

Health Risk Assessment of Groundwater Iron and Manganese in Chandrapur District, Central India.

Evaluación de riesgos para la salud del agua subterránea de hierro y manganeso en el distrito de Chandrapur, India central.

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Abstract

Groundwater iron and manganese concentration assessment was carried out in the Chandrapur district of Central India to assess their spatio-temporal variation and furthermore health risk assessment owing to their ingestion by rural inhabitants which are mainly depend on groundwater as a source of drinking water. Groundwater sampling was carried out from 36 sampling locations by grab sampling method in winter, summer, and post-monsoon to ascertain health risk assessment of groundwater iron and manganese. These heavy metals were analyzed by ICP-OES. Results revealed maximum average groundwater iron concentration was at Ballarpur [Hand Pump (HP), 18.213 mg/L] and minimum at Gunjewahi [Dug Well (DW), 0.081 mg/L] whereas; maximum average manganese concentration from Naleshwar (HP, 0.779 mg/L) and minimum average from Antargaon (HP), Gowari (HP), Morwa (HP) and Mowada (HP, 0.003 mg/L). Iron distribution on World Health Organisation (WHO), Joint FAO/WHO Expert Committee on Food Additives (JECFA) and Institute of Medicine (IOM) recommendations revealed seasonal influence on it. Distribution of iron and manganese with Indian Standard Drinking Water-Specification (2012), summer have maximum samples (n=23, 63.88%) iron concentration above the permissible limit (0.3 mg/L), on the other hand, manganese in winter (n=7, 19.44%) (Permissible limit 0.3 mg/L). At a number of samples, groundwater manganese concentration was above the WHO (2011) discontinued manganese standard of 0.4 mg/L. Chronic daily intake, hazard quotient and hazard index

were very low for these heavy metals which indicate inhabitants of the study area were no immediate or remote health threat from ingestion of this groundwater.

Keywords: Central India, Chandrapur, Chronic daily intake, Hazard quotient, Health risk assessment, Heavy metal, Iron, Manganese.

RESUMEN

La evaluación de la concentración de hierro y manganeso en las aguas subterráneas se llevó a cabo en el distrito de Chandrapur, en la India central, para evaluar su variación espacio-temporal y, además, la evaluación del riesgo para la salud debido a su ingestión por parte de los habitantes rurales, que dependen principalmente del agua subterránea como fuente de agua potable. El muestreo de aguas subterráneas se llevó a cabo desde 36 ubicaciones de muestreo mediante un método de muestreo aleatorio en invierno, verano y después del monzón para determinar la evaluación del riesgo para la salud del hierro y el manganeso en las aguas subterráneas. Estos metales pesados fueron analizados por ICP-OES. Los resultados revelaron que la concentración máxima promedio de hierro en el agua subterránea estaba en Ballarpur [Bomba manual (HP), 18.213 mg / L] y mínima en Gunjewahi [Pozo excavado (DW), 0.081 mg / L] mientras que; concentración promedio máxima de manganeso de Naleshwar (HP, 0.779 mg / L) y promedio mínimo de Antargaon (HP), Gowari (HP), Morwa (HP) y Mowada (HP, 0.003 mg / L). La distribución de hierro en las recomendaciones de la Organización Mundial de la Salud (OMS), el Comité Mixto FAO / OMS de Expertos en Aditivos Alimentarios (JECFA) y el Instituto de Medicina (OIM) revelaron una influencia estacional en ella. Distribución de hierro y manganeso con la especificación de agua potable estándar de la India (2012), el verano tiene muestras máximas (n = 23, 63.88%) de concentración de hierro por encima del límite permitido (0.3 mg / L), por otro lado, manganeso en invierno (n = 7, 19.44%) (límite permitido 0.3 mg / L). En varias muestras, la concentración de manganeso en las aguas subterráneas estaba por encima del estándar de manganeso discontinuado de la OMS (2011) de 0.4 mg / L. La ingesta diaria crónica, el cociente de riesgo y el índice de riesgo fueron muy bajos para estos metales pesados, lo que indica que los habitantes del área de estudio no representaron una amenaza inmediata o remota para la salud por la ingestión de estas aguas subterráneas.

Palabras clave: India central, Chandrapur, ingesta diaria crónica, cociente de riesgos, evaluación de riesgos para la salud, metales pesados, hierro, manganeso.

INTRODUCTION

Drinking water contaminated with different chemicals and heavy metals, released from different natural and anthropogenic sources has become a global concern (Rapant and Krcmova, 2007). The contamination of water resources has important repercussions to the environment and human health (Emmanuel *et al.*, 2009; Muhammad *et al.*, 2011). About 2.3 billion individuals in the world suffer from diseases linked to water (Kristof, 1977; United Nations, 1997).

Ingestion of high level of iron can cause hemochromatosis with symptoms such as chronic fatigue, arthritis, heart diseases, cirrhosis, diabetes, thyroid diseases, impotence, and sterility. It facilitates persistent hepatitis B or C infection, also induced malignant tumors, colorectal, liver, lung, stomach and kidney cancers (Huang, 2003). Human vulnerability analysis (Mondal, 2012) for groundwater iron was greater in regions where iron in well water was maximum (>2.11 mg/L) along with the density of population. Subba Rao (1993) and Subba Rao and Madhusudhana Reddy (2006) reported health disorders such as skin, digestive, respiratory and nervous systems, kidney, spinal cord, heart, mental imbalance, miscarriage and cancer where groundwater iron concentrations were high. Health problems such as liver diseases, amenorrhea, birth defects, pancreas damage, rheumatoid arthritis, and Parkinson's disease are reported due to high accumulation of iron (Caravati, 2004; Klaassen and Watkins, 2010; Afolabi *et al.*, 2011). On the other hand, Khan *et al.*, (2012) reported groundwater manganese above the WHO (discontinued) standard (2011) of 400 $\mu\text{g/L}$ was associated with 6.4% score loss in mathematics achievement test scores, adjusted for water arsenic and other socio-demographic variables. Hafeman *et al.*, (2007) reported that infants exposed to water manganese ≥ 0.4 mg/L (WHO standard 2003) showed an elevated mortality risk during the first year of life compared with unexposed infants. In addition, long term exposure to elevated groundwater manganese can result in Parkinson's disease. It causes neurotoxicity by increasing oxidative stress and also disturbing neurotransmitter metabolism (Erikson *et al.*, 2004).

From the review of the related literature and researches, it was observed that selected studies have been carried out pertaining to health risk assessment of groundwater heavy metals and in particular for iron and manganese (Bouchard *et al.*, 2007; Bouchard *et al.*, 2011; Ericson *et al.*, 2007; Khan *et al.*, 2011; Kim *et al.*, 2009; Menezes-Filho *et al.*, 2009; Takser *et al.*, 2003; Wasserman *et al.*, 2006; Wright *et al.*, 2006). Furthermore, a systematic human health risk assessment for individuals exposed to these two heavy metals through groundwater consumption has yet to be conducted

in the Chandrapur district (India). Therefore, the objectives of the study are (i) to assess groundwater iron and manganese concentration from the Chandrapur district, (ii) to determine spatial and temporal variability in the concentration of these two heavy metal ions, (iii) to ascertain correlation between groundwater iron and manganese with other physiochemical parameters, (iv) to assess the population health risk (adult and children) from these two heavy metals in groundwater through ingestion exposure, and (v) to carry out chronic daily intake, hazard quotient for non-carcinogenic risk assessment and hazard index. The outcome of the study will contribute to understand the theoretical aspects of the individual and synergistic effect of groundwater iron and manganese on human health. In addition, short term and long term (or both) health implications to the inhabitants.

MATERIALS AND METHODS

Study Area: Chandrapur district (19°25' N to 20°45' N and 78°50' E to 80°10' E) is situated in Vidarbha region of Maharashtra state of central India (Figure 1). The district is the easternmost district of the state. The district covers an area of 11,364 sq km with elevation ranging from 106 m to 589 m asl, the south-west part having a high level and south-east part with low level. The district comprises of 15 administrative blocks being surrounded by other districts such as Nagpur (north of northwest), Wardha (northwest), Yeotmal (west), Adilabad (south), Gadchiroli (east) and Bhandara (north). The district is bestowed with natural bounty in the form of dense forest and wildlife. However, due to abundant presence of natural resources and minerals, such as coal, limestone, iron and copper, the district has witnessed sprawling coal mines, cement industries, pulp and paper industry and a number of thermal power plants and at the same time Tadoba Andhari Tiger Reserve (TATR) which has one of the largest numbers of tigers in central India.

Geology: The geological formation of the Chandrapur district is a part of Gondwana sedimentary basin. Different stratigraphic units include *Archaean* to recent alluvium and laterites. The *Archaean formation* comprises of granites, gneisses, with schists of hornblende, mica, and quartz, and with much vein quartz, shale with some micaceous schists.

The *Purna formations* consisting mostly of sandstones, quartzitic sandstones, and quartzites, with some shales and limestones. In *Aryan formations*, *Talchir group* are generally fine buff sandstones, greenish-grey silty shales, and sandstones. The *Barakar* group contain the beds of coal with the arrangement of layers as (i) coal, (ii) sandstone

and shales, (iii) carbonaceous beds, and (iv) sandstone shales. The rocks comprising of the *Kamthi* group includes (i) grits, (ii) sandstones, coarse or fine-grained with red blotchy streaks, and (iii) sandstones, argillaceous and ferruginous. The rocks constituting the *Kota-Maleri* group are mainly red and green clays and argillaceous sandstones, the basal sandstones containing green clay-galls; limestone's beds are found in association with the clays. The Deccan Trap series is composed of volcanic lavas and has been classified into the upper, middle, and lower traps, beneath it lies basal sedimentary beds, known as Lamenta or Infratrappean.

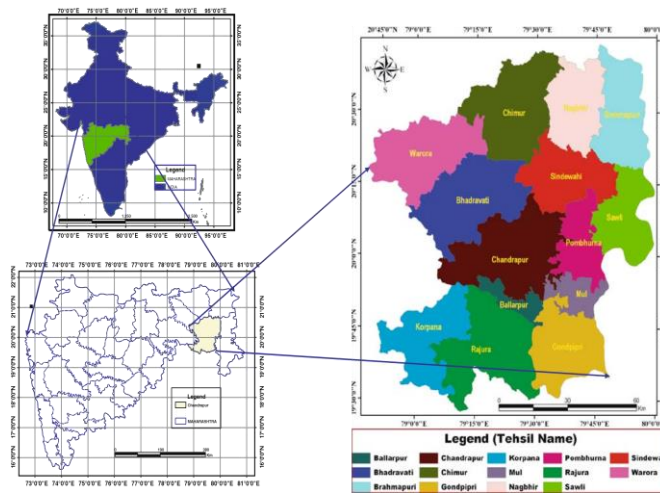


Figure 1: Chandrapur district with different administrative blocks (Satapathy *et al.*, 2009).

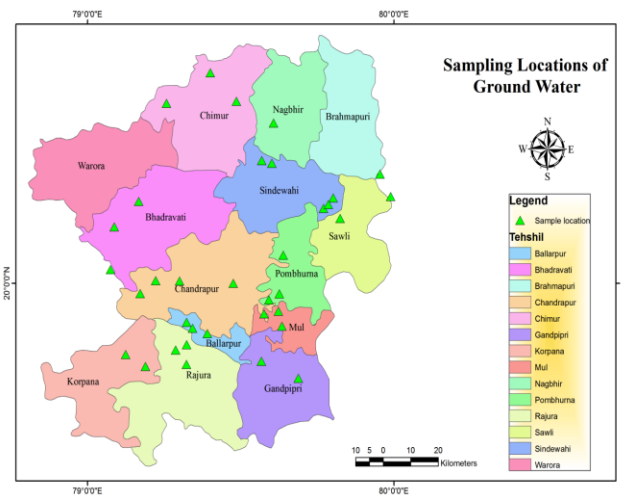


Figure 2: Groundwater sampling locations from the study area

Laterites are next in succession to the trappean rocks, and later still are the various deposits which include all the soils of the present area. *Alluvium* is mostly of fluvial origin and comprises of sand, silt, and clays (Begbie, 2005).

Hydrology: The hydrology of the district has the unconfined aquifer with extension up to a depth of 20 m below ground level with poor to moderate potential. The elevation of the water table varies from 230 m (NW part) to 160 m (SE part) above mean sea level. According to Maharashtra Pollution Control Board (MPCB) (2006), pre-monsoon (1995-2004) groundwater table has shown a declining trend (> 20 cm per year) in the district. The groundwater flow in the district is towards the Wardha river and its tributaries with hydraulic conductivity from 2.0 to 6.0 m/day. Alluvium, lower Gondwana sandstones, Deccan trap basalt, *Vindhyan* limestone and *Archaean* metamorphic are the major water-bearing formations with lower Gondwana sandstone, particularly *Kamthi* sandstone forms the most potential aquifer (Satapathy *et al.*, 2009). The annual rainfall of the district is in the range 1200-1450 mm from south-west monsoon (June-September) with a number of rainy days 60-65. The rainfall is asymmetrically distributed with Warora block receiving the minimum rainfall and Bramhapuri block with the maximum (CGWB, 2009). The rainfall in different blocks of the Chandrapur district during the study period is presented in Table 1. Rainfall data for the rainy season 2013 (June-October) was collected from www.maharain.gov.in (Rainfall in Chandrapur district, 2013). The rainfall range from 1395.9 mm (Sindhewahi) to 1916.2 mm (Pombhurna) with an average 1691.4 mm. Rainfall during the rainy seasons of 2012 and 2013 is depicted in Figure 2. From the Figure 2 it can be seen that, August 2012 have reported maximum rainfall 455.2 mm closely followed by July (444.3 mm); whereas, June with minimum 102.8 mm. In 2013, July reported maximum rainfall 785.7 mm followed by June 425.4 mm and September reported minimum 113.8 mm. On comparison of these two years rainfall months, 2013 rainfall (1642.3 mm) was comparatively higher as of 2012 (1255.5 mm); whereas, July 2013 have maximum rainfall (785.7 mm) followed by August 2012 (455.2 mm) and minimum in June 2012 (102.8 mm) (IMD, 2015).

Soil: The soil of the Chandrapur district falls into clearly defined longitudinal bands, and each of these bands displaying cropping of a wholly different kind. The soil type comprises of shallow coarse, medium black and deep black. The various kinds of soil in the district are nine in number and in local *Marathi* language are called as *Kali*, *Kanhar*, *Morand*, *Khardi*, *Wardhi*, *Retari*, *Bardi*, *Pandhari* and *Kachhar*. On the left banks of the Wardha and Godavari rivers, there is found to a deep and rich black loam overlying

trap and itself probably largely composed of the disintegrated trap. The impervious nature of the underlying trap makes the soil extremely retentive of moisture, and it is found to be peculiarly suited to the growth of open field crops such as cotton, *jawar*, and staples of the *rabi* type. The best soil of the district is black soil (*Kali*). It is confined to the riverain tracts and is only found to any considerable extent in the valley of the Wardha river. It is a trap soil of great depth and fertility, without a speck of grit. *Morand*, the most common agricultural soil of the district, is light coloured loam containing more sand that is found in *Bersi* and larger particles of stones. It grows both *kharif* and *rabi* crops well, whereas on *Wardhi* soil paddy growing areas are observed in parts of Brahampuri, Chimur and Nagbhid blocks (Begbie, 2005).

Table 1: Rainfall in different blocks of the Chandrapur district

Month	June		July		August		September		October		Total rainfall for the rainy season
	A	D	A	D	A	D	A	D	A	D	
Chandrapur	374.7	15	600.1	17	442.4	17	78.2	6	165.5	9	1660.9
Mul	389.4	14	607.8	20	319.3	15	175.0	9	216.1	12	1707.6
Gondpipari	294.8	10	746.8	15	307.4	13	164.3	9	207.7	10	1721
Warora	604.3	11	739.5	23	221.9	16	107.6	6	159.2	7	1832.5
Bhadravati	530.9	14	711.5	25	260.9	14	67.0	6	217.2	9	1787.5
Chimur	544.6	16	688.8	21	286.7	22	42.0	6	97.7	7	1659.8
Bramhapuri	503.2	14	703.5	23	403.2	16	115.1	7	186.7	10	1911.7
Nagbhid	455.5	16	507.5	23	279.2	19	70.6	8	126.8	10	1439.6
Sindhewahi	344.8	13	567.3	24	276.3	14	50.1	5	157.4	7	1395.9
Rajura	343.7	12	785.0	18	276.3	13	150.1	7	170.4	9	1725.5
Korpana	412.6	13	723.3	19	291.2	13	159.3	8	199.7	10	1786.1
Sawali	264.5	15	546.5	23	337.4	13	117.6	8	187.6	12	1453.6
Ballarpur	432.2	12	724.8	17	300.6	13	61.3	5	174.2	6	1693.1
Pombhurna	287.7	12	839.4	18	421.1	18	79.0	6	289.0	11	1916.2
Jivati	361.6	13	717.4	21	322.7	14	98.6	8	180.0	9	1680.3

Rainfall is reported in mm. A - Actual rainfall in mm, D - Number of rainy days. (Source: <http://maharain.gov.in/>)

Groundwater sampling protocol: Groundwater sampling site selections were based upon the criteria of hand pump/dug well as a source of drinking water and its use for cooking or other domestic purposes from the rural area of the district. Furthermore,

groundwater samples were collected from different blocks of the district which covers wide geographical formations, rainfall, and elevations. According to the Census of India (2011), the main source of drinking water for household in rural area of the district was 36% household use hand pump water followed by 7.2% as tube well/borehole water, thus emphasis was laid upon selection of sampling sites from rural areas and from hand pump and dug well as a source of drinking water.

In all, thirty-six groundwater sampling locations comprising of hand pumps and dug wells from the Chandrapur district were identified (Figure 3). Stratified sampling was carried out for groundwater sampling. Of these groundwater sampling locations, 34 (94.44%) were from hand pumps (HP) and 2 (5.55%) from dug wells (DW). The sampling locations were selected such that the maximum study area to be covered. Furthermore, these sampling locations were selected from rural areas where inhabitants were mostly depend upon groundwater as a source of potable water and to carry out other domestic activities. Groundwater sampling was carried out by grab sampling method.

Precise hand pump/dug well location for latitude, longitude, and altitude was recorded by using a handheld GPS (Map my India navigation 2.0). The hand pump was monitored for corrosion or other anomalies and the same was recorded in the field diary. During groundwater sampling from the source, if any, suspended matter or colour was observed the same was also recorded. The surrounding platform of groundwater source was examined for its construction type and presence of any red colour patches. To understand the influence of seasons on groundwater iron and manganese concentrations, groundwater sampling was carried out during winter, summer, and post-monsoon of 2012 and 2013. In each season, sampling was carried out from the same identified sampling location and from the same water source so as to compare them for distribution of these heavy metals.



Figure 3: Rainfall during the study period (in mm)

For collecting groundwater samples for analysis, two different capacities of polyethylene containers were selected. For analysis of general parameters (physicochemical parameters such as temperature, pH, electrical conductivity, total dissolved solids, total alkalinity, total hardness, chloride, fluoride, sulphate, and phosphate), a narrow mouth polyethylene container of 1000 mL capacity (Poly lab, India) was used; whereas, for heavy metals analysis a narrow mouth 100 mL capacity polyethylene container (Poly lab, India) was used. These both containers were thoroughly washed first with detergent then with distilled water followed by conc. HNO₃ (16 N, Merck) further by repeated washing with distilled water in the laboratory. These containers were rinsed with a hand pump or dug well water before groundwater sampling and then the sample was collected into it. Heavy metal samples were preserved by adding conc. HNO₃ (16 N, Merck), 2 mL per 100 mL at the time of sampling. All reagents used while performing physicochemical analysis were of AR grade (Merck) and glassware was of borosilicate make. Double distilled water was used for the preparation of reagents. All reagents were prepared as stated in APHA (2005).

Groundwater temperature alters soon after it gets exposed to the atmospheric environment. Thus, its analysis in the field gives accurate information about groundwater temperature. For monitoring of groundwater temperature, its measurement was carried out in the field itself by using a mercury thermometer with 0.5 °C division (Gera, GTI, India).

Laboratory analytical procedure: The concentrations of total iron and manganese were determined after acid digestion with conc. HNO₃ (16 N, Merck) (Huamain *et al.*, 1999). Groundwater samples especially collected for determination of iron and manganese were acid digested in a pre-leached glass beaker on a hot plate at 95 °C and evaporated to 5 mL without boiling. While carrying out acid digestion of groundwater samples, glass beakers were covered with a clean watch glass. This process resulted in the total extraction of metals from groundwater. After cooling, into the digested sample a small quantity of 1:1 conc. HNO₃ (16 N, Merck) was added and further refluxed for 15 min so as to dissolve any precipitate and residue resulting from evaporation. This digested sample after cooling was transferred into 25 mL volumetric flask and diluted up to 25 mL with double distilled water. This acid digested sample was used for the determination of iron and manganese concentrations. Heavy metals analysis was carried out by using ICP-OES (ICP-OES, Perkin Elmer, Germany, Dv 7000). For analysis of groundwater physicochemical parameters, standards methods as suggested by the American Public Health Association (APHA 2005) were adopted (Table 2).

Table 2: Standard methods used for analysis of groundwater

Parameter	Standard method	APHA (2005), Reference No.	Instrument particular
Temperature	Mercury thermometer	B of 2550	Gera, GTI, India
pH	Electrometric method	B of 4500-H ⁺	Digital pH meter, Electronics India, Model 101
Conductivity	Conductivity meter	B of 2510	Digital conductivity meter, Electronics India, Model 601
Total dissolved solids	Total dissolved solids dried at 180 °C	C of 2540	Hot air oven, Navyug, India
Alkalinity	Titration method	B of 2320	NA
Total hardness	EDTA titration method	C of 2340	NA
Chloride	Argentometric method	B of 4500-Cl ⁻	NA
Fluoride	SPANDS method	D of 4500-F ⁻	Double beam UV/Visible spectrophotometer, Electronics India, Model 1372
Sulphate	Turbidimetric method	E of 4500-SO ₄ ²⁻	Double beam UV/Visible spectrophotometer, Electronics India, Model 1372
Phosphate	Stannous Chloride method	D of 4500-P	Double beam UV/Visible spectrophotometer, Electronics India, Model 1372
Iron	Inductively Coupled Plasma-OES	C of 3500-Fe ⁺⁺	ICP-OES, Perkin Elmer, Germany, Dv 7000
Manganese	Inductively Coupled Plasma-OES	C of 3500-Mn ⁺⁺	ICP-OES, Perkin Elmer, Germany, Dv 7000

NA - Not Applicable

Geospatial data analysis: In this study, iron and manganese concentration in groundwater database was converted into ArcGIS coverage format and merged with the spatial database in GIS. Attributes such as latitude, longitude, and altitude of sampling locations, and concentrations of groundwater iron and manganese were used. Maps provided helpful visual displays of the spatial variability in the field and can be used for the summarization and representation of spatial data for environmental modelling (Goodchild *et al.*, 1993). The spatial variability maps prepared with the help of ArcGIS platform depict the location of the sampling site along with the concentration of iron and manganese in groundwater. Non-biodegradable nature of iron and manganese present in groundwater and their long biological half-lives, their bioaccumulation in the food chain which will enhance their concentration will have adverse effects on individual health in long term (Alloway, 1990; Kabata-Pendias and Pendias, 1992; Lee *et al.*, 2006).

Correlation of water geochemical data: The use of Person correlation coefficient in groundwater contamination assessment plays an important role in assessing how parameters are related to each other (Daraigan *et al.*, 2011). The correlation coefficient

which measures the degree of association between two variables helps to describe how parameters relate to each other and influence water quality in the way that appropriate water management strategies or options could be instituted (Kumar and Sinha, 2010). According to Pallant (2011), a correlation coefficient can be described as small correlation $0.10 \leq r \leq 0.29$, medium correlation $0.30 \leq r \leq 0.49$ and large correlation $0.50 \leq r \leq 1.0$. The positive point to the direction of the relationship indicates an increase in one variable associated with an increase in the other, while the negative correlation means an increase in one variable related to a decrease in the other.

Heavy metal distribution: Groundwater iron distribution was carried out on the basis of WHO, JECFA and IOM recommendations. In addition, groundwater iron and manganese concentrations were compared with Indian Standard (IS 10500:2012) for within and above the acceptable and the permissible limit of respective heavy metals.

Chronic daily intake: Health risk associated with ingestion of groundwater iron and manganese were assessed by using chronic daily intake (CDI) and hazard quotient parameters. The CDI through groundwater ingestion was calculated according to the modified equation from USEPA (1992) and Chrostowski (1994) as follows:

$$CDI = \frac{C \times DI}{BW} \quad (1)$$

Where, C, DI and BW represent the concentration of heavy metals in groundwater (mg/L), average daily intake rate of water (2 L/day for adult and 1 L/day for child) and body weight (72 kg for adult and 25 kg for child), respectively (USEPA, 1993; USEPA, 1999a; ECETOC, 2001; USEPA, 2001; Weyer *et al.*, 2001; USEPA, 2005; Kavcara *et al.*, 2009; USEPA, 2009).

Hazard quotient and hazard index: Hazard quotient (HQ) is primarily used by USEPA to assess health risk. It is defined as a ratio of the potential exposure to a substance and the level at which no adverse effects are expected. An $HQ \leq 1$ indicates no adverse effects and can be considered to have a negligible hazard. A value > 1 indicates exposure concentration exceeds the reference concentration (RfD). HQ as the noncarcinogenic risk was calculated by using the formula (USEPA, 1999; Gerba, 2001):

$$HQ = \frac{CDI}{RfD} \quad HQ = \frac{CDI}{RfD} \quad (2)$$

Where, HQ is hazard quotient (no unit) and RfD is originated from the risk-based concentration table ($\mu\text{g}/\text{kg}/\text{day}$) (Tahir *et al.*, 2005). To calculate elemental risk assessment, the sum of individual HQ for heavy metals forms Hazard Index (HI). If the

value of HQ and $HI > 1$, it can cause potential noncarcinogenic effects on health; whereas, $HI < 1$ indicates no risk on individual's health (Kaiser, 1960; Sikder *et al.*, 2013). $HI = HQ_1 + HQ_2 + \dots + HQ_n$

RESULTS AND DISCUSSION

Average groundwater characteristic: The average of groundwater characteristics for physicochemical parameters on winter, summer, and post-monsoon are presented in Table 3. On comparison of these with IS 10500:2012 (Second revision) it can be pointed out, average pH 6.9 which is near neutral and within the acceptable limit of the standard (6.5-8.5); whereas, chloride (170.03 mg/L) is also within the acceptable limit (250 mg/L). On the other hand, average Total Dissolved Solids (TDS), total alkalinity, total hardness, calcium hardness, magnesium hardness, fluoride, iron, and manganese concentrations are above the respective acceptable limit of the standard (IS 10500:2012). The phenolphthalein alkalinity is absent indicating absence of carbonate and hydroxyl ions. Phosphate and sulphate concentration were also absent in groundwater. Average iron concentration (1.384 mg/L) is more than 4 fold of the acceptable limit (0.3 mg/L) of the standard.

Seasonal groundwater iron and manganese: Groundwater iron and manganese concentrations in different seasons are presented in Table 4. From the table it can be seen that, the average maximum iron concentration is in Ballarpur (HP) 18.213 mg/L; whereas, minimum in Gunjewahi (DW) 0.081 mg/L. In case of manganese, maximum average concentration 0.779 mg/L is from Naleshwar (HP) and minimum 0.003 mg/L from Antargaon (HP), Gowari (HP), Morwa (HP) and Mowada (HP). Higher iron and manganese concentrations from the hand pump is in agreement with results reported by Satapathy *et al.*, (2009); Rossiter *et al.*, (2010). Hand pump owing to their close proximity to ores and minerals present in the Earth crust and water being a universal solvent tends to dissolve these may have resulted into such elevated concentrations than dug well.

Table 3: Average groundwater characteristics

Sampling location	Temp	pH	EC	Cl ⁻	TDS	T-Alkal	TH	CH	MH	F ⁻	Fe ⁺⁺	Mn ⁺⁺
Sonegaon (HP)	30.2	7.05	946.7	11.94	596.67	384.0	137.3	86.7	50.7	0.93	0.11	0.008
Telwasa (HP)	30.3	6.89	1326.7	53.73	840.00	369.3	294.7	201.3	93.3	0.90	0.251	0.004
Belora (HP)	30.5	7.27	1033.3	38.68	646.67	399.3	136.0	112.0	24.0	1.57	0.109	0.047
Sagra (DW)	28.3	7.25	1760.0	120.55	1116.67	238.7	336.0	277.3	58.7	0.62	0.081	0.007
Pethbhansouli (HP)	29.0	7.05	1316.7	91.86	833.33	416.7	288.0	185.3	102.7	1.02	5.09	0.412
Bhisi (HP)	30.3	6.8	1883.3	162.77	1200.00	375.3	470.7	336.0	134.7	1.09	0.647	0.376
Pimpalgaon (HP)	29.7	7.02	2990.0	315.41	1913.33	410.7	630.7	374.7	256.0	0.73	0.873	0.027
Mowada (HP)	29.8	7.11	1240.0	65.80	783.33	330.0	228.0	170.7	57.3	1.00	0.173	0.003
Dongargaon (HP)	30.0	6.8	2586.7	223.44	1440.00	332.7	390.7	316.0	74.7	1.72	0.871	0.372
Lohara (HP)	29.5	5.81	316.7	15.25	190.00	98.7	100.0	84.0	16.0	0.52	1.457	0.011
Chichpalli (HP)	29.0	6.93	5416.7	886.99	3496.67	506.7	1672.0	588.0	1084.0	1.32	0.124	0.144
Dabgaon (T.) (HP)	30.2	6.87	2496.7	255.54	1606.67	614.7	484.0	260.0	224.0	1.07	2.236	0.222
Naleshwar (HP)	31.5	6.57	2043.3	329.30	1296.67	333.3	457.3	357.3	100.0	1.01	0.693	0.779
Karwan (HP)	30.2	7.33	1063.3	58.68	673.33	362.0	233.3	92.0	141.3	1.41	0.128	0.053
Chikmara (HP)	30.7	6.98	1846.7	154.97	1166.67	404.0	561.3	278.7	282.7	0.98	0.41	0.022
Pathri (HP)	30.7	6.73	936.7	79.44	586.67	250.7	186.7	162.7	24.0	0.62	0.19	0.057
Gunjewahi (DW)	28.3	7.44	646.7	17.41	400.00	289.3	140.0	92.7	47.3	0.86	0.081	0.003
Mangali Chak (HP)	29.8	7.04	743.3	19.66	466.67	296.0	156.0	146.7	9.3	0.76	0.176	0.003
Govindpur (HP)	29.8	6.93	2500.0	357.68	1640.00	460.7	645.3	212.0	433.3	1.17	0.195	0.031
Ratnapur (HP)	30.8	6.87	1563.3	158.05	996.67	366.0	416.0	296.0	120.0	0.79	1.441	0.113
Antargaon (HP)	30.5	7.49	973.3	8.17	616.67	438.0	49.3	34.7	14.7	1.99	0.164	0.003
Visapur (HP)	29.7	6.31	923.3	75.74	580.00	182.7	168.0	142.7	25.3	0.71	5.766	0.131
Ballarpur (HP)	29.8	6.12	893.3	63.70	560.00	154.0	125.3	98.7	26.7	0.40	18.213	0.045
Sasti (HP)	30.0	6.83	2295.0	269.49	1980.00	507.3	786.7	498.7	288.0	1.05	2.27	0.088
Gowari (HP)	30.0	7.08	1586.7	102.43	1006.67	442.0	192.0	121.3	70.7	1.06	0.308	0.003
Arvi (HP)	30.5	6.8	1573.3	97.69	1003.33	300.7	428.0	396.0	32.0	0.94	0.524	0.005
Awarpur (HP)	30.2	7.13	2476.7	171.57	1586.67	552.7	280.0	158.7	121.3	1.51	0.23	0.034
Lakhmapur (HP)	30.3	6.88	940.0	11.45	593.33	324.0	276.0	225.3	50.7	1.14	1.28	0.006
Kem (T.) (HP)	30.5	7.11	643.3	8.53	400.00	272.0	142.7	86.7	56.0	0.78	1.779	0.057
Ganpur (HP)	30.0	6.82	4156.7	435.26	2720.00	441.3	926.7	556.0	382.7	0.89	0.601	0.004
Gondpipari (HP)	31.5	6.8	2246.7	230.97	1446.67	438.0	522.7	381.3	141.3	0.94	1.562	0.287
Pombhurna (HP)	30.5	6.96	1946.7	177.45	1246.67	435.3	552.0	260.0	292.0	0.96	0.31	0.008
Jam Tukum (HP)	30.2	6.9	2970.0	365.94	1910.00	527.3	365.3	208.0	157.3	1.27	0.257	0.06
Dongar Haldi (HP)	30.3	7.01	3073.3	349.78	1980.00	648.0	290.7	157.3	133.3	1.39	0.709	0.091
Durgapur (HP)	28.8	6.95	2894.3	219.72	1866.00	758.7	229.3	180.0	49.3	1.10	0.256	0.286
Morwa (HP)	29.5	7.04	1840.0	116.27	1180.00	388.0	301.3	172.0	129.3	0.82	0.251	0.003
Min.	28.3	5.8	316.6	8.170	190.00	98.6	49.3	34.6	9.3	0.39	0.081	0.003
Max.	31.5	7.4	5416.6	886.98	3496.66	758.6	1672.0	588.0	1084.0	1.99	18.213	0.779

	Temp	pH	EC	Cl ⁻	TDS	T-Alkal	TH	CH	MH	F ⁻	Fe ⁺⁺	Mn ⁺⁺
Average	30.0	6.9	1835.8	170.03	1182.38	390.2	377.7	230.7	147.3	1.02	1.384	0.106
SD	0.71	0.3	1059.7	172.33	699.24	133.8	300.0	136.0	192.8	0.33	3.153	0.165
BIS	NS	6.5-8.5	NS	250	500	200	200	75	30	1.0	0.3	0.1

Temp - Temperature in °C, EC - Electrical conductivity in mmhos/cm, TDS - Total dissolved solids, Cl⁻ - Chloride, T-Alkal - Total alkalinity, TH - Total hardness, CH - Calcium hardness, MH - Magnesium hardness, F⁻ - Fluoride, Fe⁺⁺ - Iron, Mn⁺⁺ - Manganese. All parameters are expressed in mg/L except temperature, pH and EC. Min. - Minimum, Max. - Maximum, SD - Standard deviation (±), NS - No standard, BIS - Bureau of Indian Standard (IS 10500:2012) (Second Revision), considered the acceptable limit of the standard for respective water characteristic.

Spatial variability of iron: Groundwater iron spatial variability maps for different seasons are depicted in Figure 4 (a-d). The iron concentration is divided into 10 classes. From the map (Figure 4a) it can be seen that, maximum groundwater iron concentration Ballarpur (HP, 47.100 mg/L, the central part of the district) followed by Pethbhansouli (HP, 14.313 mg/L, in NW direction). At both these sampling locations sandstone and variegated shale lithology exist. Thus, it can be stated that the origin of groundwater iron at these two sampling locations is from sedimentary rock i.e. sandstone.

Figure 4b depicts groundwater iron concentration for summer. Ballarpur (HP) have maximum groundwater iron concentration (3.825 mg/L) followed by Gondpipari (HP) 3.548 mg/L and Dabgaon (Tukum) (HP) 3.084 mg/L. The lithology at Ballarpur is sandstone, variegated shale; whereas, granitic gneisses and migmatite at Gondpipari and Dabgaon (Tukum). Ballarpur (HP) which has maximum groundwater iron concentration in winter is continued in summer also.

Post-monsoon groundwater iron concentration is depicted in Figure 4c. Visapur (HP) have maximum groundwater iron concentration 4.022 mg/L followed by Ballarpur (HP) 3.714 mg/L. These two sampling locations have formed a critical zone as Ballarpur emerged as a sampling location with maximum groundwater iron concentration during winter & summer and with second maximum concentration during post-monsoon. Ratnapur (HP) situated in N direction has groundwater iron concentration of 1.695 mg/L. From Figure 4d, which depicts average groundwater iron concentration, it can be seen that maximum concentration is recorded in the central part of the district which comprises of sampling locations Ballarpur (HP) and Visapur (HP), both with maximum average iron concentration 18.213 mg/L and 5.766 mg/L respectively. Other elevated groundwater average iron concentration is recorded from Pethbhansouli (HP) 5.090 mg/L in NW direction followed by Dabgaon (Tukum) (HP) 2.236 mg/L in SE direction and Ratnapur (HP) 1.441 mg/L in N direction.

The results for the asymmetrical distribution of groundwater iron from the study area corroborates with Behera *et al.*, (2012). Maximum groundwater iron concentration

from winter (47.100 mg/L), summer (3.825 mg/L) and post-monsoon (4.022 mg/L) concur with Merrill *et al.*, (2012). At number of sampling locations, the iron concentration is above permissible limit these results are in parallel with Chetia *et al.*, (2008); Borah *et al.*, (2009).

Table 4: Seasonal distribution of groundwater iron and manganese

Sampling location (Water source)	Altitude (m asl)	Age (Years)	Depth (ft bgl)	Iron concentration (mg/L)				Manganese concentration (mg/L)			
				Winter	Summer	Post- monsoon	Average	Winter	Summer	Post- monsoon	Average
Sonegaon (HP)	215	3	100	0.006	0.188	0.136	0.110	0.005	0.009	0.010	0.008
Telwasa (HP)	207	3	100	0.034	0.221	0.499	0.251	BDL	0.007	0.006	0.004
Belora (HP)	210	10	100	BDL	0.171	0.156	0.109	0.078	0.031	0.032	0.047
Sagra (DW)	240	57	50	BDL	0.164	0.080	0.081	0.004	0.011	0.007	0.007
Pethbhansouli (HP)	209	3	100	14.313	0.312	0.644	5.090	0.972	0.138	0.125	0.412
Bhisi (HP)	287	1	150	0.337	0.906	0.698	0.647	0.279	0.089	0.761	0.376
Pimpalgaon (HP)	246	25	250	0.687	0.466	1.465	0.873	0.056	0.016	0.008	0.027
Mowada (HP)	198	10	180	0.117	0.240	0.163	0.173	BDL	0.006	0.003	0.003
Dongargaon (HP)	222	30	200	1.700	0.455	0.458	0.871	0.791	0.201	0.125	0.372
Lohara (HP)	202	12	60	3.749	0.357	0.265	1.457	0.021	0.007	0.005	0.011
Chichpalli (HP)	226	12	70	BDL	0.204	0.167	0.124	0.281	0.064	0.087	0.144
Dabgaon (T.) (HP)	215	3	300	1.997	3.084	1.627	2.236	0.383	0.149	0.133	0.222
Naleshwar (HP)	215	12	140	0.982	0.446	0.651	0.693	1.853	0.474	0.009	0.779
Karwan (HP)	205	8	150	BDL	0.200	0.185	0.128	0.102	0.023	0.034	0.053
Chikmara (HP)	214	25	100	0.575	0.571	0.084	0.410	0.030	0.019	0.017	0.022
Pathri (HP)	240	20	100	BDL	0.246	0.323	0.190	0.096	0.039	0.035	0.057
Gunjewahi (DW)	230	60	35	BDL	0.188	0.055	0.081	BDL	0.006	0.002	0.003
Mangali Chak (HP)	224	25	200	0.117	0.266	0.144	0.176	BDL	0.005	0.004	0.003
Govindpur (HP)	271	25	150	0.120	0.249	0.215	0.195	0.076	0.012	0.005	0.031
Ratnapur (HP)	225	10	100	1.765	0.864	1.695	1.441	0.186	0.038	0.116	0.113
Antargaon (HP)	230	15	200	0.117	0.276	0.098	0.164	BDL	0.005	0.003	0.003
Visapur (HP)	152	9	100	11.536	1.741	4.022	5.766	0.363	0.016	0.013	0.131
Ballarpur (HP)	243	5	60	47.100	3.825	3.714	18.213	0.093	0.015	0.026	0.045
Sasti (HP)	198	10	180	5.715	0.892	0.202	2.270	0.208	0.050	0.005	0.088
Gowari (HP)	198	6	120	0.378	0.401	0.146	0.308	BDL	0.008	0.002	0.003
Arvi (HP)	202	23	100	0.317	0.901	0.354	0.524	BDL	0.010	0.006	0.005
Awarpur (HP)	216	2	200	BDL	0.569	0.120	0.230	0.060	0.025	0.018	0.034
Lakhmapur (HP)	243	8	200	2.922	0.793	0.124	1.280	0.009	0.008	0.002	0.006
Kem (T.) (HP)	178	8	150	2.927	1.134	1.276	1.779	0.037	0.113	0.022	0.057
Ganpur (HP)	199	25	160	1.364	0.281	0.157	0.601	BDL	0.011	0.002	0.004
Gondpipari (HP)	195	20	100	0.951	3.548	0.186	1.562	0.532	0.248	0.082	0.287
Pombhurna (HP)	189	20	100	0.420	0.351	0.160	0.310	0.010	0.011	0.004	0.008
Jam Tukum (HP)	174	20	250	0.030	0.627	0.115	0.257	0.101	0.062	0.016	0.060
Dongar Haldi (HP)	187	6	120	1.437	0.399	0.290	0.709	0.224	0.004	0.044	0.091
Durgapur (HP)	201	4	20	0.241	0.439	0.089	0.256	0.354	0.193	0.312	0.286
Morwa (HP)	218	15	100	0.207	0.331	0.215	0.251	0.004	0.003	0.003	0.003
Min.	152	1	20	BDL	0.164	0.055	0.081	BDL	0.003	0.002	0.003
Max.	287	60	300	47.100	3.825	4.022	18.21	1.853	0.474	0.761	0.779
Average	211	15.27	133.2	3.522	0.730	0.582	1.384	0.257	0.058	0.058	0.106
SD	26.00	13.00	63.55	9.01	0.90	0.92	3.15	0.39	0.09	0.13	0.16

HP - Hand Pump, DW - Dug Well, Altitude in meters above sea level (m asl), Age of the water source from the year of installation in years, Depth in feet of water source below ground level (ft bgl). Groundwater iron and manganese concentrations are expressed in mg/L, BDL - Below detection limit, Min. - Minimum, Max. - Maximum, SD - Standard deviation (\pm)

Spatial variability of manganese: Figure 5 (a-d) depicts spatial variability maps of groundwater manganese for winter, summer, post-monsoon, and average respectively with 10 concentration classes. From Figure 5a it can be observed, manganese concentrations have spatial and asymmetrical distribution. Naleshwar (HP) in E direction, the concentration is maximum 1.853 mg/L followed by Pethbhansouli (HP) 0.972 mg/L in NW direction. The lithology at these two sampling locations is granitic gneisses & migmatite, and sandstone, variegated shale respectively.

Groundwater manganese spatial variability for summer is depicted in Figure 5b. At Naleshwar (HP) groundwater manganese concentration is 0.474 mg/L followed by Gondpipari (HP, 0.248 mg/L) and Dongargaon (HP, 0.201 mg/L). Naleshwar (HP) which has reported maximum groundwater manganese concentration in winter also has maximum concentration in summer. Naleshwar (HP) and Gondpipari (HP) both have granitic gneisses and migmatite lithology.

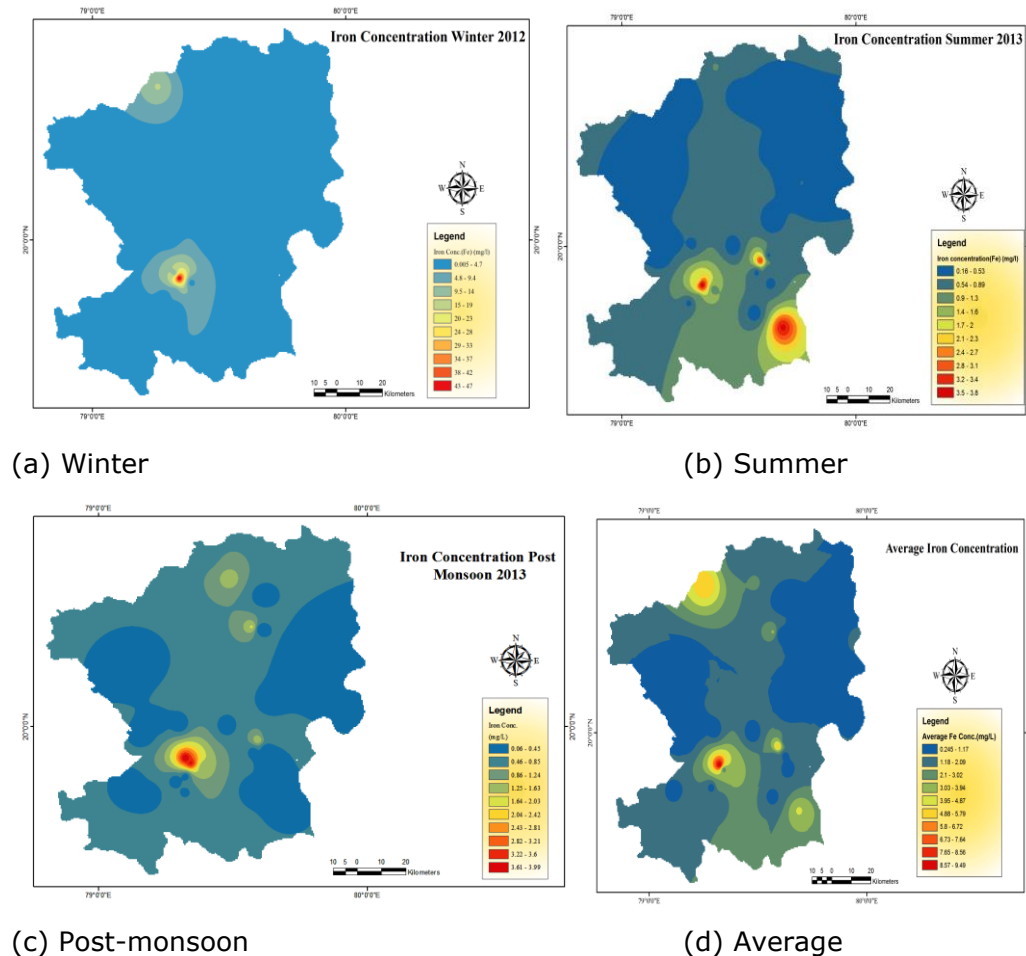


Figure 4: Spatial variation maps showing groundwater iron concentration of the study area

Groundwater manganese in post-monsoon is presented in Figure 5c. Bhisri (HP) in N direction has maximum concentration 0.761 mg/L followed by Durgapur (HP) 0.312 mg/L and Dabgaon (Tukum) (HP) 0.133 mg/L. Bhisri (HP) have granitic gneisses and granite hornblende schist, Durgapur (HP) with sandstone, variegated shale and Dabgaon (Tukum) (HP) with granitic gneisses and migmatite.

Average groundwater manganese concentrations are depicted in Figure 5d which indicates Naleshwar (HP) in E direction have maximum average groundwater manganese concentration (0.779 mg/L) followed by Pethbhansouli (HP) 0.412 mg/L and Bhisri (HP) 0.376 mg/L both in N direction. West and NE directions have comparatively minimum average manganese concentration.

Manganese concentration distribution from the study area is in parallel with observations reported by Rajmohan and Elango (2005); Savita Kumari *et al.*, (2014).

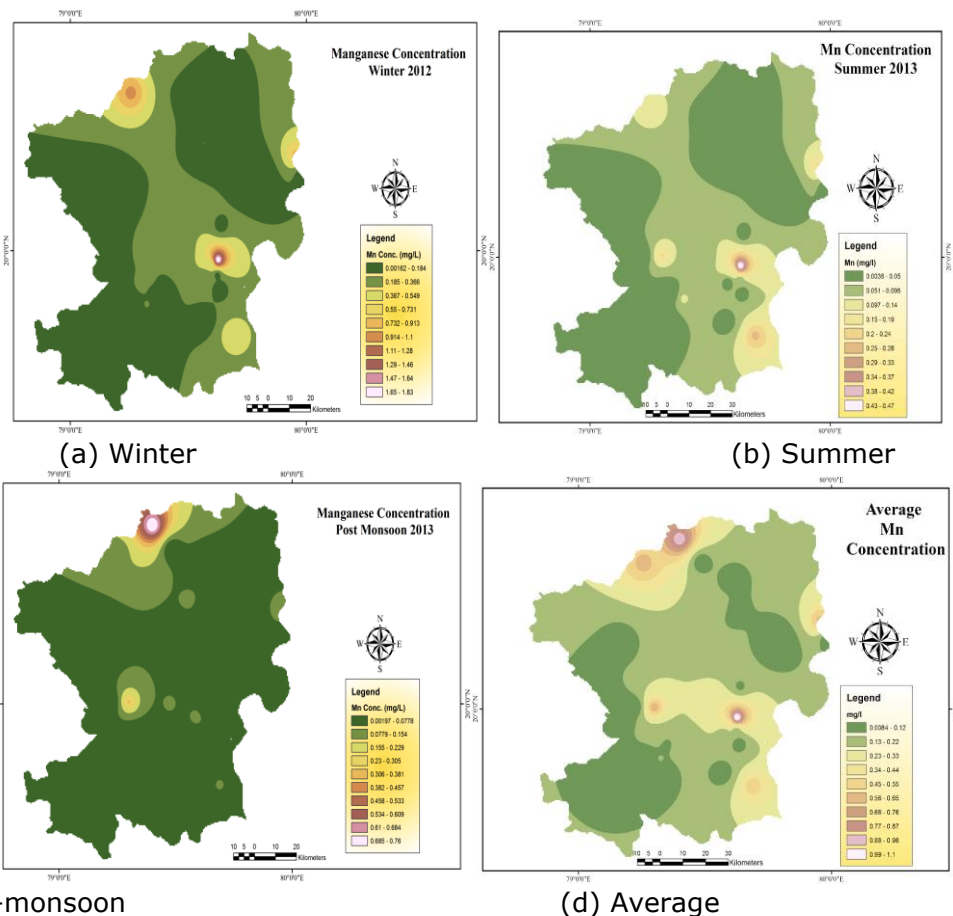
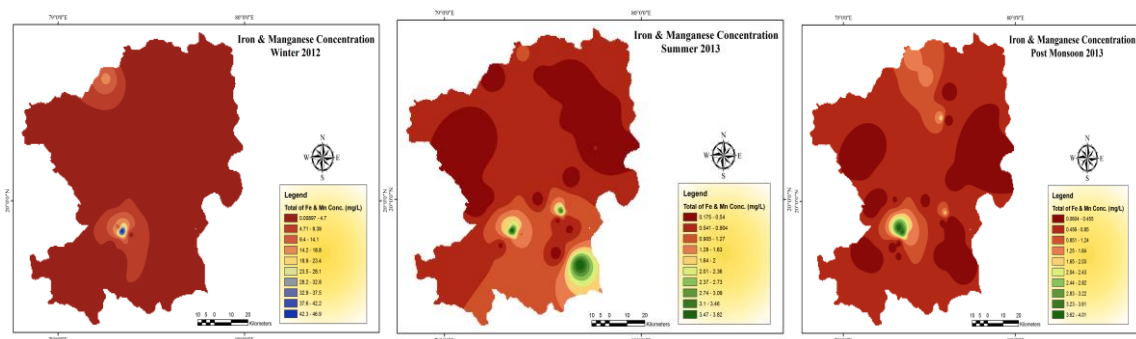


Figure 5: Spatial variation maps showing groundwater manganese concentration of the study area

Spatial variability of iron and manganese combined concentration: Combined groundwater iron and manganese concentration for winter is depicted in Figure 6a with 10 concentration classes. Maximum combined concentration from Ballarpur (HP, 47.194 mg/L, central part of the study area) followed by Pethbhansouli (HP, 15.285 mg/L, NW direction).

Figure 6b depicts spatial viability for summer. From the map it can be seen that Ballarpur (HP), Gondpipari (HP) and Dabgaon (Tukum) (HP) have elevated combined groundwater iron and manganese concentration. Combined iron and manganese concentration at Ballarpur (HP) is 3.840 mg/L followed by Gondpipari (HP) 3.796 mg/L. From the study area Naleshwar (HP) in winter and summer; whereas, Bhisi (HP) and Durgapur (HP) in post-monsoon have reported Mn>Fe.

Post-monsoon combined concentration is depicted in Figure 6c. Elevated combined concentrations are recorded at Visapur (HP) 4.035 mg/L and Ballarpur (HP) 3.740 mg/L in central part; whereas, another predominant area for combined concentration is observed in N and E directions.



(a) Winter (b) Summer (c) Post-monsoon

Figure 6: Spatial variation maps showing groundwater iron and manganese combined concentration of the study area

The results obtained are partially in accordance with results reported by Tiwari *et al.*, (2013); Dwivedi and Vankar (2014) which reported a mean value of total heavy metal content as Mn>Fe. The reasons for such findings may be due to the affinity of manganese with iron. Higher manganese concentration is not always accompanied by high iron concentration corroborates with Rossiter *et al.*, (2010).

Pearson correlation coefficient: Pearson's correlation coefficients for winter, summer and post-monsoon are presented in Tables 5, 6, and 7 respectively. From these

tables, it can be observed that iron and manganese concentrations are not correlated with each other. Furthermore, iron and total alkalinity, magnesium hardness and fluoride are significant ($p < 0.01$). In the case of manganese, it is correlated with temperature & pH ($p < 0.05$); whereas, with chloride and calcium hardness ($p < 0.01$) in winter. In summer, iron and temperature is positively correlated ($p < 0.05$); whereas, iron and pH ($p < 0.01$). Manganese is correlated with temperature, electrical conductivity and chloride ($p < 0.05$); on the other hand, with calcium hardness it was $p < 0.01$. In post-monsoon iron and pH is significantly correlated ($p < 0.01$).

Table 6: Pearson’s correlation coefficient among groundwater characteristics (Summer)

	Temp	pH	EC	TDS	Cl ⁻	T-Alka	TH	CH	MH	F ⁻	Fe ⁺⁺
Temp	1										
pH	0.00148	1									
EC	-0.1139	-0.0264	1								
TDS	-0.1208	-0.0197	0.99048*	1							
Cl ⁻	-0.0739	-0.1184	0.94393*	0.95368*	1						
T-Alkal	-0.1269	0.40003*	0.60226*	0.61856*	0.44842*	1					
TH	-0.0883	-0.0886	0.87394*	0.88898*	0.92643*	0.33154*	1				
CH	0.00721	-0.1591	0.79226*	0.79488*	0.7679*	0.29694*	0.86695*	1			
MH	-0.1328	-0.0375	0.81732*	0.83772*	0.90781*	0.31214*	0.95799*	0.6876*	1		
F ⁻	0.24911**	0.48978*	0.37581*	0.33126*	0.29204*	0.51875*	0.18013**	0.06096	0.22735**	1	
Fe ⁺⁺	0.21114**	-0.4553*	-0.0342	-0.0287	-0.0098	-0.0581	-0.0232	0.07884	-0.0791	-0.2286	1
Mn ⁺⁺	0.21062**	-0.1425	0.20392**	0.16858	0.20456**	0.18905	0.12745	0.30427*	0.0106	0.18477	0.24266

*Significant at 0.01 level; ** 0.05 level.

Temp -Temperature, EC - Electrical conductivity, TDS - Total dissolved solids, Cl⁻ Chloride, T-Alkal -Total alkalinity, TH - Total hardness, CH - Calcium hardness, MH - Magnesium hardness, F⁻ - Fluoride, Fe⁺⁺ - Iron and Mn⁺⁺ - Manganese.

Table 7: Pearson’s correlation coefficient among groundwater characteristics (Post-monsoon)

	Temp	pH	EC	TDS	Cl ⁻	T-Alka	TH	CH	MH	F ⁻	Fe ⁺⁺
Temp	1										
pH	-0.0415	1									
EC	-0.0151	0.18885	1								
TDS	-0.0123	0.18686	0.99984*	1							
Cl ⁻	-0.0428	0.05778	0.94147*	0.93769*	1						
T-Alkal	0.11602	0.56933*	0.61605*	0.61875*	0.46272*	1					
TH	-0.0863	0.0851	0.88044*	0.87718*	0.88788*	0.34462*	1				
CH	0.04763	0.04955	0.81929*	0.81882*	0.75125*	0.29848*	0.90477*	1			
MH	-0.1954	0.1039	0.79094*	0.78579*	0.86621*	0.32726*	0.91808*	0.6623*	1		
F ⁻	0.20978**	0.48259*	0.25078**	0.25047**	0.17145	0.51697*	0.07112	0.01106	0.11348	1	
Fe ⁺⁺	0.02187	-0.5462*	-0.2072	-0.2086	-0.131	-0.3775*	-0.1559	-0.1613	-0.1247	-0.3374	1
Mn ⁺⁺	0.04307	-0.0527	0.10996	0.11152	0.07737	0.17936	0.09664	0.18541	-0.007	0.13231	0.04001

*Significant at 0.01 level; ** 0.05 level.

Temp -Temperature, EC - Electrical conductivity, TDS - Total dissolved solids, Cl⁻ - Chloride, T-Alkal - Total alkalinity, TH - Total hardness, CH - Calcium hardness, MH - Magnesium hardness, F⁻ - Fluoride, Fe⁺⁺ - Iron and Mn⁺⁺ - Manganese

Pearson's correlation coefficient for groundwater iron and manganese is reported by Cobbina *et al.*, (2012) as 0.282; Agca *et al.*, (2014) as 0.082; Dwivedi and Vankar (2014) as 0.222 and Oyem *et al.*, (2015) as 0.146. These findings on comparison with results obtained from the study shows that in summer only Pearson correlation coefficient is 0.24; whereas, in winter and post-monsoon no correlation could be developed between these two heavy metals ions.

Pearson correlation coefficient for iron-manganese as reported by Amfo-Otu *et al.*, (2014) is $r=0.883$ which indicated a strong correlation. Such strong Pearson correlation coefficient among iron-manganese is not observed from the study area from different seasons. Rao (2007) and Daughney (2003) pointed out better correlation could not be observed between iron and other chemical constituents which is in agreement with the observations obtained from the study.

Iron distribution on WHO, JECFA and IOM recommendations: Distribution of water source across groundwater iron concentration categories based on WHO and JECFA water-related and IOM dietary daily iron recommendations is presented in Table 8.

In winter, 16 (44.44%) samples reported groundwater iron concentrations in minimal category (0.0-<0.3 mg/L); whereas, 13 (36.11%) in elevated (0.3-2.0 mg/L) and 6 (16.66%) from 'high' category (>2.0-22.5 mg/L). Only 1 (2.77%) sample (Ballarpur, 47.100 mg/L, HP) is in 'very high' category. On comparison with Indian Standard Drinking Water-Specification (IS 10500:2012) Acceptable limit for iron (0.3 mg/L), 16 (44.44%) samples are in minimal category. From the average groundwater iron concentration, it can be pointed out elevated, high and very high concentration categories for winter are above the acceptable limit of the standard. Elevated category reported more than 3 fold increase in average iron concentration; whereas, in high category ~23 fold increase and in very high category ~157 fold increase.

In the minimal category (0.0-<0.3 mg/L of iron), during summer reduction in groundwater level leads to an increase in average groundwater iron concentration (0.222 mg/L). In monsoon, precipitation led to augmentation of groundwater which may have resulted into dilution of the concentrated heavy metal ion as compared to summer (Average iron concentration 0.154 mg/L). During winter, reduction in the dissolution of ores and dilution of groundwater iron concentration may have resulted in minimum average concentration (0.100 mg/L). During post-monsoon, leaching activities from different minerals and ores from the Earth crust may have resulted in elevated average groundwater iron concentration (0.154 mg/L) as that of winter. The leaching activity

perhaps got reduced in winter as no more precipitation led to percolation, leaching, and accumulation of heavy metals into groundwater.

On comparison of observations during summer with IS 10500:2012 it is seen that, 13 (36.11%) samples are within the acceptable limit; whereas, 23 (63.88%) above it. Elevated and high category average groundwater iron concentrations are found to be two fold and ~11 fold respectively more than Indian Standard acceptable limit for iron. The average groundwater iron concentration from minimal category (0.222 mg/L) is more than two fold as compared with winter (0.100 mg/L).

Post-monsoon observations on comparison of with IS 10500:2012 for iron revealed, 23 (63.88%) samples are within the acceptable limit; whereas, 13 (36.1%) above it. Average groundwater iron concentration from elevated (0.880 mg/L) and high category (3.868 mg/L) is found to be about three fold and 13 fold respectively higher than the acceptable limit of the Indian Standard for iron.

Merrill *et al.*, (2010) reported maximum (73%) iron concentration contribution was from categories of high and very high; whereas, minimum contribution (27%) from minimal and elevated categories which on comparison with results from the study revealed a reverse trend. Minimal and elevated iron concentration categories contributed to maximum sampling locations (~80%) and high and very high categories contributed minimum (~20%) in winter. Furthermore, this trend was continued in summer and post-monsoon too.

Distribution with Indian standard: Distribution of groundwater iron and manganese concentrations in different seasons with Indian Standard (IS) Drinking Water-Specification (IS 10500:2012, Second revision) for iron and manganese is presented in Table 9.

Iron distribution: During winter, 16 (44.44%) samples have iron concentration within the acceptable limit (0.3 mg/L) of the standard; whereas, 20 (55.55%) above the permissible limit (Permissible limit "no relaxation"). In case of summer, 13 (36.11%) samples are within the acceptable limit; whereas, 23 (63.88%) above the permissible limit. In post-monsoon, 23 (63.88%) samples have groundwater iron concentration within the acceptable limit and 13 (36.11%) above the permissible limit.

In case of above the permissible limit, it is in the order of summer (n=23, 63.88%) > winter (n=20, 55.55%) > post-monsoon (n=13, 36.11%). Minimum number of samples within the acceptable limit during summer can be attributed to decrease in groundwater level which may have resulted in an increase in the concentration of metal ion in groundwater. Maximum (n=23, 63.88%) samples in post-monsoon have

groundwater iron concentrations within the acceptable limit which can be attributed to dilution of heavy metal ion in groundwater due to precipitation in monsoon. Furthermore, in winter, samples within the acceptable limit got reduced to 16 (44.44%), which indicates a reduction in dilution activity.

Table 8: Iron distribution on WHO, JECFA and IOM recommendations

Iron conc. category	Winter		Summer		Post-monsoon	
	n (%)	Average	n (%)	Average	n (%)	Average
Minimal 0.0-<0.3* mg/L	16 (44.44%)	0.100	13 (36.11%)	0.222	23 (63.88%)	0.154
Elevated 0.3-2.0† mg/L	13 (36.11%)	0.980	20 (55.55%)	0.647	11 (30.55%)	0.880
High >2.0-22.5‡ mg/L	6 (16.66%)	6.860	3 (8.33%)	3.485	2 (5.55%)	3.868
Very high >22.5 mg/L	1 (2.77%)	47.100	--	--	--	--

n Number of sampling locations. Average values are reported in mg/L.

*WHO (2006) aesthetic cut-off and IS 10500: 2012, Acceptable limit for iron (0.3 mg/L).

†JECFA provisional maximum tolerable daily intake for iron in water (WHO 1984, 2004).

‡Per litre equivalent of the Institute of Medicine (IOM) recommended tolerable upper intake level of 45 mg iron/day for daily iron intake for adults (excluding iron supplements) assuming 2 L/day water consumption (Otten *et al.* 2006; WHO 2006).

Manganese distribution: During winter, 22 (61.11%) samples have groundwater manganese concentration within the acceptable limit (0.1 mg/L) and 7 (19.44%) above the permissible limit (0.3 mg/L) of IS 10500:2012 (Second revision). In summer, 29 (80.55%) samples are within the acceptable limit (0.1 mg/L) and 1 (2.77%) above the permissible limit; whereas, in post-monsoon, 30 (83.33%) within the acceptable limit and 2 (5.55%) above the permissible limit. During winter, the average manganese concentration is ~2.5 fold more than the acceptable limit (0.1 mg/L). Maximum manganese concentrations from all seasons are above the acceptable and the permissible limit of the standard.

In summer, due to decrease in groundwater level 29 samples manganese concentration is within the acceptable limit; whereas, in monsoon, precipitation resulted into increase in groundwater level and brought 30 samples within the acceptable limit of IS 10500:2012. Furthermore, reduction in dilution activity in winter may have resulted

in 22 samples manganese concentration within the acceptable limit; whereas, 7 (19.44%) above the permissible limit. The percolation of rainwater through soil during monsoon and post-monsoon may have resulted into decrease in groundwater manganese concentration as compared with summer for above the permissible limit of the standard. Post-monsoon have maximum samples (n=30, 83.33%) within the acceptable limit and winter with minimum 22 (61.11%).

Table 9: Distribution of iron and manganese with Indian Standard Drinking Water-Specification (IS 10500: 2012)

Heavy metal	Season	IS 10500:2012		Observed concentration (mg/L)			Number of sampling location (%)		
		Acceptable limit (mg/L)	Permissible limit (mg/L)	Min	Mix	Average	Within the acceptable limit	Above the permissible limit	
Iron									
	Winter	0.3	No relaxation	BDL	47.100	3.522	16 (44.44%)	20 (55.55%)	
	Summer			0.16	3.825	0.730	13 (36.11%)	23 (63.88%)	
	Post-monsoon			0.05	4.022	0.582	23 (63.88%)	13 (36.11%)	
Manganese									
	Winter	0.1	0.3	BDL	1.853	0.257	22 (61.11%)	7 (19.44%)	
	Summer			0.00	0.474	0.058	29 (80.55%)	1 (2.77%)	
	Post-monsoon			0.00	0.761	0.058	30 (83.33%)	2 (5.55%)	

Min - Minimum, Max - Maximum, BDL - Below detection limit

Rajmohan and Elango (2005) reported pre-monsoon (summer) samples exceed the permissible limits of EPA (2002) and ISI (50 and 100 µg/L) for groundwater iron concentration; whereas, post-monsoon were within the permissible limit which is in accordance with the results obtained in this study. The seasonal variation in groundwater iron concentration as summer with maximum samples above the permissible limit and post-monsoon with the minimum is in accordance with observations reported by Laluraj and Gopinath (2006); Demirel (2007). Idoko (2010) reported 35% of boreholes have high iron concentration above WHO standard for drinking water. From the results, only post-monsoon (36.11%) have comparable results; whereas, winter and summer are comparatively higher 55.55% and 63.88% respectively. Merrill *et al.*, (2010) reported only 3% of surveyed tubewell have below WHO aesthetic cut-off of 0.3 mg/L iron

concentration which is significantly lower than these results. Haloi and Sarma (2011) reported 65% of sampling locations were contaminated by iron is observed during summer (63.88%). Cobrina *et al.*, (2012) reported 11% of boreholes have iron concentration above WHO recommended guidelines (0.3 mg/L) which indicate, in Chandrapur district presence of groundwater iron is more with temporal variation. Groundwater iron and manganese concentrations above the permissible limit of IS 10500:2012 (Second revision) for various seasons is in agreement with results reported by Daughney (2003); Cheng *et al.*, (2004); Chakrabarty and Sarma (2010); Homoncik *et al.*, (2010); Singh *et al.*, (2012); Khan *et al.*, (2013); Tiwari *et al.*, (2013); Huang *et al.*, (2015).

Chronic daily intake: Results of CDI is presented in Table 10 suggest groundwater contains dissolved heavy metals. CDI values for adult from groundwater iron ranged BDL-1.308 mg/kg/day in winter, 0.005-0.106 mg/kg/day in summer and in post-monsoon 0.002-0.112 mg/kg/day. In case of groundwater manganese it is BDL-0.051 mg/kg/day in winter, 0.0001-0.0131 mg/kg/day in summer and 0.0001-0.0211 mg/kg/day in post-monsoon. Therefore, the order of heavy metal toxicity for groundwater is Fe>Mn. In case of CDI for children, for iron, during winter it is in the range BDL-1.884 mg/kg/day, 0.0066-0.153 mg/kg/day in summer and in post-monsoon 0.002-0.160 mg/kg/day. For groundwater manganese during winter it ranged BDL-0.074 mg/kg/day, in summer 0.0001-0.019 mg/kg/day and 0.000-0.030 mg/kg/day in post-monsoon. Children's CDI on comparison with adult revealed they are at marginally higher health risk. These CDI values, however, gives an indication of possible toxicity of these heavy metals found in the aquifer of the study area. Since CDI is below the reference dose (RfD) values for iron (0.7 mg/kg/day) and manganese (0.14 mg/kg/day) (USEPA 2005), except from Ballarpur for groundwater iron in winter (1.308 mg/kg/day for adult and 1.884 mg/kg/day for child), it can be stated that at other sampling locations health risk of consuming groundwater with these heavy metals concentrations perhaps may be negligible for inhabitants.

Hazard quotient and hazard index: Hazard quotient on the health of inhabitants (adult and children) through regular consumption of groundwater is also presented in Table 10. The hazard quotient for an adult for iron ranged BDL-1.869 in winter, 0.007-0.151 in summer and 0.003-0.160 in post-monsoon; whereas, for groundwater manganese, it is BDL-0.364 in winter, in summer 0.0007-0.0936 and in post-monsoon 0.0007-0.1500, the order of toxicity being Fe>Mn. In case of HQ for children, for iron during winter it ranged BDL-2.691, 0.009-0.219 in summer and in post-monsoon 0.003-

0.229. On the other hand for manganese it is BDL-0.529 in winter, 0.001-0.136 during summer and in post-monsoon 0.000-0.214.

Meanwhile, hazard index (HI) for adult is calculated from the sum of average hazard quotients of contaminants

Hazard Index_{mean} = HQ_{Fe}+HQ_{Mn} (USEPA and US 2006)

0.14+0.05, Hazard Index_{mean}= 0.19 for winter,

0.028+0.011, Hazard Index_{mean}= 0.039 for summer, and

0.022+0.009, Hazard Index_{mean}= 0.031 for post-monsoon.

Hazard index for children is found to be

0.201+0.071, Hazard Index_{mean}= 0.272 for winter,

0.041+0.014, Hazard Index_{mean}= 0.055 for summer, and

0.033+0.014, Hazard Index_{mean}= 0.047 for post-monsoon.

Since the hazard index is <1.00 (Khan *et al.*, 2008; Krishna and Mohan, 2013), groundwater is confirmed as being safe with reference to the studied heavy metals and results reported.

The carcinogenic risk was measured from the calculation of CDI_{oral} (mg/kg/day) (Kundu *et al.*, 2008). Scales for chronic and carcinogenic risk assessment is presented in Table 11 (USEPA, 1999a; Bortey-Sam *et al.*, 2015). As reported by Rahman *et al.*, (2019), hazard quotient for children from iron and manganese is relatively very low which is in agreement with results obtained in the study. According to Hafeman *et al.*, (2007) infants exposed to winter manganese levels greater than or equal to WHO 2003 guideline (0.4 mg/L) have an elevated mortality risk during the first year of life compared with unexposed infants. From the study area, few sampling locations (viz. Naleshwar, HP; Pethbhansouli, HP) have groundwater manganese concentration >0.4 mg/L which may lead to infant mortality if such groundwater is used without any treatment for the potable purpose. In winter, groundwater can cause a potential threat to infants. The results obtained from this study are in agreement with Oyem *et al.*, (2015). The CDI by Giri *et al.*, (2012) 1.94 and 1.05 mg/kg/day for iron and manganese respectively is significantly higher than the results obtained from this study. Hazard quotient value through oral ingestion from northern Pakistan for iron and manganese was >1.00 (Begum *et al.*, 2015) which is not the case from this study area. The elevated groundwater iron concentration from the study area which is ingested by inhabitants may pose a threat to their health in the light of results reported by Huang (2003). Furthermore, it can be pointed out that till date iron standard is restricted with the

aesthetic aspect only, now it needs to be looked at with respect to health perspective also.

Table 10: Chronic daily intake and hazard quotient indices with reference dose for iron and manganese

Heavy metal	Statistics		CDI, mg/kg/day		HQ	RfD, mg/kg/day ^a
Iron						
Winter	Min BDL, Max 47.100, Average 3.52, SD 9.01	Adult	BDL, 1.308, 0.098, 0.250	Adult	BDL, 1.869, 0.14, 0.357	0.7
		Child	BDL, 1.884, 0.140, 0.360	Child	BDL, 2.691, 0.201, 0.514	
Summer	Min 0.164, Max 3.825, Average 0.73, SD 0.90	Adult	0.005, 0.106, 0.020, 0.025	Adult	0.007, 0.151, 0.028, 0.036	
		Child	0.006, 0.153, 0.029, 0.036	Child	0.009, 0.219, 0.041, 0.051	
Post-monsoon	Min 0.055, Max 4.022, Average 0.58, SD 0.92	Adult	0.002, 0.112, 0.016, 0.026	Adult	0.003, 0.160, 0.022, 0.037	
		Child	0.002, 0.160, 0.023, 0.036	Child	0.003, 0.229, 0.033, 0.051	
Manganese						
Winter	Min BDL, Max 1.853, Average 0.25, SD 0.39	Adult	BDL, 0.051, 0.007, 0.010	Adult	BDL, 0.364, 0.05, 0.071	0.14
		Child	BDL, 0.074, 0.010, 0.015	Child	BDL, 0.529, 0.071, 0.111	
Summer	Min 0.003, Max 0.474, Average 0.058, SD 0.09	Adult	0.0001, 0.0131, 0.0016, 0.0025	Adult	0.0007, 0.0936, 0.0114, 0.0179	
		Child	0.0001, 0.019, 0.002, 0.004	Child	0.001, 0.136, 0.014, 0.029	
Post-monsoon	Min 0.002, Max 0.761, Average 0.058, SD 0.13	Adult	0.0001, 0.0211, 0.0013, 0.0036	Adult	0.0007, 0.1500, 0.0092, 0.0257	
		Child	0.000, 0.030, 0.002, 0.005	Child	0.000, 0.214, 0.014, 0.036	

CDI - Chronic Daily Intake, HQ - Hazard Quotient, RfD - Reference dose, Min - Minimum, Max - Maximum, SD - Standard deviation (\pm), BDL - Below detection limit

^aRfD (USEPA 2005)

Table 11: Scales for chronic and carcinogenic risk assessment (USEPA 1999a; Bortey-Sam *et al.* 2015)

Risk level	HQ or HI	Chronic risk	Calculated cases of cancer occurrence	Cancer risk
1	< 0.1	Negligible	< 1 per 1000,000 inhabitants (10^{-6})	Very low
2	$\geq 0.1 < 1$	Low	> 1 per 1000,000 inhabitants (10^{-6})	Low
3	$\geq 1 < 4$	Medium	< 1 per 100,000 inhabitants (10^{-5}) > 1 per 100,000 inhabitants (10^{-5})	Medium
4	≥ 4	High	< 1 per 10,000 inhabitants (10^{-4}) > 1 per 10,000 inhabitants (10^{-4})	High
5			< 1 per 1000 inhabitants (10^{-3}) > 1 per 1000 inhabitants (10^{-3})	Very high

As conclusions, the results obtained in this study reported the spatial and temporal distribution of groundwater iron and manganese concentration from the Chandrapur district and analyzed the health risk assessment of these two heavy metals. At a number of sampling locations, groundwater manganese concentration was >0.4 mg/L, which was discontinued WHO standard (2011). The results highlight, in the natural aquatic environment elevated groundwater manganese concentration exists. Ballarpur and Ratnapur for iron and Naleshwar for manganese have emerged as hotspots from the district for these heavy metals into consideration. Pearson correlation coefficient revealed iron and manganese concentrations were not correlated with each other which reflect a lack of correlation between the total amount of iron and manganese in aquifer minerals. Iron distribution on WHO, JECFA and IOM recommendations revealed seasonal influence on it. Maximum sampling locations were from minimal and elevated iron concentration categories. Seasonal distribution of these two heavy metals with Indian Standard (IS 10500:2012) reported the concentration of these heavy metals is governed by percolation of precipitation through the soil, dilution of heavy metal concentration accumulated in groundwater, and dissolution of ores and minerals present in the Earth crust. The results of the study indicate no significant human health risk by chronic daily intake and non-carcinogenic hazard quotient through the ingestion of groundwater from the district. Inhabitants of this study area were under no immediate or remote health threat from ingestion of these groundwater sources. Ballarpur (HP) for iron and Naleshwar (HP) for manganese may pose a health risk in the long term to the inhabitants which need further in-depth studies and particularly on school going children. It is further recommended to initiate mitigation measures in Ballarpur and Naleshwar with an objective to reduce the concentration of these two heavy metals. It is suggested to carry out public health awareness through education, public health camps, identifying contaminated sampling locations with suitable colour coding for a sustainable environment. The study is carried out for iron and manganese in groundwater from limited identified locations. The results do not provide complete information about other locations in the district. Therefore, an extension of this study can be carried out by investigating other heavy metals from additional sampling locations from the study area. Furthermore, the effects of elevated groundwater iron concentration on women iron level in blood need to be ascertained. Health effects of groundwater manganese need to be assessed by carrying out long term exposure studies especially on children. This study

could provide a future framework for assessing and monitoring of heavy metals from the study area.

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