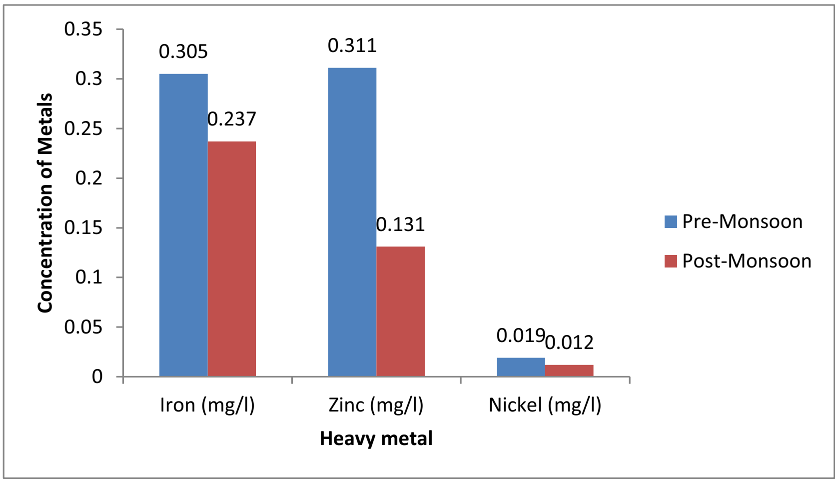


Fig. 4 Comparative analysis of metal compositions of Fe, Zn and Ni during different seasons

Table 4 Physico-chemical properties of water in post-monsoon period

Sample no.	pH	Turbidity (NTU)	Electrical cond. (µS/cm)	TDS (mg/l)	Total alkalinity (mg/l)	Total hardness as $CaCO_3$ (mg/l)	Ca^{++} (mg/l)	Mg^{++} (mg/l)	SO^{-}_4 (mg/l)	Cl^{-} (mg/l)	NO^{-}_3 (mg/l)	PO^{-}_4 (mg/l)	Na^{+} (mg/l)	K^{+} (mg/l)	Bicarbonate (mg/l)	Fluoride (mg/l)
GW-1	7.3	1.4	708	425	173	243	64	20	67	70	9	0.38	35	23	211	0.7
GW-2	7.1	1.3	1405	843	346	429	97	45	154	149	10	0.25	115	34	422	0.7
GW-3	7.5	1.0	1565	939	420	1015	142	161	159	369	29	0.26	48	7	512	0.6
GW-4	7.1	0.7	2014	1208	316	650	133	77	594	304	31	0.27	335	8	385	0.6
GW-5	6.8	2.0	2618	1571	276	741	137	97	629	378	36	0.08	330	28	336	0.5
GW-6	7.1	0.7	911	547	253	319	45	50	129	97	5	0.15	95	3	309	0.5
GW-7	7.1	2.3	1067	640	308	333	55	48	97	101	8	0.20	99	7	376	0.8
GW-8	6.9	1.2	1411	846	260	504	128	45	80	239	26	0.23	88	6	318	0.4
GW-9	6.8	1.0	1958	1175	251	522	147	37	223	387	32	0.12	232	21	306	0.3
GW-10	7.1	1.1	901	541	234	207	65	11	101	107	3	0.20	124	13	285	0.4

Fly ash and its effect on groundwater

Most of the power requirements of developing nations are met with coal fuelled power plants. Generation of fly ash is inevitable during such processes. Fly ash composition depends on the composition and type of coal from which it is generated (Wang 2018). Certain varieties of coal produce less fly ash than the others. Fly ash has found various productive uses in the building material industry. It is often added to enhance the strength of concrete (Wang and Lu 2018). Fly ash can be captured at source level by electrostatic precipitators and other particle filtration equipments to reduce the impact of fly ash pollution (Pandey et al. 2011). Thermal power industries require various devices to capture the escaping fly ash. They can be deposited in ponds. If the deposition ponds are not properly layered with impermeable material, some amount of fly ash can be intermixed with leachant (water) and percolate to groundwater (Pal et al. 2016). Many a times toxic elements are also involved with the fly ash leachate thus making water sources harmful (Wang et al. 2016). It can be referred to as a secondary source of pollution.

The ionic concentration of the region was due to high concentration of elements like bicarbonate, calcium, sodium and sulphate ions. The Piper's trilinear diagram shows that the majority of the cations were supplied by calcium, sodium and potassium ions, while the anion was supplied by bicarbonate ions. The ionic concentration can increase the electrical conductivity of the water (Khan and Umar 2019). The present study showed that the leading sources of cation supply during both the pre-monsoon and post-monsoon season were made by sodium ions followed by calcium, magnesium and potassium ions (Figs. 5 and 6). The significant amount of calcium ions can also be linked with the presence of fly ash pollution in the region because fly ash contains a high amount of calcium (Wang 2018).

Interpretation of groundwater quality in Koradi Region

Interpretations of groundwater quality reveal its suitability for human use (Bhakar and Singh 2018). Ash ponds are man-made ponds situated near power plants where the FA and bottom ash are disposed as sludge. The ash ponds contain significantly higher quantities of FA when compared to the quantity of bottom ash. Studies conducted earlier in the Koradi region suggest that limited interactions take place between the ash pond and groundwater (Spadoni et al. 2014; Voltaggio et al. 2015). Several regulatory reforms have been initiated in developing countries like India to curb excessive pollution caused by Industries and power plants. Ghosh and Kathuria (2016) obtained the relative efficiency score (RTE) of several power plants around India with Koradi TPS receiving an RTE score of 88.2, while the most efficient plant scored 92.9. Plant size, plant age,

Table 5 Heavy metal analysis of water in post-monsoon period

	Sample no.	Iron (mg/l)	Copper (mg/l)	Manganese (mg/l)	Cadmium (mg/l)	Lead (mg/l)	Total arsenic (mg/l)	Zinc (mg/l)	Total chromium (mg/l)	Nickel (mg/l)
Desirable limit by WHO 2004		0.3	2	0.04	0.0003	0.01	0.01	4	0.05	0.07
Desirable limit by IS 10500:2012		0.3	0.05	0.1	0.0003	0.01	0.01	5	0.05	0.02
	GW-1	0.11	< 0.03	0.06	< 0.001	< 0.001	< 0.01	0.24	< 0.03	0.01
	GW-2	0.21	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.05	< 0.03	0.02
	GW-3	0.24	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.08	< 0.03	< 0.01
	GW-4	0.32	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.15	0.04	< 0.01
	GW-5	0.33	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.12	< 0.03	< 0.01
	GW-6	0.25	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.24	< 0.03	0.01
	GW-7	0.31	< 0.03	0.08	< 0.001	< 0.001	< 0.01	0.12	< 0.03	< 0.01
	GW-8	0.27	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.14	< 0.03	0.01
	GW-9	0.27	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	0.07	< 0.03	0.02
	GW-10	0.06	< 0.03	< 0.05	< 0.001	< 0.001	< 0.01	< 0.1	< 0.03	< 0.01

the type of fuel used and amount of power generated are plant level factors affecting their environment and overall efficiency (See and Coelli 2012). Larger plant size can be linked to higher efficiency (Meibodi 1998). KTPS generates Class F FA which have low CaO content and a high percent of Al_2O_3 (37.72%) and Fe_2O_3 (7.41%) (Spadoni et al. 2014).

Numerous FA-based brick industries are situated near the villages included in the study. The groundwater in the region is high in salinity and TDS. The results of this study are synonymous with a previous study conducted by Spadoni et al. (2014) which suggested that the levels of Mg^{2+}, Ca^{2+}, NO_3^-, SO_4^{2-} and TDS levels of the groundwater sources exceed the desirable limits for potable water recommended by BIS (2012). The levels of SO_4^{2-} in samples GW-4 and GW-5 collected from the villages Khairy and Mhasala were notably high and needs to be checked (Fig. 7). These sources could have been influenced by the chemical and brick manufacturing industries in the region as well. In 2015, regulatory norms for sulphur emissions were imposed for the first time in India which limits the emission level of SO_2 to 200 mg/Nm^3 and 600 mg/Nm^3 for large and small power plant boilers, respectively (MoEFCC 2015). Such measures will reduce the chances of sulphur toxicity originating from drinking water.

Conclusion

The ash residues remaining after coal combustion generally contain significantly higher levels of ions of calcium, magnesium, chloride and bicarbonates. This can cause the contamination of groundwater. Contamination occurs due to leaching effect of FA when it is disposed of in ash ponds. The groundwater sources which were sampled from bore wells located nearby the ash disposal site of thermal power plant generally showed higher concentrations of electrical conductivity, total dissolved solids, alkalinity, hardness, bicarbonates and

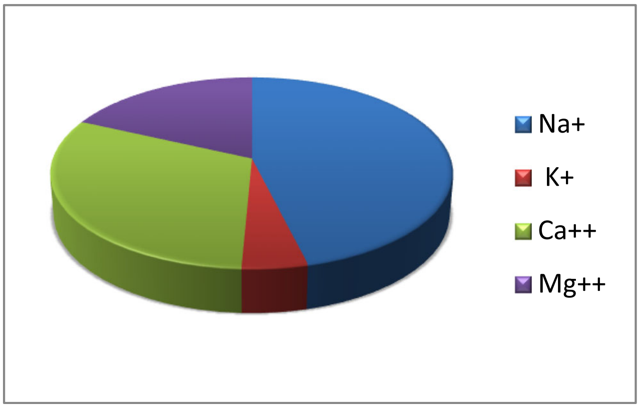


Fig. 5 Cation generators in groundwater during post-monsoon season

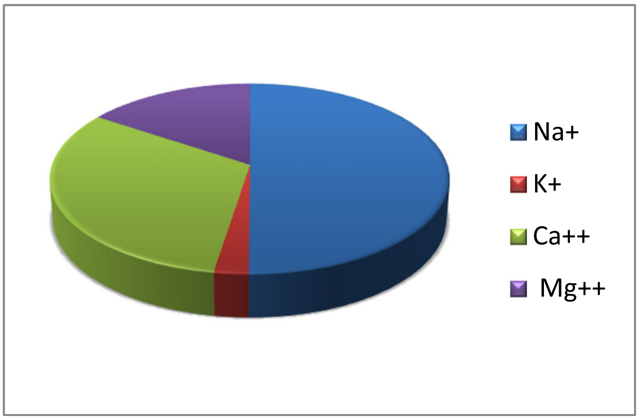


Fig. 6 Cation generators in groundwater during pre-monsoon season

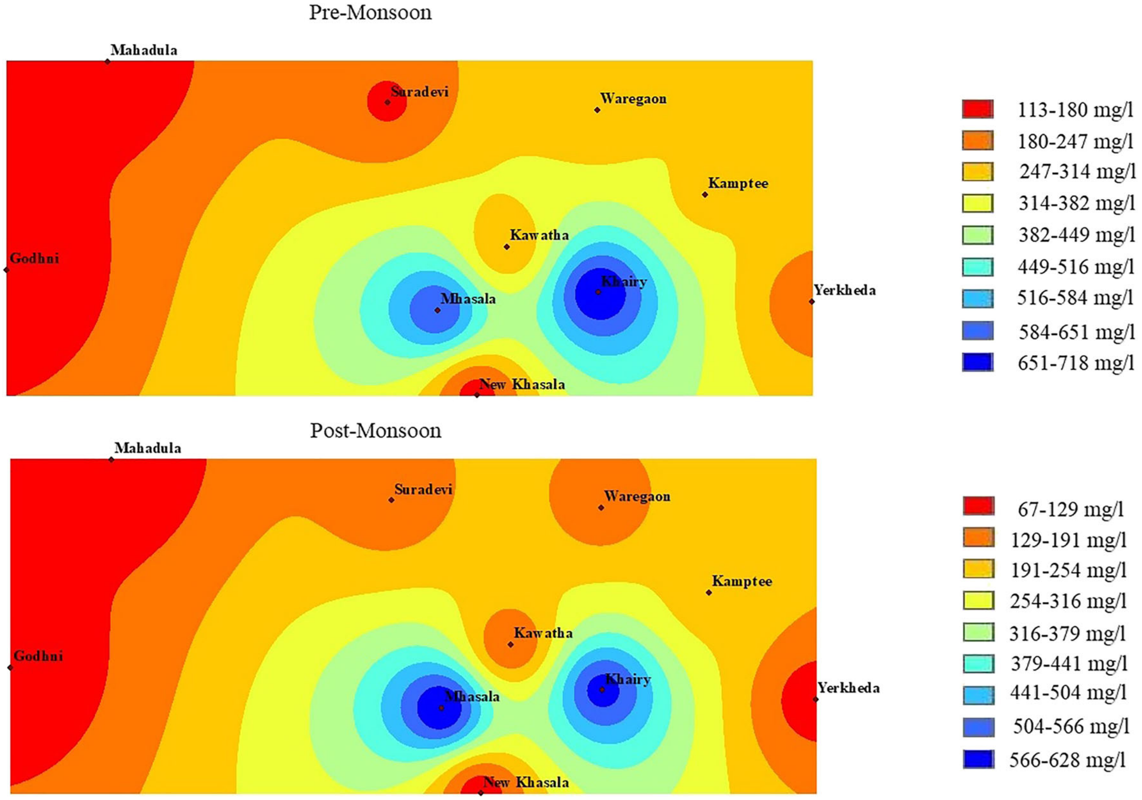


Fig. 7 Spatial distribution of sulphate ions in sample locations

magnesium ions exceeding the desirable limits prescribed by regulatory authorities. From the present study, it can be concluded that there is a significant impact of ash pond on groundwater contamination. The statistical analysis of the physico-chemical parameters suggests that the concentrations of sulphur, TDS, total hardness and electrical conductivity were dominant factors in governing the groundwater quality of Koradi Region. However, trace metal concentrations were within desirable limits. This can be attributed to new environmental regulations introduced by the Government. The utility of advanced technological tools to curb environmental pollution was not accounted for in this study. Further investigations in the coming years will display the role of regulatory norms in reducing pollution.

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