Oral and dermal risk assessment and statistical source identification of dissolved metals in the Subernarekha River, India.

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Abstract: *Surface waters are highly vulnerable to pollution due to their easy accessibility to the disposal of wastewaters, since river basins generally constitute areas with a high population density owing to favorable living conditions. Natural processes, such as precipitation, erosion and weathering, as well as anthropogenic influences, urban, industrial, and agricultural activities and increasing exploitation of water resources, determine the quality of surface water in a region. The study is carried out in Subernarekha River which flows through the East Singhbhum district, which is one of India's important industrialised areas known for ore mining, steel production, power generation, cement production and other related activities. Surface water samples were collected from 21 sampling sites throughout the river from its origin to mouth during pre monsoon season. The concentrations of metals were determined using inductively coupled plasma-mass spectrometry (ICP-MS) for the source apportionment and risk assessment studies. The results demonstrated that concentrations of the metals showed significant spatial variation and most variables exhibited higher levels in the locations near to industrialized and mining areas. Also, higher metal concentrations were observed in the locations in proximity to the ocean. On comparison with drinking water guidelines by WHO, 2006; US EPA, 2006 and Indian standards, there were a number of metals (Al, As, Cu, Fe, Ni and Se) with concentrations higher than the levels for drinking water in different sampling locations. Principal Component Analysis (PCA) outcome of four factors together explained 81.7% of the variance with >1 initial eigenvalue also indicated both innate and anthropogenic activities are contributing factors as source of metal profusion in Subarnarekha river. Risk of metals on human health was then evaluated using Hazard Quotients (HQ) by ingestion and dermal pathways for adult and child and it was indicated that As with $HQ_{ingestion}>1$, was the most important pollutant leading to non-carcinogenic concerns. The largest contributors to chronic risks were As, V and Co. The HQ_{dermal} of all the elements for adult and child were below unity, suggesting that the metals posed little hazards via dermal absorption indicating that the oral intake was the primary exposure pathway. The study concludes that higher values of metals in the rivers imply additional inputs from unusual geochemical enrichment, which in turn may be attributed to the geological sources coupled with anthropogenic inputs from the catchments.*

Keywords: *Subernarekha river, Metals, Risk assessment, Hazard Quotients, Source evaluation*

1. Introduction:

Surface waters are highly vulnerable to pollution due to their easy accessibility to the disposal of wastewaters, since river basins generally constitute areas with a high population density owing to favorable living conditions [1]. Natural processes, such as precipitation, erosion and weathering, as well as anthropogenic influences, urban, industrial, and agricultural activities and increasing exploitation of water resources, determine the quality of surface water in a region [2]. Identification and quantification of these sources should form an important part of managing land and water resources within a particular river catchment [3]. Simultaneously, seasonal variations in agricultural activity, storm water runoff, interflow and atmospheric deposition has strong effects on river water quality [4]. Thus, characterization of seasonal variability in surface water quality is imperative for evaluating temporal variations of river pollution from natural or anthropogenic contributions.

Heavy metals contamination is important due to their potential toxicity for the environment and human beings [5]. Some of the metals such as Cu, Fe, Mn, Ni and Zn are essential as micronutrients for the life processes in animals and plants while many other metals such as Cd, Cr, Pb and Co have no known physiological activities [6]. Metals are non-degradable and can accumulate in the human body system, causing damage to nervous system and internal organs [5]. They enter into river water from mining areas through various ways such as mine discharge, run-off, chemical weathering of rocks and soils, wet and dry fallout of atmospheric particulate matter [7] or from industrial areas via discharge of untreated industrial effluent in the river [8]. Rivers in urban areas have also been associated with water quality problems because of the practice of discharging of untreated domestic and small scale industries into the water bodies which leads to the increase in the level of metals concentration in river water [9].

Risk assessment modelling is subdivided into main four stages, i.e. hazard identification, exposure assessment, toxicity (dose–response) assessment and risk characterisation. Exposure of human being to trace metals could occur via three main pathways including direct ingestion, inhalation through mouth and nose, and dermal absorption through exposures skin. Ingestion and dermal absorption are common for water pathway [10, 11]. In order to assess exposure, it is necessary to calculate the average daily dose (ADD) of contaminant via the identified pathways. In dose–response assessment for noncarcinogens, reference doses (R_fD) are calculated and that for carcinogens, slope factors (SF) are obtained by United States Environment Protection Agency (US-EPA) Integrated Risk Information System (IRIS) database. In risk characterisation, the results of toxicity assessment calculate the risk or hazard resulting from potential exposure to chemicals via the pathways and routes of exposure determined appropriate for the source area.

In view of the above facts, the present study was taken up with the objectives of evaluating surface water quality of Subernarekha river pertaining to metals, source identification and assessment of human health risk through the ingestion and dermal absorption of the river water. This would make it possible to understand the present contamination level and plan management strategy accordingly.

2. Materials and methods:

2.1. Site description:

The study is carried out in Subernarekha River which flows through the East Singhbhum district, which is one of India's important industrialised areas known for ore mining, steel production, power generation, cement production and other related activities. The Subarnarekha River is the 8th river of India by its flow (12.37 billion m^3/year) and length. The River Subarnarekha is a rain fed river originating near Nagri village ($23^0$18’02’’N, $85^0$11’04’’E) in the Ranchi district runs through several major cities and towns such as Jamshedpur, Chaibasa, Ranchi, Bhadrak, etc. covering a distance of about 400km. It finally joins the Bay of Bengal at Kirtania port ($21^0$33’18’’N, $87^0$23’31’’E) in Orissa. Before falling in the Bay of Bengal, the river flows through Ranchi, Saraikela and East Singhbhum districts of Jharkhand, West Midnapore district of West Bengal and Balasore district of Orissa. Of its total length 269 km are in Jharkhand and 64 km in West Bengal and 62 in Orissa. The Subernarekha basin covers an area of 19,300 km^2. This area is nearly 0.6% of the total national river basin area and yields 0.4% of the country's total surface water resources.

2.2. Sampling and Analysis:

Water samples were collected from the river in 21 sites along the Subernarekha River from its origin to mouth during pre monsoon (May 2012). The sampling stations are given in Figure 1. In each site, three replicates were collected and subsequently mixed *in situ*. Water samples were collected in pre-conditioned acid-washed High density polyethylene (HDPE) containers. The samples were filtered through pre-washed 0.45 μm Millipore nitrocellulose filters. The initial portion of the filtration was discarded to clean the membrane, and the following ones destined for metal determination were acidified to pH<2 using supra pure nitric acid and then stored refrigerated in pre-cleaned HDPE bottles until analysis [12].

2.3. Determination of metals:

Concentrations of Al, As, Ba, Cr, Co, Cu, Fe, Mn, Ni, Se, Sr and V were determined in water using inductively coupled plasma-mass spectrometry (ICP-MS, Perkin Elmer Elan DRC-e.). A calibration blank and an independent calibration verification standard was analyzed every 15 samples to confirm the calibration status of the ICP-MS. Matrix interference (Blank) was <1% for all elements. Recovery rates of metals spiked in water ranged from 89% to 107%. Triplicates of samples analysis yielded relative percent differences of <5%.

2.4. Principal Component Analysis (PCA):

Principal component analysis (PCA) is a powerful pattern recognition tool that attempts to explain the variance of a large dataset of intercorrelated variables with a smaller set of independent variables [13]. PCA technique extracts the eigenvalues and eigenvectors from the covariance matrix of original variables. The Principal Components (PC) are the uncorrelated (orthogonal) variables obtained by multiplying the original correlated variables with the eigenvector, which is a list of coefficients (loadings or weightings). Thus, the PCs are weighted linear combinations of the original variables. PC provides information on the most meaningful parameters, which describe the whole data set while affording data reduction with a minimum loss of original information [1]. Factor Analysis further reduces the contribution of less significant variables obtained from PCA and the new group of variables obtained from PCA and the new group of variables known as varifactors (VF) is extracted through rotating the axis defined by PCA [1]. FA further reduces the contribution of less significant variables obtained from PCA and the new group of variables obtained from PCA and the new group of variables known as VF is extracted through rotating the axis defined by PCA.

PCA with varimax rotation of standardized component loadings were conducted for maximizing the variation among the variables under each factor, and those PCs with eigenvalue >1 were retained [4].

2.6. Risk assessment on human health:

Exposure of human being to metals could occur via three main pathways including direct ingestion, inhalation through mouth and nose, and dermal absorption through exposures skin, while ingestion and dermal absorption are common for drinking water [10, 11]. The dose received through the individual path- way considered was determined using Eqs. (1) and (2) modified from the US Environmental Protection Agency [10].

$$ADD_{ing} = (C_w \times IR \times ABS_g \times EF \times ED) / (BW \times AT) \quad \ldots\ldots (1)$$

$$ADD_{dermal} = (Cw \times SA \times K_p \times ET \times EF \times ED \times 10^{-3}) / (BW \times AT) \quad \ldots\ldots (2)$$

where ADD, average daily dose by ingestion ($ADD_{ingestion}$) and dermal absorption (ADD_{dermal}), unit in µg/kg/day; BW, bodyweight, unit in kg; EF, exposure frequency, unit in days/year; ED, exposure duration, unit in years; IR, ingestion rate, unit in l/day; ABS_{GI}, gastrointestinal absorption factor (dimensionless); C_w, average concentration of metals in water, unit in µg/l; SA, exposed skin area, unit in cm^2; K_p, dermal permeability coefficient in water, unit in cm/h; ET, exposure time, unit in h/day; AT, averaging time (days). Their values originated from the USEPA [10] except ABS_{GI} for Al, Co, Cu, Fe, Si and Sr from Rodriguez-Proteau and Grant (2005) [14]. The average value of B_w of 52 kg for Indian man [15, 16] and the average water consumption of 1.48 m^3 $year^{-1}$ by an Indian adult [17] was used for the calculations.

Risk characterization was quantified by potential non-carcinogenic risks, reflected by the hazard quotient (HQ), were estimated by comparing exposure or average intake of contaminants from each exposure route (ingestion, dermal) with the corresponding reference dose (R_fD) using Eqs. (3) and (4). If the HQ exceeds 1, there might be concern for non carcinogenic effects. To evaluate the total potential non carcinogenic risks posed by more than one pathway, the hazard index (HI) was introduced, which was the sum of the HQs from all applicable pathways. HI > 1indicated a potential for an adverse effect on human health or the necessity for further study [10].

$$\text{Hazard Quotient (HQ)} = ADD / R_fD \quad \ldots\ldots..(3)$$

$$R_fD_{dermal} = R_fD \times ABS_{GI} \quad \ldots\ldots.(4)$$

where $R_fD_{ingestion}$ originate from risk based concentration table, the USEPA, 1993 [18].

3. Results and discussion

3.1. Distribution of metals in water:

The results of the metal analysis for the study area is provided in Table 1. The average of Al, As, Ba, Cr, Co, Cu, Fe, Mn, Ni, Se, Sr and V of all the samples was found to be 64.3, 5.41, 39.8, 0.89, 0.57, 16.6, 133.8, 12.0, 25.2, 4.66, 405.6 and 14.1, respectively. High concentrations of Co, Ni and Cu is observed at Mosabani which is under the influence of copper mining. The highest concentration of Al and V was noted at the sampling location with Al industry i.e. Muri. Tatanagar which is known for its Iron and Steel Industry, recorded the highest concentration of Cr. The sampling locations near the mouth of the river are under the oceanic influence with high salinity. These locations recorded the high concentrations of Se, Sr, As and Fe.

When compared with drinking water guidelines by WHO, 2006 [19]; US EPA, 2006(a) [20] and Indian standards (IS 1993) [21] there were a number of metals (Al, As, Cu, Fe, Ni and Se) with concentrations higher than the levels for drinking water in different sampling locations.

3.3. Principal Component Analysis (PCA):

Inter-element correlation was studied in the sediment and the results of PCA are provided in the Table 2. PCA was adopted to assist the interpretation of elemental data. This powerful method allows identifying the different groups of metals that correlate and thus can be considered as having a similar behaviour and common origin [22]. The number of significant principal components is selected on the basis of Kaiser criterion with eigen value higher than 1 [23].

The Principal component analysis of sediment of Subarnarekha basin shows that the variables are correlated to four principal components in which 81.74% of the total variance is justified. The number of significant principal components is selected on the basis of Kaiser criterion with eigen value higher than 1 [23]. According to this criterion, only first four principal components are retained because the subsequent eigen values are less than 1. After Varimax rotation, four components (factors) are extracted. These components are related to the sources of the elements.

The first factor (PC1) seems to be associated to the earth's crust and the geological formation of the area. The first component with 31.14% of variance comprises of Fe, As, Se, Sr and V with high loadings.

The second component (PC2) contributes Cu, Ni and Co at 23.66%. This factor may be attributed to the mining activities of the area. Extensive Cu mining is associated with the area and may have lead to the concentration of Cu, Ni and Co. Ni and Co have been studied to be associated with Cu mining and smelting [24].

The third component (PC3) explains 13.66% of variance of our result and is associated with Al and V. This component is also attributed to the industrial source in particular the Aluminium industry. V_2O_5 is produced as a by product of the Bayers process in the Alumina production, the bauxite being one of the major sources of Vanadium with average V_2O_5 content ranging from 0.05% to 0.25%. During the production of alumina from bauxite by the Bayer's Process, by-product containing fairly high quantity of Vanadium as V_2O_5 ranging from 6% to 20% [31, 32]. Thus the waste from the industry has high concentration of Al and V.

The fourth component (PC4) explains 13.29% of variance of our result and is associated with Ba, Cr and Mn. This component seems to be arisen from anthropogenic sources; like the industrial wastes and vehicular pollution. Ba is reported to be associated with many industries like manufacture of alloys, paints, soaps, paper, rubber, glass, ceramics, television picture tubes, brick and tile refractories, plastics stabilisers, fireworks and in lubricating additives [25, 26]. Environmental pollution with various forms of Cr results from its numerous uses in the chemical industry, production of dyes, wood preservation, leather tanning, chrome plating, manufacturing of various alloys, and many other applications and products [27]. The major industrial sources for Mn can be attributed to iron-and steel-related industries, power plants and coke ovens, paper and newsprint mills, fossil fuel electric power generation, manufacturing of heating and commercial refrigeration equipment, dry-cell battery and welding industries [28].

All the three metals are also identified to be allied with vehicular pollution. Barium is present in fuel additives and in fillers, which are used in the brake linings (in the form of barite) and tyres of vehicles [29]. The wearing down of vehicular brake linings that contain asbestos and the use of catalytic converters represents vehicular source of chromium [30]. Manganese may also be released to the environment through the use of MMT as a gasoline additive [31].

3.4. Risk assessment on human health:

Table 3 presents the Hazard Quotient (HQ), Hazard Index (HI) and risk values for the oral and dermal pathways for the study area relating to adult and child. The $HQs_{ingestion}$ (hazard quotient by ingestion) of all elements except As for adult were less than 1, suggesting that these elements posed little hazard. However, $HQ_{ingestion}$ of As was more than 1 (1.35) implying that As may cause adverse health effects and potential non carcinogenic concern. The HQ_{dermal} (hazard quotient by dermal absorption) of all the elements for adult were below unity, indicated that these metals posed little hazards via dermal absorption. For child, $HQs_{ingestion}$ of As (4.67) was much higher than unity and V (0.73) was nearing unity indicating their serious health concerns. Similar to adult, HQ_{dermal} of elements for child was below unity, and the largest value was 0.046 for V. Overall, HI of As for adult and child exceeded 1, and HI of V for child was near unity. It can be concluded that the largest contributors to chronic risks were As, V, Co and Ni, while the least were Al, Fe and Ba for both the adult and child, respectively.

The risk assessment indicated that As was the most important pollutant in the Subernarekha River. Previous studies reported adverse health effects including hypertension, neuropathy, diabetes, skin lesions, and cardiovascular and cerebrovascular diseases through high arsenic intake [11]. Therefore, special attention should be paid to arsenic for local residents particularly for the sensitive children, and measures needed to be taken for sustaining the healthy aquatic ecosystem.

However, there existed uncertainties for risk characterization, which was emphasized by the USEPA and other documents [10]. Uncertainties in some methodological aspects such as water and dermal contact factor (K_p), varied exposure condition due to different age and receptor, temporal and spatial variations in contaminant concentrations could not be quantified. In addition, exposure parameters employed in the study were from the USEPA and WHO, which might not be specific to Indian conditions. However, daily water intake rate and body weight was considered from Indian reference for better estimation of the risk. Therefore, further precise risk characterization should be defined and risk assessment approaches may be modified through the investigation on the risk levels in the Subernarekha River.

4. Conclusions:

Concentrations of dissolved metals (Al, As, Ba, Cr, Co, Cu, Fe, Mn, Ni, Se, Sr and V) in the surface water of the Subernarekha River demonstrated great seasonality. Irrespective of the locations, the elemental concentrations were lower in rainy monsoon season as compared to the other seasons due to pronounced dilution effect. When compared to drinking water guidelines established by WHO, India and the US EPA, much greater attention should be paid to Al, As, Cu, Fe, Ni and Se though the concentrations were below the critical values in the monsoon season for some elements. The higher values of metals in the rivers imply additional inputs from unusual geochemical enrichment, which in turn may be attributed to the geological sources coupled with anthropogenic inputs from the catchments. PCA outcome of four factors together explained 76.9% of the variance with >1 initial eigenvalue also indicated both innate and anthropogenic activities are contributing factors as source of metal profusion in Subarnarekha river. This study has revealed that enhanced concentrations of metals are recorded near to industrial and mining establishments indicating that their concentrations have been strongly affected by anthropogenic influences. Thus, it is reasonable to conclude that the increased concentrations of metals in water of the Subarnarekha river is considerably due to direct discharge of industrial, urban and mining wastes into the river. Human risk was assessed in people exposed to metals using exposure risk assessment model indicated As was the most important pollutant causing non carcinogenic concerns, particularly for sensitive children. It can be concluded that As, V and Co were the largest contributors to chronic risks in all the seasons and the oral intake was the primary exposure pathway.

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Table 1: *Dissolved metals in pre monsoon season in Subernarekha river, India (unit: µg/l)*

Code	Location	Al	As	Ba	Cr	Co	Cu	Fe	Mn	Ni	Se	Sr	V
W-1	Nagri	1.00	0.17	52.0	0.56	0.08	1.91	48.3	1.29	1.40	0.31	21.7	0.69
W-2	Namkom	70.1	3.30	96.5	0.95	1.27	2.16	201.9	50.6	7.64	1.28	405.4	2.55
W-3	Tatisilwai	56.3	5.02	102.7	1.44	0.90	19.2	368.6	21.9	9.11	1.31	371.8	3.10
W-4	Hundru	2.58	0.92	79.2	0.57	0.09	0.30	81.2	3.25	10.6	1.37	103.0	1.46
W-5	Muri	215.3	11.5	50.8	0.57	0.18	1.20	51.9	3.45	11.6	1.24	96.9	141.9
W-6	Chandil	89.5	1.23	27.5	0.81	0.07	1.52	58.6	5.66	11.5	1.56	71.5	0.85
W-7	Barabinda	74.4	0.83	22.9	0.75	0.06	1.86	61.1	5.66	13.5	1.43	70.2	1.11
W-8	Kanderbera	85.3	1.09	23.7	0.72	0.07	6.33	60.4	5.77	15.1	1.55	71.2	1.10
W-9	Tatanagar (Sonari)	13.0	1.10	31.0	0.60	0.12	5.28	75.1	11.3	18.1	1.23	81.0	1.27
W-10	Tatanagar (Mango)	41.5	1.08	29.4	2.62	0.13	7.52	69.5	12.2	18.1	1.66	80.8	1.39
W-11	Galudih	62.9	0.78	30.5	0.78	0.16	10.4	175.1	51.0	21.6	2.27	85.7	1.44
W-12	Mosabani (u/s Sankh)	81.5	1.04	32.3	0.75	2.19	90.0	92.2	15.3	112.5	1.49	97.5	1.93
W-13	Mosabani (d/s Sankh)	92.2	1.03	31.6	0.74	3.18	94.4	85.0	12.2	123.8	1.02	97.2	1.91
W-14	Shyamsunderpur	42.9	0.86	35.9	0.84	0.16	14.5	84.9	16.1	40.2	1.16	98.7	1.71
W-15	Baharagora	80.7	1.00	32.2	0.75	0.14	7.18	74.5	5.26	15.5	1.48	91.8	2.32
W-16	Gopiballavpur	70.5	0.83	33.0	0.89	0.13	5.40	71.0	6.52	13.6	1.49	93.1	2.36
W-17	Mahapal	91.4	0.87	32.6	0.85	0.13	3.68	71.8	4.12	12.9	1.40	98.2	2.53
W-18	Sonakaniya	57.8	0.70	26.3	0.75	0.10	2.87	60.1	3.70	12.2	1.37	87.2	3.42
W-19	Jaleswar	64.2	0.75	28.6	0.86	0.10	2.98	62.5	7.64	12.0	2.29	85.3	3.25
W-20	Pontai	33.7	42.2	15.9	0.96	1.46	30.9	486.6	2.37	21.8	1.57	3025.1	60.5
W-21	Kirtania	22.7	37.5	19.9	0.87	1.36	39.5	470.0	6.95	26.0	69.4	3274.8	58.8
Average		**64.3**	**5.41**	**39.8**	**0.89**	**0.57**	**16.6**	**133.8**	**12.0**	**25.2**	**4.66**	**405.6**	**14.1**
Standard error		**9.8**	**2.6**	**5.2**	**0.1**	**0.2**	**5.9**	**29.6**	**3.0**	**7.0**	**3.2**	**200.3**	**7.4**

Table 2: *Principal component loadings (varimax normalized) for the metals in the water of Subarnarekha River*

Elements	PC1	PC2	PC3	PC4
Al	-0.230	0.085	0.901	0.032
As	0.963	0.058	0.141	-0.110
Ba	-0.105	-0.134	0.032	0.830
Cr	0.097	-0.063	-0.333	0.580
Co	0.282	0.916	0.052	0.174
Cu	0.147	0.978	0.006	-0.062
Fe	0.908	0.112	-0.106	0.288
Mn	-0.065	0.144	-0.116	0.802
Ni	-0.118	0.976	0.036	-0.109
Se	0.761	0.069	-0.090	-0.162
Sr	0.979	0.092	-0.046	-0.103
V	0.505	-0.098	0.809	-0.062
Eigenvalues	3.74	2.84	1.64	1.60
%Total variance	31.14	23.66	13.66	13.29
Cumulative variance	31.14	54.79	68.45	81.74

Table 3: *Reference dose, Hazard quotient and Hazard Index for each element in the Subernarekha river*

Metal	R_fD_{ing} (µg/kg/ day)	R_fD_{der} (µg/kg/ day)	$HQ_{ingestion}$		HQ_{dermal}		HI=∑HQs	
			Adult	**Child**	**Adult**	**Child**	**Adult**	**Child**
Al	1000	200	4.80E-03	1.66E-02	6.18E-05	1.36E-04	4.86E-03	1.68E-02
As	0.3	0.285	1.35E+00	4.67E+00	3.66E-03	8.02E-03	1.35E+00	4.68E+00
Ba	200	14	1.48E-02	5.15E-02	5.47E-04	1.20E-03	1.54E-02	5.27E-02
Cr	3	0.075	2.21E-02	7.66E-02	4.55E-03	9.98E-03	2.66E-02	8.65E-02
Co	0.3	0.06	1.43E-01	4.95E-01	7.36E-04	1.61E-03	1.43E-01	4.96E-01
Cu	40	8	3.10E-02	1.08E-01	4.00E-04	8.77E-04	3.14E-02	1.08E-01
Fe	700	140	1.43E-02	4.95E-02	1.84E-04	4.03E-04	1.45E-02	4.99E-02
Mn	24	0.96	5.22E-02	1.81E-01	3.37E-03	7.37E-03	5.56E-02	1.88E-01
Ni	20	0.8	9.40E-02	3.26E-01	1.21E-03	2.66E-03	9.52E-02	3.29E-01
Se	5	0.15	6.96E-02	2.41E-01	5.98E-03	1.31E-02	7.56E-02	2.54E-01
Sr	600	120	5.04E-02	1.75E-01	6.50E-04	1.42E-03	5.11E-02	1.76E-01
V	5	0.13	2.10E-01	7.29E-01	2.08E-02	4.57E-02	2.31E-01	7.75E-01

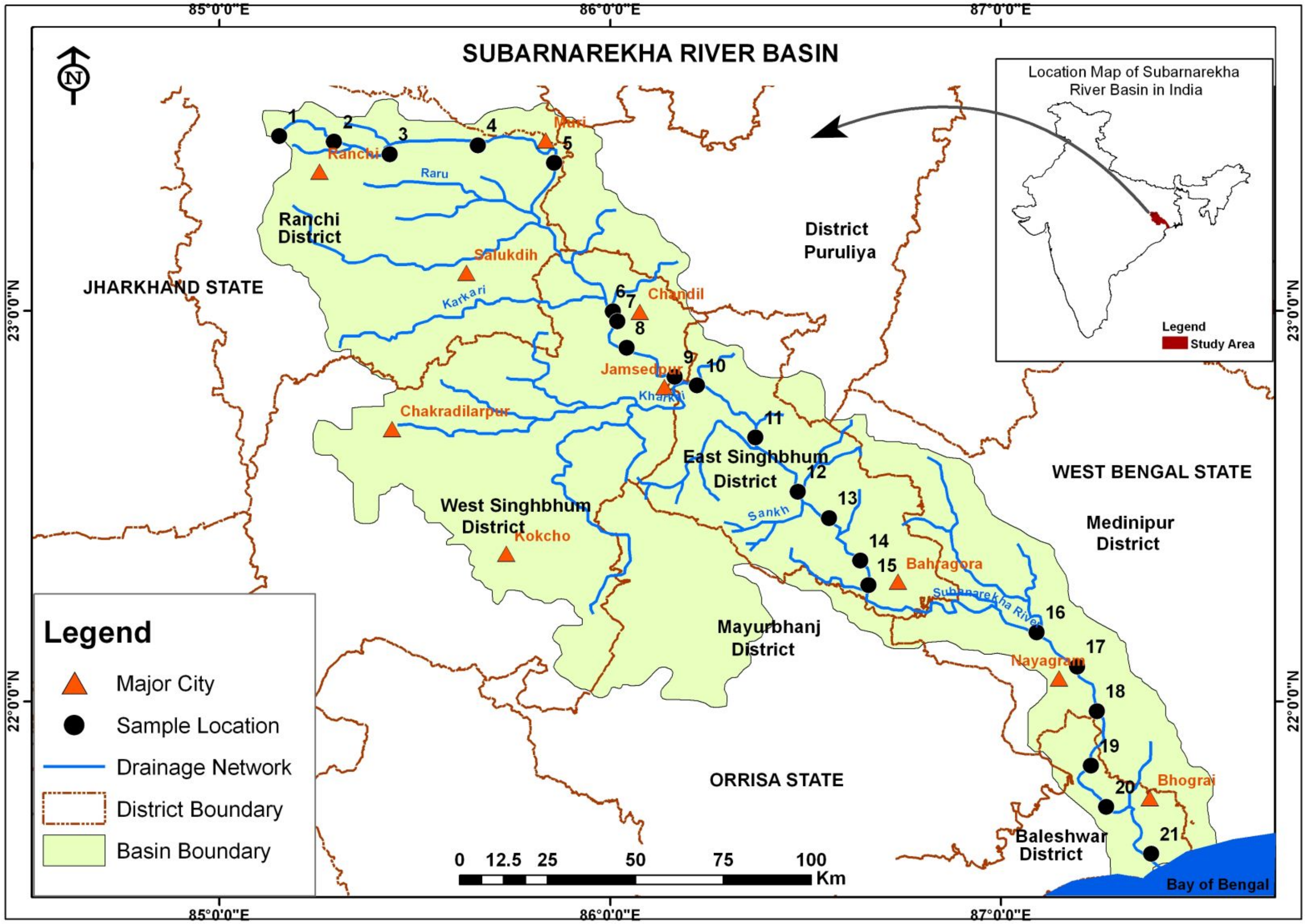

Figure 1: Map of the study area with sampling locations