Below this temperature, NMR signals may vary from the actual. For accurate analysis seed temperature should be 40°C. Since room temperature is around 25°C during the analysis, it is obvious that while transferring the sample tube from conditioning block to NMR, the temperature will go below 40°C. Castor seed has a hard outer layer (seed coat) compared to other oilseeds crops and its oil is positioned in the endosperm rather than kernel of the seed. At 40°C, viscosity of castor oil is 2.7135 × 10–1 Pa,S (ref. 8) which is high compared to sunflower oil 0.3627 × 10–1 Pa,S (ref. 7) and safflower oil 0.2999 × 10–1 Pa,S (ref. 9) at the same temperature. In case of sunflower and safflower, NMR magnet conditioning before the actual analysis is adequate to bring the desired temperature (Figure 1 *a* and *b*), but in case of castor results show that by conditioning the castor seeds at 44°C, temperature loss can be compensated (Figure 2 *a* and *b*). To study the actual variation in oil content, six reference castor seed samples were analysed by making a calibration curve at 40°C and 44°C respectively (Table 3). It was found that calibration made at 40°C gave 0.91% variation in oil content, while that made at 44°C gave only 0.15%. Hence, by keeping sample conditioning temperature at 44°C, a good calibration curve and precise oil content of castor seeds can be determined.

NMR spectroscopy is one of the most important and widely used methods for oil content determination in the oilseed crops. In this study, the effect of change in sample conditioning temperature on calibration statistics and calibration linearity was described, and NMR spectrometry has been calibrated with respect to conditioning temperature for castor seed oil measurements. The study concludes that optimum sample conditioning temperature for sunflower and safflower seeds is 40°C, while for castor seeds it is 44°C.

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Arsenic and other metals in the groundwater samples of Ranchi city, Jharkhand, India

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This study was aimed to monitor and quantify the metals present in the groundwater of Ranchi city, state capital of Jharkhand, India. Samples were collected from 44 locations during three seasons. The results show that arsenic concentration ranged from 0 to 0.2 and 0 to 0.015 mg/l in monsoon and pre-monsoon seasons respectively, but was below detection limit in the post-monsoon season. Manganese varied from 0 to 4.199, Nickel from 0 to 0.077, Selenium from 0 to 0.14, and Fe varied from 0 to 0.047 mg/l. Presence of toxic metals, especially arsenic, above acceptable limits is alarming and needs immediate attention.

Keywords: Arsenic, groundwater, land use, metal contamination.

DEGRADATION of freshwater resources in terms of quality and quantity is posing a great threat to human civilization. Moreover, metal contamination in freshwater resources can lead to serious public health concern. Metals in groundwater generally originate from weathering of minerals and rocks which can cause contamination of water resources. However, anthropogenic activities like disposal of industrial effluents from metal processing, storage, battery, chemicals and glass industries, release of

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mining effluents, pesticide run-offs, and leachate from waste dumps can also be the sources of metal contamination[1]. The metals in water can cause cerebral malfunction, lung and kidney problems, gastro-intestinal distress, pulmonary fibrosis, and skin dermatitis and cancer[2,3]. However, the most alarming contaminant and threat to public health in the northeastern parts of India is arsenic in groundwater. The source of arsenic in groundwater can be either of geological origin from the local bedrock or from man-made products like paints, rat poisoning, fungicides and wood preservatives. Leachate from sewage sludge, coal burning, use of pesticides and industrial discharge can also be potential sources of arsenic in water[4,5]. Even arsenic contaminated irrigation water can move the metal into the food chain through the agricultural systems causing bio-magnification[6]. In Jharkhand, 17 villages of Sahibgunj district in the middle Gangetic plain were reported arsenic affected[7,8]. The concentration of arsenic was above 0.05 mg/l in three blocks of Sahibgunj[9]. However, arsenic contamination was not reported in the other parts of the state.

Ranchi city being the state capital is undergoing rapid and unplanned urbanization with an expansion rate of 10.16 sq. km/year. It has a total population of 1,073,440 (Census, 2011)[10,11]. So, anthropogenic pressure on the water resources is inevitable. Geologically, the study area is a plateau with a height of 654 m amsl and underlain by the hard igneous and metamorphic rocks where fracture porosity is the controlling factor for groundwater recharge. The network of horizontal and vertical joints and fracture make up the aquifer system[12]. Till date metal contamination has not been reported in Ranchi. Thus the present study was aimed to find out the levels of heavy metals in the groundwater of Ranchi city and surrounding areas. During our study in December 2014, skin lesions related to arsenic poisoning were reported in local newspapers. But till date no literature has been published regarding arsenic contamination in the area.

Sampling was done during monsoon, post-monsoon and pre-monsoon seasons in 2014 from the municipal corporation area of Ranchi city. Groundwater samples were collected from bore wells, hand pumps and wells from various locations, including residential, commercial, industrial and agricultural areas (Figure 1). There were totally 44 sampling sites and from each site three water samples were collected for each season. So the total sample number for each season was 132. Table 1 gives the average data of the three samples for each sampling site. The zonation of areas was done by consulting the land-use/land-cover map of Ranchi district. Water samples from hand pumps were collected after pumping for 15 min. Untreated groundwater is used mostly for drinking and domestic purpose, and partly for irrigation and in industries. The samples were preserved using 1% HNO_3. Metals (As, Mn, Ni, Se, Pb, Cd, Co, Cr, Cu and Fe) were analysed using Perkin Elmer Optical 2100 DV inductively coupled plasma – atomic emission spectrophotometer (ICP-OES). For quality control and quality assurance, Millipore water and Merck standards were used to prepare the calibration standards. The regression coefficient of the calibration curve was 0.995. A moderate concentration of multi-element standard was used at the interval of 10 samples to check the detector stability. Table 2 gives the detectable range of the instrument for each metal studied. All the samples were analysed on triplicate basis. For statistical analysis of the data, ANOVA and Pearson's correlation were calculated using MS-EXCEL 2007 version.

Table 1 lists the concentration of As, Mn, Ni, Se and Fe in groundwater samples during the three seasons. Cr, Cu, Cd, Co and Pb studied were below detection limit in the samples and hence are not shown in the table. In the monsoon season arsenic was found above the acceptable limits of Bureau of Indian Standards (BIS), which is 0.01 mg/l at almost all the sampling locations. Arsenic ranged from 0 to 0.2 mg/l. In this season maximum arsenic (0.2 mg/l) was found at GW20, namely at Tunkitoli which is in the peri-urban region near Kokar industrial area. The area has foundry-forge industry and automobile servicing centres. Manganese varied from 0 to 4.199 mg/l. Maximum 4.199 mg/l Mn was found at GW21, Barhitoli, which is a peri-urban residential area. Nickel and selenium concentrations varied from 0 to 0.077 and 0.032 to 0.14 mg/l respectively. In the monsoon season 15.91%, 70.45% and 93.18% locations showed metal concentration within acceptable limits of BIS for As, Mn and Ni respectively. Whereas the BIS acceptable limits for Mn, Ni and Fe are 0.1 mg/l, 0.02 mg/l, and 0.3 mg/l respectively. Iron was below detection limit in all the samples. Selenium was above acceptable limits (0.01 mg/l) in all the 44 locations. Arsenic was below detection limit in the post-monsoon, while Mn, Ni and Se varied from 0 to 1.025, 0.001 to 0.017 and 0.004 to 0.028 mg/l respectively. Fe concentration ranged from 0 to 0.047 mg/l. Mn and Se concentrations were above acceptable limits at 27.5% and 72.5% in the 44 locations, whereas Ni was within acceptable limits in all the locations. In the pre-monsoon season, As and Mn varied from 0 to 0.015 and 0 to 0.604 mg/l respectively. Ni and Fe were found below detection level and Se varied from 0 to 0.029 mg/l. In the pre-monsoon season, 3.13%, 12.5% and 21.87% locations were found with As, Mn and Se concentrations above acceptable limits. In all the three season, four locations, i.e. GW4, GW7, GW8 of Sector 2 Dhurwa, and GW24 (Near Kanke dam) showed high concentration of various metals. However, according to ANOVA, the zonal variation of metal concentration at 0.05 level of significance for monsoon season was non-significant, except Fe ($F = 10.59$, $F_{\text{crit}} = 2.6$) and Se ($F = 5.42$). In the post-monsoon season As ($F = 23.46$) and Se ($F = 58.52$) showed significant zone-wise variation. Whereas, in post-monsoon season Ni and Se showed

Table 1. Metal concentration (mg/l) in groundwater samples of Ranchi city

Sample id	Latitude	Longitude	Classification	Source	Monsoon season					Post-monsoon season					Pre-monsoon season				
					As	Mn	Ni	Se	Fe	As	Mn	Ni	Se	Fe	As	Mn	Ni	Se	Fe
GW 1	23.274	85.261	Rural/residential	Well	**0.081**	BDL	BDL	**0.064**	BDL	BDL	BDL	0.001	**0.02**	0.033	0.001	0	BDL	**0.02**	BDL
GW 2	23.301	85.263	Rural/residential	Tube well	**0.09**	BDL	0	**0.102**	BDL	BDL	0.009	BDL	**0.022**	0.022	0.001	0.07	BDL	0.008	BDL
GW 3	23.3	85.272	Peri-urban residential	Well	**0.069**	BDL	BDL	**0.131**	BDL	BDL	0	BDL	**0.025**	0.017	0.004	0	BDL	**0.015**	BDL
GW 4	23.299	85.272	Rural/residential	Tube well	**0.066**	**0.359**	BDL	**0.105**	BDL	BDL	**0.293**	BDL	**0.024**	0.019	0.009	**0.604**	BDL	0.014	BDL
GW 5	23.324	85.282	Peri-urban/residential	Tube well	**0.02**	0.131	BDL	**0.099**	BDL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
GW 6	23.311	85.292	Peri-urban/residential	Tube well	**0.044**	0.018	0	**0.112**	BDL	BDL	**0.172**	BDL	**0.02**	0.047	NA	NA	NA	NA	NA
GW 7	23.324	85.293	Peri-urban/residential	Tube well	**0.068**	**0.53**	BDL	**0.122**	BDL	BDL	**0.382**	BDL	**0.022**	0.012	0.005	**0.286**	BDL	0.006	BDL
GW 8	23.324	85.299	Peri-urban/residential	Tube well	**0.016**	**0.384**	BDL	**0.135**	BDL	BDL	**0.474**	BDL	**0.028**	0.01	0.004	**0.477**	BDL	0.007	BDL
GW 9	23.411	85.334	Rural/residential	Tube well	**0.032**	0.058	0.007	**0.069**	BDL	BDL	0.01	BDL	**0.024**	0.009	0.003	0	BDL	**0.015**	BDL
GW 10	23.41	85.336	Rural/residential	Well	**0.042**	BDL	0.003	**0.09**	BDL	BDL	0	BDL	**0.022**	0.006	NA	NA	NA	NA	NA
GW 11	23.411	85.335	Rural/residential	Bore well	**0.08**	**0.39**	BDL	**0.062**	BDL	BDL	0	BDL	0.006	0.005	0.007	BDL	BDL	**0.017**	BDL
GW 12	23.406	85.335	Rural/residential	Bore well	**0.068**	0.008	BDL	**0.098**	BDL	BDL	0.012	0.002	**0.017**	0.039	NA	NA	NA	NA	NA
GW 13	23.404	85.368	Rural/residential	Well	**0.087**	BDL	BDL	**0.077**	BDL	BDL	BDL	BDL	**0.015**	0.003	0.004	0	BDL	**0.018**	BDL
GW 14	23.404	85.35	Rural/residential	Well	**0.053**	BDL	BDL	**0.069**	BDL	BDL	BDL	BDL	**0.021**	0.002	0.005	0	BDL	0.007	BDL
GW 15	23.406	85.349	Rural/residential	Tube well	**0.096**	0.091	0	**0.063**	BDL	BDL	0.079	BDL	0.012	0	BDL	0.139	BDL	0.011	BDL
GW 16	23.409	85.346	Rural/residential	Tube well	**0.015**	0.056	0.003	**0.058**	BDL	BDL	0.015	BDL	0.01	0.004	0.004	0.034	BDL	**0.016**	BDL
GW 17	23.384	85.35	Peri-urban/residential	Well	**0.022**	BDL	0.002	**0.115**	BDL	BDL	BDL	BDL	0.011	BDL	BDL	0	BDL	0.009	BDL
GW 18	23.39	85.35	Peri-urban/residential	Tube well	**0.058**	BDL	BDL	**0.096**	BDL	NA	NA	NA	NA	NA	0.012	0.059	BDL	0.007	BDL
GW 19	23.383	85.351	Peri-urban/residential	Well	**0.047**	BDL	BDL	**0.082**	BDL	BDL	BDL	BDL	0.013	0	NA	NA	NA	NA	NA
GW 20	23.383	85.35	Peri-urban/residential	Tube well	**0.2**	**0.196**	**0.077**	**0.139**	BDL	BDL	**0.254**	BDL	**0.018**	0.002	0.002	0	BDL	0.017	BDL
GW 21	23.379	85.35	Peri-urban/residential	Tube well	0.004	**4.199**	0.002	**0.14**	BDL	BDL	**1.025**	0.002	**0.021**	BDL	NA	NA	NA	NA	NA
GW 22	23.364	85.344	Urban/residential	Tube well	0.004	**0.191**	0.012	**0.109**	BDL	BDL	0.099	BDL	**0.022**	0	NA	NA	NA	NA	NA
GW 23	23.364	85.341	Urban/residential	Boring	**0.093**	**0.391**	BDL	**0.082**	BDL	BDL	**0.405**	BDL	**0.025**	BDL	0.008	0	BDL	0.007	BDL
GW 24	23.407	85.31	Urban/residential	Tube well	0.01	0.068	BDL	**0.069**	BDL	BDL	**0.156**	BDL	**0.02**	BDL	0.008	**0.241**	BDL	0.004	BDL
GW 25	23.385	85.319	Urban/residential	Tube well	**0.022**	0.085	BDL	**0.06**	BDL	BDL	0.043	BDL	0.013	0	0	0	BDL	0.007	BDL
GW 26	23.392	85.351	Urban/residential	Tube well	**0.086**	**0.412**	BDL	**0.066**	BDL	BDL	**0.341**	BDL	**0.017**	BDL	0	0	BDL	0.007	BDL
GW 27	23.352	85.358	Industrial	Tube well	**0.053**	0.106	BDL	**0.094**	BDL	BDL	0.064	BDL	**0.017**	BDL	0.007	0	BDL	BDL	BDL
GW 28	23.352	85.365	Peri-urban/residential	Tube well	**0.06**	0.116	BDL	**0.05**	BDL	BDL	0.023	BDL	0.01	0	0.006	0	BDL	0.004	BDL
GW 29	23.356	85.354	Peri-urban/residential	Well	**0.065**	BDL	BDL	**0.064**	BDL	BDL	BDL	BDL	**0.022**	BDL	0.007	BDL	BDL	BDL	BDL
GW 30	23.372	85.349	Industrial	Tube well	**0.03**	**0.195**	BDL	**0.032**	BDL	BDL	0.134	BDL	**0.019**	BDL	NA	NA	NA	NA	NA
GW 31	23.375	85.358	Industrial	Tube well	**0.05**	0.051	0.004	**0.1**	BDL	BDL	**0.197**	BDL	**0.019**	0.005	0.004	0.035	BDL	0.007	BDL
GW 32	23.372	85.353	Industrial	Well	**0.052**	BDL	BDL	**0.029**	BDL	BDL	0	BDL	0.012	BDL	0.011	0	BDL	0	BDL
GW 33	23.359	85.359	Peri-urban/residential	Bore well	**0.054**	0.136	0.006	**0.081**	BDL	BDL	0.087	0.002	**0.021**	BDL	0.002	0.084	BDL	0.008	BDL
GW 34	23.354	85.303	Urban residential	Well	**0.097**	BDL	BDL	**0.046**	BDL	BDL	BDL	BDL	**0.015**	BDL	0.011	0	BDL	0.001	BDL
GW 35	23.353	85.304	Urban residential	Boring	0.008	**0.663**	**0.045**	**0.097**	BDL	BDL	0.015	0.017	**0.019**	BDL	0.004	0	BDL	0.011	BDL
GW 36	23.372	85.319	Commercial	Tube well	0.010	0.1	BDL	**0.137**	BDL	BDL	0.028	BDL	**0.021**	0	0.002	0.032	BDL	0.01	BDL
GW 37	23.372	85.32	Commercial	Tube well	0.010	**0.617**	**0.034**	**0.114**	BDL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
GW 38	23.375	85.319	Commercial	Tube well	**0.026**	**0.373**	0.005	**0.107**	BDL	BDL	**0.178**	BDL	0.01	BDL	0.007	0	BDL	0.009	BDL
GW 39	23.375	85.32	Commercial	Tube well	**0.038**	0.021	BDL	**0.099**	BDL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
GW 40	23.366	85.324	Commercial	Tube well	BDL	0.005	BDL	**0.113**	BDL	BDL	0.014	BDL	0.014	BDL	BDL	0	BDL	0.01	BDL
GW 41	23.364	85.325	Commercial	Tube well	**0.075**	0.039	BDL	**0.14**	BDL	BDL	0.023	BDL	0.004	BDL	0.003	0.05	BDL	**0.029**	BDL
GW 42	23.357	85.324	Commercial	Tube well	**0.058**	0.022	BDL	**0.122**	BDL	BDL	0.048	BDL	**0.021**	BDL	NA	NA	NA	NA	NA
GW 43	23.362	85.325	Commercial	Tube well	**0.02**	0.03	BDL	**0.133**	BDL	BDL	0.046	BDL	**0.019**	BDL	NA	NA	NA	NA	NA
GW 44	23.352	85.357	Industrial	Well	**0.048**	BDL	BDL	**0.078**	BDL	BDL	0	BDL	**0.015**	BDL	**0.015**	0	BDL	0.004	BDL

BDL, Below detection level; NA, Not available; Bold font, Concentration of metals exceeding acceptable limits of BIS Standard (Second Revision of IS 10500) for drinking water.
Acceptable limits: As, 0.01 mg/l, Mn, 0.1 mg/l, Ni, 0.02 mg/l, Se, 0.01 mg/l, Fe, 0.3 mg/l.

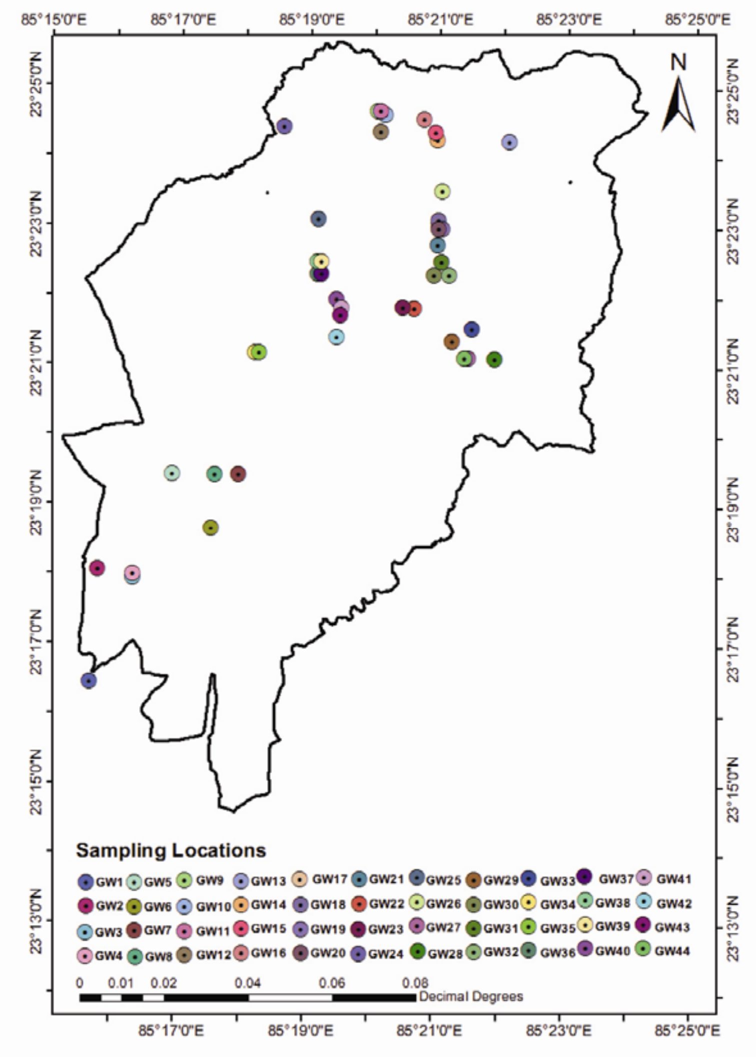

Figure 1. Sampling sites in the study area.

Table 2. Detectable range of metals

Elements	Detectable range of the metals (ppm)
As	0.002–200.0
Ca	0.005–5.0
Cd	0.01–10.0
Co	0.02–20.0
Cr	0.02–20.0
Cu	0.04–40.0
Fe	0.01–10.0
Mg	0.004–4.0
Mn	0.001–10.0
Ni	0.05–50.0
Pb	0.01–100.0
Se	0.004–400.0

significant zone-wise variation ($F = 3.37$ and 4.01 respectively). The seasonal variations of metal concentration were significant, except Mn. The F values were 61.78, 1.58, 3.16, 230.76 and 10.19 for As, Mn, Ni, Se and Fe respectively ($F_{\text{crit}} = 3.08$). The sources of metals may be geogenic or/and anthropogenic in the water samples. Since the seasonal variation of the metals was pronounced, it may be related to geological weathering too. Especially, in the monsoon season the rate of chemical weathering increases and hence releases metals from the bedrock in substantial amounts, which is evident from the data. The study area is mostly underlain by Chotanagpur granite-gneiss of Archaean age, which is consolidated in nature. Some areas have unconsolidated alluvium of Quarternary age and a small portion is comprised of consolidated formation consisting of shale, quartzite and schist of pre-Cambrian age. Metals can be released from various types of the above-mentioned geological foundations due to chemical weathering. Fe and Mn contamination may be of geogenic origin as the anthropogenic sources such as steel and alloy processing industries are not present in the study area. The primary source of nickel in drinking water is leaching from pipes and fittings. However, nickel may also be present in groundwater as a consequence of dissolution from nickel ore-bearing rocks. Selenium is present in the earth's crust, often in association with sulphur-containing minerals. Leachate from solid waste dumping sites can also contribute many metals like Fe, Mn, As, Ni and Cu in the groundwater. The city does not have a proper leachate treatment, and solid and municipal waste management facility. Hence leaching from the dumping sites can be a possibility, especially during the monsoon season. In the pre-monsoon season too leachate can cause contamination due to less chance of dilution. Whereas in the post-monsoon season, the water is diluted after heavy rainfall and due to surface run-off metal loading in leachates can decrease. Other than leachate from solid waste dumping ground, metals (especially arsenic sources) can also be present due to application of pesticides in the rural areas practising agriculture. Reductive dissolution of iron–manganese oxides and oxidation of arsenopyrite are the governing mechanisms of arsenic release in alluvial plains[13]. However, in the present study correlation of arsenic with iron and manganese was found to be weak in all the seasons (r^2 = 0.13 and –0.23 for Fe and Mn respectively, in monsoon season). Further, the data should be correlated with oxidation–reduction potential, pH, depth and sulphate before jumping into any conclusion regarding the source. Biological weathering of sulphur-containing minerals can also release arsenic and hence the relation with sulphate and dissolved organic matter needs to be studied[14]. Arsenic contamination from similar geogenic sources of granitic terrain in Rajnandgaon district, Chattisgarh has also been reported[15]. The possible reason for the contamination in Chattisgarh is weathering of arsenic-bearing rocks with pegmatitic intrusions and water–rock interactions. In Ranchi too, most of the aquifers are of granite-gneiss origin. The aquifers in the study area are semi-confined in nature and the water level is replenished due to rainfall and not by seepage of river water as the rivers in this area are effluent in nature. So, leaching and weathering can be the most probable sources of arsenic and other metals in groundwater. As arsenic contamination in this region has never been reported, a detailed study is required to understand the geochemistry and identify the source. We are carrying out studies by analysing and correlating various parameters to identify the probable source. Mukherjee *et al.*[16] reported that out of the total samples analysed in the affected areas of Sahibganj, 30% had arsenic above 10 μg/l, whereas in Bihar, 39.02% samples had arsenic above 10 μg/l. Nine districts of West Bengal and 20 districts of Assam had arsenic concentration above 50 μg/l (ref. 16). But in these areas most of the terrain has alluvial sediments and so the release mechanism is different.

Finally, from the results it can be inferred that groundwater of Ranchi city is contaminated with arsenic, selenium and manganese, as these methods are found well above the acceptable limits for drinking water. Metal contamination is prominent in the monsoon and pre-monsoon seasons. Probable source for contamination can be the weathering of rocks. However, a detailed investigation is necessary for source identification. Water from the contaminated sites should not be used for drinking or domestic purpose and immediate attention and intervention by the Government need for providing alternative sources.

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