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## Hydrogeochemical processes, mixing and isotope tracing in hard rock aquifers and surface waters from the Subarnarekha River Basin, (East Singhbhum District, Jharkhand State, India

Philippe Négrel, Bruno Lemièrre, Hubert Machard de Gramont, Pierre Billaud,  
B. Sengupta

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# **HYDROGEOCHEMICAL PROCESSES, MIXING AND ISOTOPE TRACING IN HARD ROCK AQUIFERS AND SURFACE WATERS FROM THE SUBARNAREKHA RIVER BASIN, (EAST SINGHBHUM DISTRICT, JHARKHAND STATE INDIA)**

PH. NÉGREL

*BRGM, BP 6009, F 45060 Orléans Cedex 2.*

e mail: [p.negrel@brgm.fr](mailto:p.negrel@brgm.fr),

B. LEMIERÈ

*BRGM, BP 6009, F 45060 Orléans Cedex 2.*

e mail: [b.lemiere@brgm.fr](mailto:b.lemiere@brgm.fr)

H. MACHARD DE GRAMMONT

*BRGM, BP 6009, F 45060 Orléans Cedex 2.*

e mail: [h.machard@brgm.fr](mailto:h.machard@brgm.fr)

P. BILLAUD

*BRGM, BP 6009, F 45060 Orléans Cedex 2.*

e mail: [p.billaud@brgm.fr](mailto:p.billaud@brgm.fr)

B. SENGUPTA

*GSI ER, New Karunamayee Building, DK VI Sector II, Bihdan Nagar, Kolkata  
700 091.*

## Abstract

The chemical and isotopic compositions of river and groundwater reflect the different natural processes that provide chemical elements to the dissolved load, i.e. mainly the weathering of rocks and soils, atmospheric inputs and anthropogenic disturbances.

This study reports on the geochemistry of surface- and groundwater along a part of the Subarnarekha River system (north-eastern India) collected during monsoon and dry season, during a monitoring program aimed at evaluating impacts of mining and metallurgy on the river system.

The aquifer is of fracture type and the seasonal behaviour, groundwater flow conditions and pollutant transfer were observed through a network of 69 wells with typical depths of 50 meters. Geochemical observations, including major cations and anions, trace element concentrations and isotopic tracing (stable isotopes of the water molecule, strontium isotopes) come to conclusions on the origin and the relationships between the surface- and groundwater in the studied catchment.

A large range of salinities is observed in surface- and groundwater, both for dry or wet periods. Surface water samples plot within the field  $\text{HCO}_3\text{-Ca}$  during both water stages. Most groundwater samples plot within the field of  $\text{Ca-SO}_4$  water type and  $\text{HCO}_3\text{-Ca}$  water type. This reflects the high Ca input in groundwater, other than weathering. Such inputs could be related to (i) carbonate amendments used in agricultural practices and (ii) residues from ore processing.

With regards to stable isotopes  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ , many groundwater samples plot between local meteoric water lines and the global meteoric water line, reflecting a meteoric origin for the water without any major transformation like evaporation. This suggests that transfer from rainfall towards groundwater storage through soils and the non-saturated zone is fast. The scatter of  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures in surface- and groundwater cannot be explained by less than 3 end-member compositions. The most dilute end-member should be compatible with rainwater inputs. The most mineralised end-member has isotopic compositions very similar to the dilute one, and is believed to represent anthropogenic inputs. The third end-member is characterised by an intermediate Sr content and a more radiogenic signature. It is believed to be controlled by a natural background, however affected by human activities (e.g. drainage of mine waste).

Potential flow paths were investigated north of the area. Under the light of different geochemical tools, all groundwater types in this area seem to evolve more as in close pockets than along a flow path. This is consistent with groundwater head contour maps that do not reflect any groundwater flow directions, as groundwater bodies evolve in discontinuous or isolated units.

The limited extent of transfer and the predominance of natural phenomena contribute to explain the moderate level of groundwater contamination and the characteristics of surface water contamination by mining and metallurgy.

Keywords: hydrochemistry, fracture type aquifer, strontium isotopes, weathering, stable isotopes

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## Introduction

The chemical and isotopic compositions of waters reflect the different natural processes that provide chemical elements to the dissolved load, i.e. mainly the weathering of rocks and soils, atmospheric inputs and anthropogenic disturbances (Drever, 1988). Detailed studies focused on the exogenic cycle of the elements were carried out on large- to medium-size river systems, including the Amazon, the Congo, the Ganga-Brahmaputra, the Indus, the Huanghe... (Sarin *et al.*, 1989; Négrel *et al.*, 1993; Pande *et al.*, 1994; Gaillardet *et al.*, 1997; Zhang *et al.*, 1990). For small catchments, the application of geochemical tools may provide constraints on runoff, on the natural and anthropogenic end-members and on their respective contributions (Ben Othmann *et al.*, 1997; Négrel and Deschamps, 1996),

In India, as in other fast developing countries, groundwater use for domestic, industrial and agricultural activities is fast growing. For example, the number of dug wells increased from around 4 up to 10 millions between 1952 and 1992 (Ballukraya and Sakthivadivel, 2002). Ground water resource use needs to be concerted. The concept of sustainable use is quantitatively related to such factors as the volume of the existing resource, its recharge and environmental impacts. From the quality point of view, sustainability implies the prevention of deterioration of ground water quality beyond acceptable limits.

Groundwater flow and storage in hard rock areas has always been a major issue for both researchers and water managers (De Silva and Weatherhead, 1997; Krishnamurthy et al., 2000; Ballukraya and Sakthivadivel, 2002) either with regards to water quantity (Gupta and Singh, 1988), water quality (Robins and Smedley, 1994) as well as delimitation of resources and aquifers (Singhal et al., 1988) and long-term sustainability (Foster et al., 2000). Pumping affects groundwater quality through salinity increase and heavy metal contamination, (Kamra et al., 2002; Singh et al., 2002).

These issues are more complex in hard rocks terranes due to strong heterogeneity and anisotropy, with irregular distribution of pathways of groundwater flow.

“Groundwater accounts for over 80 per cent of the domestic water supply (...) and 50 per cent of irrigation requirements” (Morris et al, 2003); “in weathered and fractured aquifers throughout India, shallow groundwater is widely used for small-scale irrigation and village potable supplies. Increasing abstraction from these low storage aquifers has resulted in severe seasonal water shortages in some areas.” (ibid).

This paper uses geochemistry and isotope tracing to determine groundwater characteristics in a copper-mining region located in northeastern India. Data were collected in a larger surface and groundwater as well as soil and sediment monitoring program in the vicinity of mining and metallurgical industries along with extensive agricultural use of land (Billaud et al., 2003).

This paper investigates the recent hydrogeological and hydrogeochemical conditions of the site through the isotopic composition of strontium and oxygen and hydrogen in different groundwater types collected from a network of wells. Strontium isotope ratios are used to trace the degree of water-rock interaction and mixing processes in groundwater (Négrelet et al., 2001; Négrelet and Pauwels, 2004) while stable isotopes provide an insight of the water origin (Négrelet and Lachassagne, 2000).

## **General features of the catchment**

The Subarnarekha river basin is located in north-eastern India, rising in southern Bihar state (Figure 1). The Subarnarekha river flows eastwards through the Singhbhum copper

mining region. Continuing eastwards, it enters the Bay of Bengal after a 470-kilometre course.

The selected area is about 17 km long on 7 km wide, along the Subarnarekha River, with a mean altitude of 90 m. It is located around 40 km south-east of Jamshedpur (East Singhbhum district, Jharkhand state). It is underlain by folded and fractured Precambrian metasediments, mainly mica schists, locally with quartzite and hornblende schists (Ghosh et al., 2002) and show dominant vertical fracturation (Fig. 1). Mineral resources, mainly copper (Cu) but also uranium (U), are associated with a Precambrian shear zone.

Three zones can be individualised:

- the southwesternmost zone is a hilly area belonging to the Singhbhum belt, reaching an altitude of 450 to 500 m. This area is covered by a fairly dense forest with scattered small settlements in the valleys and little paddy fields close to the settlements;
- the area comprised between the bottom of the hills and the Subarnarekha River on its right bank is a 17 km long and 1.5 km to 3.5 km wide stripe. This area is almost flat with paddy fields, small forested areas, barren land on rock outcrops, and with important settlements in relation with the Cu or U mining sites;
- the left bank of the Subarnarekha River is similar to the right bank, but it does not bear any mining activity. The Cu smelter was built close to the main agglomeration of the area (Ghatsila).

Only fissured aquifers were identified. Frequent quartzite outcrops in the river bed itself imply that alluvial formations are discontinuous and cannot host continuous alluvial aquifers.

Total annual rainfall is nearly 1300 mm, with around 300 mm per month during the monsoon season between mid-June and mid-September, and 50 mm per month between mid-September and mid-June. The temperature varies between 7°C and 36°C in winter and between 22°C and 45°C in summer. The Subarnarekha River discharge has a steep increase in response to monsoon rains (level up by 2 to 3 meters). This is enhanced because the upper catchment dams are cleared at the beginning of rains for safety.

However, monsoon rains do not cause an immediate increase in the tributaries (hereafter referred to as nallahs) flow rates, early precipitation being collected and stored in the paddy fields, or recharging the shallow aquifers.

Groundwater occurs under unconfined condition in the hard rock areas of the district. The potential aquifers comprise two units with thick weathered residuum and underlying fractured hard rock up to a depth of at least 100 m. Altered formations above metamorphic rocks usually behave as a seasonal water reservoir from which water is percolating to the fissured rock aquifer below. Areas with a thick alteration cover have better potential for groundwater than areas with exposed rock outcrops.

The altered layer is rather thin in the study area (usually less than 7 meters). Nevertheless, a large number of open dug-wells exist almost everywhere in the valley, with a typical depth of about 10 meters, with a few meters inside the fractured rock. Small diameter tube wells are also very frequent, with a typical depth of about 50 meters and usually equipped with Indian-type hand-pumps. This large number of wells shows that the area probably has a well-distributed fracturation network. However no lithological logs were available, and therefore no indication on the depth of the alteration, or on the depth of fracturation below. Water depletion in a well seems to affect little the level of the neighbouring ones, suggesting a poor interconnection of aquifers. Direct and roughly immediate correlation between rainfall events and groundwater raising is observed. Isopotential curves drawn from monthly measurements (Billaud et al., 2003) show that there is a complete recovery of the water table from one year to the other. The global water abstraction in the monitored wells, mainly for domestic uses, is not important compared to the aquifer recharge through precipitation. Annual rainfall is therefore sufficient to replenish the fissured aquifer with any excess discharging through the surface runoff network.

On the hill slopes, rice fields spreading over large areas are favourable features for the recharge of the fissured aquifer during the monsoon and the irrigation periods.

Groundwater is used mostly for domestic uses (drinking, washing, gardening), and for very limited industrial uses. Smelting and mining activities use surface water (mainly river water).

# **Geochemical sampling procedures and analytical methods**

## **Sampling strategy**

Surface water samples were collected from the river at two sites upstream and downstream of the study area, e.g. Subarnarekha Barrage and Subarnarekha Kanas. Small or medium-sized tributaries (nallahs) were also sampled over the study area and include Nallah Dhutra, Garra Nallah Barrage, Nallah Royam and Sankh Nallah. One sample was collected from a wastewater canal.

Groundwater samples were collected from tube wells used for drinking (plus one dug well). Sampling strategy was to take groundwater samples from the most used tube well in each village. This allows picking up water from a well renewed resource. Groundwater data will be grouped for detailed examination, based on the location of the wells on the right or left bank of the Subarnarekha River. This presentation is intended to highlight the possible effects of the mining activity, which is localised only on the right bank of the Subarnarekha River. The left bank is geologically similar but without any mining activity. Sampling was carried out two times, during a low water stage in February 2001 and during a higher water stage in November 2001 (Figure 1).

## **Sampling procedure and field measurements**

Master variables of each sample were measured on site, results are presented in Table 1. Electrical conductivity (EC) and water temperature were measured using a WTW conductivity meter standardised to 25°C. EC data in the water samples collected during the low water stage are scattered between low EC values (115  $\mu\text{S}/\text{cm}$ ) and higher ones (~1400  $\mu\text{S}/\text{cm}$ ). The pH was measured on site using a WTW pH-meter calibrated using standard buffers, groundwaters display pH in the range 5.60-7.25, higher values are observed in surface waters (range 7.40-9.10)

All water samples were collected in polyethylene bottles and filtered through precleaned 0.45 $\mu\text{m}$  acetate cellulose filters using a precleaned Nalgene filter apparatus. The filtrate was separated into three aliquots: 100 + 500 ml were acidified with suprapure nitric acid and stored in precleaned polyethylene bottles for major cations, trace elements analysis and strontium isotopes determination, 250 ml were stored in polyethylene bottles, unacidified, for anion determination.

## Major- and trace-element determination, stable and strontium isotopic measurements

Chemical analyses of water samples were performed by atomic absorption spectrometry (Ca, Na, K), colorimetry (Si), ion chromatography (Cl, SO<sub>4</sub>, NO<sub>3</sub>), inductively coupled plasma mass spectrometry (Mg, trace elements), HCl titration and Gran's method for HCO<sub>3</sub>. Precision was greater than ± 5% for the determination of major elements.

The deuterium and oxygen isotopic ratios are reported in per mil deviations from the international SMOW standard following  $\delta = [(R_{\text{sample}} / R_{\text{standard}}) - 1] \times 1000$  where R is the isotopic ratio of the heaviest isotope over the lighter (e.g. <sup>18</sup>O/<sup>16</sup>O). The deuterium and oxygen isotopic ratios were analyzed using a Finnigan MAT 252 mass spectrometer. The average precision, based on multiple analyses of various samples and laboratory standards was ± 0.1 ‰ for δ<sup>18</sup>O and ± 0.8 ‰ for δ<sup>2</sup>H.

The standard procedure was adopted for the chemical separation and mass spectrometry of strontium (Négre and Deschamps, 1996). After chemical separation, 1/5 of the sample was loaded onto a single tungsten filament and analysed using a Finnigan MAT 262 multiple collector mass spectrometer. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios were normalized to a <sup>86</sup>Sr/<sup>88</sup>Sr ratio of 0.1194. The overall precision of the <sup>87</sup>Sr/<sup>86</sup>Sr determination is approximately ± 10. 10<sup>-6</sup> (2σ errors). The reproducibility of <sup>87</sup>Sr/<sup>86</sup>Sr measurement was tested by duplicate analyses of the NBS 987 standard; the mean value obtained during the study was 0.710227 ± 17. 10<sup>-6</sup> (2σ, n = 70).

## Results and Discussion

### Surface- and ground waters geochemistry

#### *Chemistry of the dissolved load*

Total Dissolved Solid (TDS, mg/l, Table 1) is generally close to 300 mg/l in most surface waters, except nallah Royam (975 mg/l during the low water stage and 510 mg/l during the higher water stage). In the Subarnarekha River, the upstream sample is more saline during the higher period, whereas the downstream sample shows a similar salinity for both periods. In groundwater during the low water stage the TDS values ranged from 180 up to 1485 mg/l while during the higher water stage, the TDS ranged from 264 mg/l up to 1289 mg/l. The average TDS does not vary much between the two seasons despite the extreme discharge variations in the river ( $615 \pm 341$  mg/l and  $687 \pm 343$  mg/l, respectively)

The range of total cationic charge ( $\Sigma^+ = \text{Na}^+ + \text{K}^+ + 2 \text{Mg}^{++} + 2\text{Ca}^{++}$ , expressed in  $\mu\text{eq/l}$ ) in surface water samples is 3500  $\mu\text{eq/l}$  to 5000  $\mu\text{eq/l}$ , clearly higher than the 'world average river water' (1200  $\mu\text{eq/l}$ , Meybeck, 1979). In groundwater, the range of  $\Sigma^+$  is large, (1000 to 15000  $\mu\text{eq/l}$ , without any discrepancy between the right and left banks of the river). The charge imbalance, estimated by the Normalised Inorganic Charge Balance ( $\text{NICB} = 2\{\Sigma^- - \Sigma^+ / \Sigma^- + \Sigma^+\} * 100$ ) is within the +5/-5% admissible interval for most chemical analyses. There is no evidence of any link between the NICB and the salinity of water, represented by  $\Sigma^+$ . A minor deficit in negative charges suggests the presence of anions other than those analysed, such as organic anions.

The order of cation abundance in surface waters is  $\text{Na} > \text{Ca}$  or  $\text{Mg} > \text{K}$  during the low water stage and  $\text{Ca} > \text{Na} > \text{Mg} > \text{K}$  during the higher water stage. For anions, the order is  $\text{HCO}_3 > \text{SO}_4$  or  $\text{Cl} > \text{NO}_3$  during both the low and higher water stages. In groundwater, the order is  $\text{Na}$  or  $\text{Ca} > \text{Mg} > \text{K}$  and  $\text{HCO}_3$  or  $\text{Cl} > \text{SO}_4 > \text{NO}_3$  during both the low and higher water stages. Water types are often used in the characterisation of waters as a diagnostic tool (Leybourne et al., 1998; Pitkänen et al., 2002). Surface water samples are of the  $\text{HCO}_3\text{-Ca}$  type during both water stages, with the exception of the Royam nallah that plots within the field of  $\text{Ca-SO}_4$  water type during the low water stage, and within the field  $\text{HCO}_3\text{-Ca}$  during the higher water stage. Most groundwater samples are of  $\text{Ca-SO}_4$  water type and  $\text{HCO}_3\text{-Ca}$  water type, in agreement with the fresh and mined- water types defines by Sikdar et al. (2001) in the Quaternary aquifer of Calcutta and Howrah (India). However, two samples plot within the field  $\text{HCO}_3\text{-Na}$  (TW4052 and 4033) during the

higher water stage and their low water stage equivalents fall within the  $\text{HCO}_3\text{-Ca}$  field, reflecting a higher Ca input during the low water stage.

### ***Inter-element relationships***

The chemical composition of the surface- and ground waters is efficiently examined through binary diagrams between two chemical species X and Y expressed in  $\mu\text{mol/l}$ . The seawater dilution line is classically added to the diagram as seasalt aerosols are often a source of chemicals in the dissolved load (Krishnaswami et al., 1992; Edmond et al., 1995; Gaillardet et al., 1997). It is also generally agreed that Cl is used as reference element in such diagrams (Leybourne et al., 1998; Négrel and Pauwels, 2004; Négrel et al., 2004). Unless evaporites occur in the catchment, Cl ions do not participate in weathering reactions and thus behave conservatively through the hydrological cycle. Cl originates from rain inputs (seasalts aerosols) and human activities.

In the Na vs. Cl plot (Figure 2), the highest concentrated samples plot along the sea water dilution line while towards lower concentrations, the waters display Na enrichment generally related to silicate weathering. When plotted versus Cl in Figure 2, Ca,  $\text{SO}_4$  (and K) also display enrichments that could be partly related to silicate weathering.

Seasonal fluctuations can be best observed with individual sampling site variations of selected chemical elements (Figure 3). The upstream river sample shows a similar Cl (and Na) content during the dry and wet periods, which is not consistent with TDS variations. The downstream river sample, which shows similar TDS for both periods, shows a higher Cl content during the dry period than during the wet one. The fluctuations between wet and dry periods for the Ca and  $\text{SO}_4$  contents of surface waters suggest that the divergence in the TDS for the upstream sample is certainly due to the large increase in the Ca and  $\text{SO}_4$  contents (Figure 3). This implies that at least one specific source of these two species is predominant during the wet period, the origin of which might be from agriculture and/or ore deposits weathering and/or mining activities.

For groundwater, the Cl graph (Figure 3, in log scale) evidences some enrichment during the wet period whereas only two samples show minor Cl enrichment during the dry period. A similar evolution is observed for Na. A larger scatter of Cl (and Na) variation is thus observed in surface water samples, whereas for many groundwater samples, there is no evidence of large fluctuations in the Cl contents even during the wet period. The good correlation observed between Cl and  $\text{SO}_4$  (Figure 2) departs from the results of Leybourne et al. (1988) whom reported low Cl (0.1 – 10 mg/l) associated with high  $\text{SO}_4$  (up to 10 – 100 mg/l) on groundwater at sulphide deposits. This suggests that fertilisers may be responsible of the correlation between Cl,  $\text{SO}_4$  and Ca. Due to the absence of evaporites in the basin, part of the Cl input could be due to fertiliser application, this is

further supported by the relationship between Cl and NO<sub>3</sub>, especially with regard to the highest concentrations. As no carbonate formations were recognised in the catchment, the large Ca contents could also be derived from agricultural inputs (Figure 2 and 3). Comparing Ca and SO<sub>4</sub>, most points display a Ca/SO<sub>4</sub> mole ratio close to 1.03, lower than that of the gypsum or anhydrite dissolution. Therefore, Ca seems depleted compared to SO<sub>4</sub>, suggesting that the additional source of SO<sub>4</sub> did not provide Ca to the water. The higher Ca and SO<sub>4</sub> contents in the river sample upstream during the wet period are not accompanied by a significant increase in the NO<sub>3</sub> content. Conversely, the highest NO<sub>3</sub> content is observed during the dry period. It is therefore suggested that the source of Ca and SO<sub>4</sub> in surface waters is independent from that responsible of NO<sub>3</sub> inputs. River chemistry variations during the wet period could be explained by a large input of water with a lower salinity (and therefore a lower content in chemical elements), hence the decrease in most elements in the river. The decrease in the contents downstream by a dilution scheme involving less concentrated waters (e.g. groundwater), is supported by the chemical composition of some groundwaters, all located downstream. (e.g. Narsingharh, Patargorah and Deuli). On the other hand, during the dry period, most elements are almost constant downstream, excepted NO<sub>3</sub> that exhibits a decrease. The lack of variation seems to highlight the lack of groundwater input, and/or another influence that is not reflected by the geochemistry. This will be further investigated with the use of strontium isotopes. NO<sub>3</sub> enrichment is locally observed during the wet period, but most wells show identical values between the two periods. Much of Ca and SO<sub>4</sub> inputs in groundwater can therefore be related to agricultural practice.

## ***The carbonate system and the origin of Ca and SO<sub>4</sub>***

The carbonate system in waters can be investigated by using calcium and bicarbonate which are the dominant ions. Samples plot above and below the Ca = HCO<sub>3</sub> equivalent line (calculated in µeq/l). The fact that points fall off this line implies that both cation(s) and anion(s) are necessary to reach the balance. This could be refined by comparing Ca + Mg as a function of HCO<sub>3</sub> + SO<sub>4</sub> (Figure 4) that shows a better scatter of the points around the 1:1 line (Edmond *et al.*, 1995). This observation highlights the important role of calcium and sulphate in the Subarnarekha River system and induces that sulphate must be taken into consideration in the carbonate system equilibrium.

The PHREEQC geochemical code (Parkhurst and Appelo, 1999; available at [www.usgs.org](http://www.usgs.org)) was used to compute the saturation indices on selected groundwater samples, covering the large Ca range. The saturation indices are hereafter referred as SI, a value of zero indicates equilibrium, a positive value indicates oversaturation and a negative value undersaturation. The values obtained for the relevant solid phases were used as criteria to determine the solids likely to precipitate under the measured physico-chemical conditions. Among the main species available using PHREEQC, Table 2 summarises the SI for carbonate species (calcite and dolomite) and sulphate species (gypsum and celestite) on selected samples.

For the less Ca-concentrated samples carbonate and sulphate phases are generally undersaturated during both low and higher stages, implying that neither Ca nor SO<sub>4</sub> and Sr are controlled by solid phases. However, carbonate phases are undersaturated in one samples (Kesarpur) during the dry period (SI: -1.32 / -1.71) but surprisingly become oversaturated during the higher period (SI: 0.17 / 1/15). For the highest Ca-concentrated samples, SI values always indicate oversaturation for carbonate phases while sulphate phases are always undersaturated whatever the period is. These trends are more marked for the various species of dolomite.

With large and frequent oversaturation of carbonate phases, PHREEQC geochemical calculations confirm the large Ca and Mg contents in groundwaters, reflecting the role of the Ca and Mg source(s). However, the origin of this source remains in debate. Calcite saturation indices suggest that part of the Ca depletion compared to SO<sub>4</sub> can be linked with the precipitation of calcite; sulphate phases are never oversaturated. However, the relatively low SI with regard to calcite associated with the good linkage between Cl and Ca and the weaker linkage with SO<sub>4</sub> plead in favour of a common source for Cl and Ca and a specific one for SO<sub>4</sub>. The first source can be related to agricultural practices via fertiliser application and the second one can be related to mining activities.

## $\delta^2\text{H}$ and $\delta^{18}\text{O}$ isotopic signature and origin of the waters

The stable isotopic signature in continental waters is mainly controlled by precipitation input, evaporation and mixing processes (IAEA, 1981). In the Subarnarekha River system, stable isotopes fall in the range 0.4 to -6.0‰ for  $\delta^{18}\text{O}$  and 10.4 to -39.0‰ for  $\delta^2\text{H}$  in surface waters, including sample WW2038 which contains a wastewater component. For groundwaters, the range for  $\delta^{18}\text{O}$  is -3.3 to -6.8‰ and -28.5 to -45.5‰ for  $\delta^2\text{H}$ , including the sample DW2017 from Tentuldenga. All ranges are in accordance with values given by Stüber et al. (2003), Majumdar et al. (2005) and Gupta et al. (2005). Stable isotope measurements in water are plotted in a classical  $\delta^{18}\text{O}$  vs.  $\delta^2\text{H}$  diagram (Figure 5). The global meteoric water line (GMWL,  $\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ ) is indicated, and the GNIP Database (from the Global Network for Isotopes in Precipitation, IAEA/WMO, 2001) allows drawing four significant local meteoric water lines over India (Allahabad, Hyderabad, Schillong, and Shiliguri stations) that fall either above or below the GMWL. Many of the groundwater samples plot between the local and the global meteoric water line(s), reflecting a meteoric origin for the water without any major transformation, e.g. mainly evaporation. This suggests that the transfer from rainfall towards groundwater storage through soil and the non-saturated zone is fast, and that post-precipitation evaporation during the passage in soil is not an active process on the Subarnarekha River system. This is contrary to the observations of Majumdar et al. (2005) and Gupta et al. (2005), but in agreement with the study by Stüber et al. (2003) in West Bengal. With regard to the groundwater samples plotting along the GMWL (Figure 5), the ranges of  $^{18}\text{O}$  and  $^2\text{H}$  isotopes are narrow, e.g. from -5 to -7‰ for  $\delta^{18}\text{O}$  and -30 to -45‰ for  $\delta^2\text{H}$ . This suggests that groundwater recharge occurs during a limited period (i.e. the monsoon). Moreover, there is no evidence of stable isotopes variation with regard to the location of the samples or altitude, reflecting a similar input during the recharge period. In accordance with the monsoon system, Deshpande et al. (2003) evidenced a geographic distribution of the  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  isotopic signature in precipitations. Hence, groundwaters from southern India (Deshpande et al., 2003; Négrel et al., 2007) are strongly influenced by the different features in rain input, which is not the case in the Subarnarekha River system. Our values are depleted in heavy isotopes, like those of Gupta et al. (2005) in their study from the west to the east coast of India but further south. Gupta et al. (2005) showed an average  $\delta^{18}\text{O}$  in groundwater around  $1 \pm 1$ ‰, but a decrease in  $\delta^{18}\text{O}$  up to -7‰ towards the northeast of their zone is clearly evidenced. They related these depleted values to atmospheric inputs marked by depressions and cyclonic storms originating from the Bay of Bengal.

A few of the surface- and groundwater samples show a significant shift of more than 1‰ to the right of the GMWL. Comparison of the  $\delta^{18}\text{O}$  in the surface- and ground- waters in the Subarnarekha River system between the wet and dry periods shows that all surface waters display  $\delta^{18}\text{O}$  enrichment more marked during the dry period (Table 1). These  $^{18}\text{O}$  and  $^2\text{H}$  enrichments in surface waters may be linked to evaporation processes in soils, to evapotranspiration or sometimes to surface evaporation from the river water masses (Negrel and Lachassagne, 2000). Some of the groundwaters are also shifted on the right of the GMWL in relation with either an evaporation processes linked with a poor isolation of the tube well or to water return flow with a depleted value as illustrated by Négrelet et al. (2007) in the Maheshwaram watershed (Andhra Pradesh, India). However, most of the groundwater display similar  $\delta^{18}\text{O}$  between dry and wet periods reflecting few variations during the infiltration of recharge waters.

## **Strontium contents and Strontium isotope ratios**

### ***Variations in the concentrations and strontium isotopes***

Strontium content varies greatly in groundwater samples and less in surface water samples. The range is between 1 and 2  $\mu\text{mol/l}$  in surface waters, either in wet or dry periods. The observed range in surface water agrees with that found in rivers in the Ganga-Brahmaputra-Indus river system (Krishnaswami et al., 1992; Pande et al., 1994; Singh et al., 1998) and Himalayan rivers (Galy et al., 1999). However, Sr contents in groundwater vary by 2 order of magnitude from less than 0.4 up to 10  $\mu\text{mol/l}$  on both banks of the Subarnarekha River. Few studies deal with the Sr content and Sr isotopes in India. The Sr content in the Subarnarekha hydrosystem agrees with that found by Dowling et al. (2003) in groundwater near rivers of the Ganga- Brahmaputra floodplain in the Bengal Basin. They related the lowest values (around 1  $\mu\text{mol/l}$ ) to silicate weathering while the highest are related to carbonate inputs.

However, the fluctuations of the Sr contents in the Subarnarekha hydrosystem are correlated with those of Cl (Table 1). This relationship reflects that the source of chloride is also a potential source of Sr. On the other hand, the similar behaviour of Sr and Ca is widely recognised, due to their similar geochemical properties. The plot of Sr vs. Ca (Figure 6) shows different linear relationships, resulting from the weathering of shale, silicate and carbonate. Different Ca/Sr ratios reflect indicate the geological homogeneity of sub-watersheds draining single rock-type areas (Meybeck, 1986) as stated by Edmond et al. (1995) and Huh et al. (1998). No points in the Subarnarekha River system were found along the shales weathering line. Most points are located on the "silicate line", while some of them are scattered closer to the carbonate one, either with low or high Ca

and Sr contents. As most of the studied area is underlain by silicate rocks, the position of most points along the "silicate line" is consistent with the nature of the rocks. When comparing the Sr vs. Ca variations in some groundwater between dry and wet periods, an opposite behaviour can be observed. For example, the sample from Amdah is located on the "silicate line" during the wet period and shifts towards lower-Sr/higher-Ca during the dry period. Conversely, the sample from Sabisa plots on the "silicate line" during the dry period and shifts towards higher -Sr/ lower -Ca during the wet period.

Inasmuch as there is no carbonate outcrops, the shift of most points towards the "carbonate line" agrees and confirms Ca inputs from another source than weathering. Such Ca inputs (and therefore Sr) could be related to (i) carbonate amendments used in agriculture and (ii) residues of ore processing.

Strontium isotopes display a wide variation both in the low and high water stages from 0.71844 to 0.80518 in surface waters and from 0.719997 to 0.76866 in ground waters. The observed range in surface- and groundwater, with relatively high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios is similar to the range for rivers draining old cratons (Guyana Shield, Edmond et al., 1995; French Guiana, Négrel and Lachassagne, 2000; Lena River basin, Huh and Edmond, 1999) and for the Ganga- Brahmaputra -Indus River system (Krishnaswami et al., 1992; Pande et al., 1994; Singh et al., 1998). Similar ranges are observed in Himalayan rivers (Galy et al., 1999). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios range given by Dowling et al. (2003) in groundwater from rivers of the Ganga- Brahmaputra floodplain in the Bengal Basin are lower as water draining silicate displays  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7143 and 0.724 while that draining carbonate displays  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios between 0.7155 and 0.7273. The time evolution of strontium and its isotopes shows a good consistency between dry and wet period values as illustrated in Table 1.

### ***Mixing processes***

The Sr isotope studies of rivers and lakes have shown that variations in  $^{87}\text{Sr}/^{86}\text{Sr}$  and Sr contents are caused primarily by mixing of waters of various origins with different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Sr contents, such as mixing between different water pools, each of them possibly reflecting water-rock interaction with different rock types (Gaillardet et al., 1997; Bullen et al., 1996; Galy et al., 1999). A comparison of the  $^{87}\text{Sr}/^{86}\text{Sr}$  vs. Sr contents shows that all the water samples from the Subarnarekha River system are largely scattered either with regard to Sr isotope and Sr contents. It is worth noting that (i) the large variation in the Sr contents corresponds to a relatively restricted range of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and (ii) the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios correspond to relatively low Sr contents. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vs.  $1/\text{Sr}$  diagram (Figure 7) is classically used to evaluate two-component mixing and end-member water compositions. The  $1/\text{Sr}$  logarithmic scale

is used for easier viewing (Négrel et al., 2001; Négrel and Casanova, 2005). The samples are scattered amongst 3 directions that suggest the existence of at least 3 end-member compositions (Hogan et al., 2000). The most dilute end-member should be compatible with the rainwater inputs (hereafter referred to as rainwater) which characteristics are usually  $^{87}\text{Sr}/^{86}\text{Sr}$  close to 0.720, Sr content around 0.1  $\mu\text{mol/l}$ . The most mineralized end-member has very similar isotopic compositions, and Sr concentrations around 100  $\mu\text{mol/l}$ . It is believed to represent anthropogenic inputs, mainly agricultural in origin. The third end-member is characterized by a Sr content around 1  $\mu\text{mol/l}$  and a more radiogenic signature ( $^{87}\text{Sr}/^{86}\text{Sr} > 0.760$ ). This end-member is represented by Royam nallah, which drains a large area of mines tailings. This very high  $^{87}\text{Sr}/^{86}\text{Sr}$  reflects the weathering of the Rb-rich minerals which are enriched in the tailings. This end-member reflects a natural background component, though enhanced by human activities.

Comparing the Sr isotope ratios and the chloride contents argues further in favour of these three end-members. Rainwater inputs display the lowest Cl contents while anthropogenic inputs shows the highest Cl contents, and the natural background has a low Cl content (around 100  $\mu\text{mol/l}$ ). These three end-members can also be observed by comparing Sr and  $\text{SO}_4$  contents,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and  $\text{SO}_4$  and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and Ca contents (all not shown).

In the case of water mixing, the mixture of two or more components and the end-member water compositions can be evaluated with the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios vs.  $1/\text{Sr}$  diagram (Faure, 1986; Hogan et al., 2000; Grosbois et al., 2001). In the case of a multi-end member mix, several linear mixing lines have to be considered, and the main difficulty is the identification of the different end members (Négrel and Pauwels, 2004; Négrel and Casanova, 2005). The isotope systematics of two-component mixtures, described in detail by Faure (1986), can be expressed as follows:

$$^{87}\text{Sr}/^{86}\text{Sr}_m \times [\text{Sr}]_m = \alpha (^{87}\text{Sr}/^{86}\text{Sr}_1 \times [\text{Sr}]_1) + (1-\alpha) (^{87}\text{Sr}/^{86}\text{Sr}_2 \times [\text{Sr}]_2) \quad (1)$$

where  $^{87}\text{Sr}/^{86}\text{Sr}_m$  is the measured isotopic ratio in the mixture,  $^{87}\text{Sr}/^{86}\text{Sr}_1$ ,  $^{87}\text{Sr}/^{86}\text{Sr}_2$  represent the isotopic ratios of the first and second end member, respectively.  $[\text{Sr}]_m$ ,  $[\text{Sr}]_1$ ,  $[\text{Sr}]_2$  are the Sr content of the mixture, and of the first and second end members, respectively. The mixing parameter  $\alpha$  derived from equation (1) is represented by

$$\frac{\text{Sr}_1}{\text{Sr}_1 + \text{Sr}_2} \text{ and } 1 - \alpha \text{ by } \frac{\text{Sr}_2}{\text{Sr}_1 + \text{Sr}_2}; \quad \alpha \text{ represents the proportion of the two components}$$

in the mixture.

Different mixing trends exist between the end-members in Figure 7. The application of equation (1) allows the calculation of the mixing curves RW-NAT1 and RW-NAT2 on

Figure 7 which end-members are rainwater ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.720$ ;  $\text{Sr} = 0.1\ \mu\text{mol/l}$ ) and the two natural backgrounds NAT1, represented by Royam nallah ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.80518$ ;  $\text{Sr} = 1\ \mu\text{mol/l}$ ) and NAT2 ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.77354$ ;  $\text{Sr}$  content =  $1\ \mu\text{mol/l}$ ).

The application of equation (1) allows the calculation of the second mixing curve RW-ANT on Figure 7 which end-members are rainwater ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.720$ ;  $\text{Sr} = 0.1\ \mu\text{mol/l}$ ) and the anthropogenic end-member ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.720$ ;  $\text{Sr} = 30\ \mu\text{mol/l}$ ), as well as that of the third mixing curves ANT-NAT1 and ANT-NAT2 on Figure 7 which end-members are the anthropogenic end-member ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.720$ ;  $\text{Sr}$  content =  $30\ \mu\text{mol/l}$ ) and the two natural backgrounds NAT1 and NAT2.

Considering the mixing diagram in Figure 7, it is worth noting that sample(s) lies directly on a mixing line reflecting binary mixing (one groundwater sample lying on the mixing lines RW-NAT2 and other samples on the mixing line RW-ANT). All other samples are located between the mixing lines, reflecting inputs from all end-members.

## Groundwater circulation, existence of flow paths?

According to the piezometric levels, some areas can be focussed on for flow path investigations. Within the studied catchment, the most probable flow path area, located north, including Kesarpur, Bagalkora, Jarisa and Galudih wells, can be further detailed. Figure 8 summarises the chemical indicators for the dry and wet periods with regards to their evolution along the suggested flowpath. The piezometric levels indicated a possible flowpath as indicated on the map in Figure 8. Along this possible flowpath, the chloride contents display a similar behaviour both between the samples and between the dry and wet period. The Cl contents fluctuate between 280 and 680  $\mu\text{mol/l}$  in Kesarpur, Bagalkora and Jarisa and a larger value (up to 2200-2600  $\mu\text{mol/l}$ ) is observed in Galudih. The large increase in solutes in the Galudih samples, both during the dry and wet periods suggests anthropogenic inputs, along with the increased nitrate contents (not shown). Na displays a roughly similar behaviour to Cl (not shown). Sulphate contents seem to increase regularly from Kesarpur up to Galudih, whatever the period is.  $\text{SO}_4$  contents, as well as numerous other chemical indicators not shown in Figure 8 (e.g. K,  $\text{HCO}_3$ , ...), do not show variations between dry and wet periods. Mg and Ca contents show similar trends to Cl, but with a supplementary increase in the Bagalkora samples. Sr contents display the same trend along the possible flowpath as Ca and/or Mg, that is to say an increase in the Bagalkora samples compared to Kesarpur and Jarisa and a large increase in the Galudih samples, and very few differences between the dry and wet periods. Regarding the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, several features can be pointed out. First, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is identical for Kesarpur samples during the dry and wet periods, close to 0.720. This is also observed in Galudih samples, but the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is higher (e.g.

0.724) than in Kesarpur samples. This reflects for Kesarpur a large homogeneity for the water resource, both for meteoric inputs and for water-rock interactions (i.e. no variations between dry and wet periods). For Galudih, this is true for meteoric inputs and for water-rock interactions, but also for anthropogenic activities. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios differ in Bagalkora and Jarisa samples between the dry and wet periods, the wet period ratio being higher. Overall,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios increase from Kesarpur up to Jarisa, and therefore decrease up to Galudih.

As discussed previously on Figure 8 with further evidence on Figure 9 ( $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $1/\text{Sr}$  ratios), Sr isotopes and Sr contents in Kesarpur and Galudih samples have similar values in dry and wet periods, which is not the case at Jarisa and Bagalkora. In Bagalkora, the main variation is an increase of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio during the higher water stage, while Sr remained similar. In Jarisa, the main variations are a decrease of the Sr content during the higher water stage, together with a slight but significant increase of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. The increase of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios showed in Figure 8 between Kesarpur and Jarisa is not supported by a binary mixing trend between two end-members, as illustrated in the plot  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $1/\text{Sr}$  ratios by the lack of any linear relationship (Figure 9). This suggests that all groundwaters evolved more as in close pockets than along a flow path. This could be related to a possible over exploitation of groundwater resources in hard rock aquifers. The shallower part of the aquifer is increasingly desaturated due to the large exploitation of groundwater resources for domestic, agricultural and mining activities, leading to the formation of exploited groundwater pockets. This can easily be related to the heterogeneous and anisotropic fractured rock aquifer system characteristics, in which flow is very significantly influenced by the fracture characteristics (Gupta and Singh, 1988; Neretnieks, 2002; Talbot et al., 2003).

## Conclusions

This study reports on the geochemistry of surface- and groundwaters along the Subarnarekha River system in the vicinity of the Singhbhum mining district, distinguishing between dry and wet seasons (low and high stages). The dedicated geochemical tools included major cations and anions, traces elements concentrations and isotopic tracing (stable isotopes of the water molecule, strontium isotopes) and this study comes to the following conclusions on the origin and the relationships between surface- and groundwaters in the studied catchment.

A large range of salinities in surface- and groundwaters was observed in the system, both for dry or wet periods. On a TDS (mg/l) vs. Na/Na+Ca diagram, data from both surveys plot between the evaporation-crystallisation dominance and rock dominance fields, suggesting fluctuations between low-salinity and high-salinity water types.

Water characterisation can be done by using ternary diagrams. Surface water samples plot within the field  $\text{HCO}_3\text{-Ca}$  during both water stages. Most groundwater samples plot within the field of  $\text{Ca-SO}_4$  water type and  $\text{HCO}_3\text{-Ca}$  water type. This reflects the high Ca input in groundwaters.

In X vs. Cl diagrams (X being major ions), the most concentrated samples plot along the sea water dilution line while at lower concentrations water samples display enrichment, generally related to silicate weathering. However, in the absence of any evaporites, part of the Cl could come from fertiliser application, inducing part of the major ions vs Cl relationships.

With regards to stable isotopes of the water molecule ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ), many of the groundwater samples plot between the local meteoric water lines and the global meteoric water line, reflecting a meteoric origin for the water without any major transformation, e.g. mainly evaporation. This suggests a rapid transfer from rainfall towards groundwater through soils and the non-saturated zone.

Sr and Ca show different linear relationships resulting from the weathering of shale, silicate and carbonate. No sample of the Subarnarekha River system plotted along the line reflecting the weathering of shales. Most points are located closer to the "silicate line" with some of them being scattered towards the carbonate one, either with low or high Ca and Sr contents. Inasmuch as there is no carbonate outcrops, the shift of most points towards the "carbonate line" should reflect another source of Ca inputs than weathering. Such Ca inputs (and therefore Sr) could be related to (i) carbonate amendments used in agricultural practice or (ii) residues of mining treatment.

The scatter of  $^{87}\text{Sr}/^{86}\text{Sr}$  signatures needs to be explained by at least 3 end-member compositions. The most dilute end-member should be compatible with rainwater inputs. The most mineralised end-member has isotopic compositions very similar to the dilute one and is believed to represent anthropogenic inputs. The third end-member is characterised by an intermediate Sr content and a more radiogenic signature. It represents a natural background, but modified by human activities (e.g. drainage of tailings). Potential flow paths were investigated north of the area. In the scope of the different geochemical tools used, all groundwaters in this area seem to evolve more as in close pockets than along a flow path.

These observations on groundwater and recharge explain the limited extent and irregularity of groundwater contamination. Groundwater plays a minor part in pollutant transfer. The observations on surface water chemistry show clearly the influence of human activities, but also the predominance of natural phenomena (mineral weathering and monsoon regime). The role of mining and metallurgy can be observed in sulphate and Sr behaviour, but it is not clearly greater than the role of agriculture.

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## Figure Captions

Figure 1 General setting of the studied site in the Subarnarekha River system

Figure 2. Plot of major ions (Na, Ca, K, SO<sub>4</sub> and NO<sub>3</sub>, all in μmol/l) vs. chloride contents from the Subarnarekha River system. Note that contents are represented in log scale for better viewing.

Figure 3. Plot of Ca + Mg vs. HCO<sub>3</sub> + SO<sub>4</sub> (in μeq/l). The 1 : 1 line is calculated in μeq/l.

Figure 4. Plot of Cl, Ca and SO<sub>4</sub> contents (expressed in μmol/l) between the dry and wet periods for surface- and groundwaters in the Subarnarekha River system. The Cl contents scale is expressed in logarithmic units for the groundwaters for easier viewing.

Figure 5. Plot of the δ<sup>18</sup>O vs. the δ<sup>2</sup>H in rainwater (data are from the IAEA/WMO, 2001) and in the Subarnarekha River system. GMWL corresponds to the global meteoric water line (δ<sup>2</sup>H = 8 δ<sup>18</sup>O + 10).

Figure 6. Plot of strontium vs. calcium contents (expressed in μmol/l) in the the Subarnarekha River system. The dashed lines correspond to the weathering of shales, silicate and carbonate, respectively.

Figure 7. Plot of <sup>87</sup>Sr/<sup>86</sup>Sr vs. 1/Sr (Sr concentration expressed in μmol/l) for the surface- and ground- waters samples during dry and wet periods in the Subarnarekha River system. The 1/Sr scale is reported in logarithmic units for easier viewing. Curves represent calculated mixing lines according to equation 1 (see text).

Figure 8. Plot of selected chemical indicators (Cl, Ca, SO<sub>4</sub>, Sr, μmol/l) and Sr isotopes for the ground- waters samples during dry and wet periods in the supposed flowpath between Kesarpur and Galudih (North of the Subarnarekha River system).

Figure 9. Plot of  $^{87}\text{Sr}/^{86}\text{Sr}$  vs.  $1/\text{Sr}$  contents (Sr concentration expressed in  $\mu\text{mol/l}$ ) for the ground- waters samples during dry and wet periods in the supposed flowpath between Kesarpur and Galudih (North of the Subarnarekha River system).

Table 1. Results of the master variables (EC in  $\mu\text{S/cm}$ , T in  $^{\circ}\text{C}$ , pH), TDS (in  $\text{mg/l}$ , calculated by summing cation and anion contents), major ions (in  $\mu\text{mol/l}$ ), total cationic and anionic charge (in  $\mu\text{eq/l}$ ), Normalised Inorganic Charge Balance (NICB), Sr contents, (expressed in  $\mu\text{mol/l}$ ), Sr isotope values ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios) and stable isotopes of the water molecule ( $\delta^{18}\text{O}$  and  $\delta^2\text{H}$ ) of water samples from the aquifers and surface waters from the Subarnarekha river basin. Samples SW refer to surface water, TW refer to groundwater collected by tubewells, DW refer to groundwater collected by dugwell. Low water stage corresponded to February 2001 and high water stage to November 2001.

Table 2. Saturation indices on selected samples from the aquifers from the Subarnarekha river basin.

Location	ID Code	C µS/cm (25°C)	T (°C)	pH	TDS mg/l	Ca µmol/l	Mg µmol/l	Na µmol/l	K µmol/l	HCO <sub>3</sub> µmol/l	Cl µmol/l	NO <sub>3</sub> µmol/l	SO <sub>4</sub> µmol/l	Σ+ µeq/l	Σ- µeq/l	NICB %	Sr µmol/l	<sup>87</sup> Sr/ <sup>86</sup> Sr	δ <sup>2</sup> H ‰ SMOw	δ <sup>18</sup> O ‰ SMOw
<b>Low water stage</b>																				
<i>Surface water</i>																				
Nallah Dhutra	SW/2001	310	20.7	8.75	298	495	576	1348	23	3230	197	ld	40	3514	3506	-0.225602	1.27	0.71836	-10.4	0.4
Gara Nala Barrage	SW/2002	365	21	7.87	305	678	630	1288	84	2869	417	ld	326	3986	3937	-1.237254	1.44	0.72341	-24.8	-2.5
Nallah Royat	SW/2003	500	22.6	7.4	975	1140	1016	513	171	1082	192	8	1883	4998	5048	1.0142618	1.32	0.80518	-37.7	-5.4
Subarnarekha Barrage	SW/2008	340	21.5	9.13	276	760	362	1140	123	1885	701	208	332	3507	3459	-1.379909	1.22	0.72544	-27.2	-3.1
Subarnarekha Kanas	SW/2009	340	21.7	8.52	255	768	379	1131	128	1885	679	85	385	3551	3420	-3.769271	1.23	0.72530	-26.6	-2.9
Nallah Nala	SW/2023	345	21.9	8.02	334	913	695	739	54	3590	231	ld	58	4009	3938	-1.797245	1.32	0.71844	-21.5	-2
<i>Groundwater</i>																				
Kanikola	Tw/2004	210	28.2	6.46	304	338	148	1292	38	2016	152	61	21	2302	2271	-1.31669	0.84	0.73318	-40	-5.8
Baheradih	Tw/2005	270	28.2	6.44	379	703	259	1100	26	1984	462	94	54	3050	2647	-14.12079	1.88	0.72930	-35.5	-5.2
Pathargorah Camp GSI	Tw/2013	325	25.5	6.68	436	560	346	1366	90	2639	485	ld	83	3267	3290	0.7217059	1.03	0.76866	-39.1	-5.8
Deuli	Tw/2022	535	28.2	6.83	643	1813	424	1318	31	5525	223	53	104	5821	6008	3.1627804	1.84	0.72605	-42.8	-6.2
Benasol	Tw/2024	875	28	5.93	1050	1903	658	2445	38	1230	4254	1273	347	7605	7449	-2.074461	4.83	0.72858	-34.1	-5
Surda	Tw/2025	240	28	6.47	294	573	329	513	18	2148	310	8	41	2335	2547	8.6873264	1.14	0.75150	-41.7	-6.2
Kumirmuri	Tw/2026	880	27.5	7.03	1004	2493	609	3249	33	7770	1031	8	510	9486	9829	3.5591103	4.38	0.72766	-34	-5
Sohada	Tw/2027	675	27.6	6.81	724	963	387	4093	15	5115	541	ld	700	6807	7056	3.594115	2.68	0.73448	-33.2	-4.9
Kendadih	Tw/2028	1125	27.8	6.28	1495	2600	988	3589	41	3475	5099	73	803	10805	10253	-5.237959	6.69	0.73575	-38.7	-5.6
Upper Royam	Tw/2029	420	29	6.49	397	1165	218	1135	15	2197	969	518	176	3917	4035	2.9768205	2.00	0.73471	-30.2	-4.5
Mosabani	Tw/2037	765	27.5	7.12	853	1518	1947	1196	240	8066	439	ld	211	8365	8927	6.510514	2.48	0.75221	-29.5	-4
Sundarkanali	Tw/2006	230	27.8	6.17	269	568	235	757	43	1738	358	85	72	2404	2325	-3.380384	1.53	0.72836	-44.4	-6.4
Deuli	Tw/2007	520	26.3	6.92	566	1643	749	1122	31	4328	577	113	327	5936	5672	-4.551114	1.94	0.72008	-30.6	-4.2
Sabisa	Tw/2010	1085	27.6	6.45	1059	2825	1053	2897	128	4393	5099	68	310	10782	10180	-5.742092	7.50	0.73807	-39.2	-5.9
Derang	Tw/2011	680	27.9	6.82	833	1948	877	1592	87	4066	1938	247	330	7327	6910	-5.856987	3.49	0.73810	-35.9	-5.4
Amdah	Tw/2012	1005	28.2	6.98	795	3475	1132	1653	77	5344	3183	508	575	10943	10186	-7.162408	7.42	0.73018	-38.6	-5.7
Narsingharh	Tw/2014	195	27.4	6.68	250	578	296	361	79	2098	39	6	5	2188	2155	-1.531277	1.61	0.73034	-37.4	-5.6
Doba	Tw/2015	490	27.4	6.3	645	1130	477	1562	51	1770	1972	458	145	4827	4490	-7.25038	2.77	0.73261	-41	-6
Tentuldanga	Tw/2016	1420	27.3	6.57	1485	4200	1420	3789	61	4934	6169	556	1134	15089	13928	-8.002857	8.70	0.72695	-35	-5.3
Kesarpur	Tw/2018	230	27.7	6.6	394	473	255	892	33	2164	341	ld	3	2380	2511	5.3481124	1.39	0.72000	-38.2	-5.7
Bagalkora	Tw/2019	340	27.8	6.49	639	895	383	970	56	2803	569	ld	41	3582	3453	-3.645322	1.99	0.72912	-40.3	-6.2
Jarisa	Tw/2020	115	27	5.63	178	183	107	448	26	541	279	218	26	1053	1090	3.4580847	0.38	0.73168	-41.3	-6.1
Bankaikotcha	Tw/2030	300	26.3	6.7	414	538	794	387		3180	54	ld	4	3051	3242	6.0886152	0.86	0.72342	-45.5	-6.8
Kharoti	Tw/2031	340	26.8	6.6	460	783	420	1279	43	3443	417	ld	36	3727	3932	5.3677862	2.35	0.72941	-28.6	-4
Gopalpara	Tw/2032	345	26.3	6.92	295	858	329	966	31	1934	662	95	373	3370	3437	1.9644096	2.16	0.72506	-28.5	-3.3
Moubandha	Tw/2033	390	27.4	6.79	508	953	391	1005	28	2475	997	208	82	3720	3845	3.315881	2.61	0.72498	-37.7	-5.3
Kapajora	Tw/2034	495	28.1	6.58	503	893	239	2427		2148	1890	40	288	4690	4654	-0.749599	2.15	0.72578	-28.9	-4.3
Paitalpur	Tw/2035	595	28.1	6.51	531	1280	383	2271	10	2344	2541	87	287	5606	5547	-1.068947	3.66	0.72423	-37.6	-5.5
Galudih	Tw/2036	570	28.2	6.28	479	1188	498	1896	51	1639	2217	705	341	5319	5244	-1.416478	3.57	0.72417	-35.6	-5.4
Tentuldanga	DW/2017	2630	23.5	7.6	1578	3350	3082	1135	1307	3443	14535	240	3039	25307	24295	-4.078996	6.98	0.73220	-37.4	-5.3
Mouth of waste canal	W/2038	515	23.5	8.08	376	920	527	1622	279	2410	946	250	606	4795	4818	0.4751921	1.44	0.75012	-23.5	-2.2

Location	ID Code	C μS/cm (25°C)	T (°C)	pH	TDS mg/l	Ca μmol/l	Mg μmol/l	Na μmol/l	K μmol/l	HCO <sub>3</sub> μmol/l	Cl μmol/l	NO <sub>3</sub> μmol/l	SO <sub>4</sub> μmol/l	Σ+ μeq/l	Σ- μeq/l	NICB %	Sr μmol/l	<sup>87</sup> Sr/ <sup>86</sup> Sr	δ <sup>2</sup> H ‰ SMOW	δ <sup>18</sup> O ‰ SMOW
<b>High water stage</b>																				
<i>Surface water</i>																				
Nallah Dhutra	Sw/4044	333	26.1	8.24	332	763	621	887	20	3623	135	0	26	3676	3810	3.5958836	1.57	0.71866	-27	-3.5
Gara Nallah Barrage	Sw/4045	408	27	8.03	293	750	551	835	51	3082	217	0	128	3489	3555	1.8646914	1.50	0.72208	-29.1	-3.9
Nallah Royam	Sw/4046	324	26.3	7.5	512	695	753	352	84	1803	130	5	747	3333	3432	2.9290359	0.89	0.77354	-39	-6
Subarnarekha Barrage	Sw/4047	491	27.1	8.12	431	1315	539	1227	79	2770	676	48	853	5014	5201	3.6688543	1.80	0.72785	-29.6	-4
Subarnarekha Kanas	Sw/4037	280	27.1	8.18	238	688	379	705	72	2344	299	35	164	2908	3007	3.3367461	1.26	0.72340	-31.2	-4.3
<i>Groundwater</i>																				
Pathargorah Camp GSI	Tw/4034	125	28.6	6.89	459	300	165	618	56	1459	203	5	0	1603	1667	3.885727	0.37	0.75608	-38	-6.1
Deuli	Tw/4033	710	28.5	7.18	708	1335	535	4050	66	7656	245	0	132	7856	8165	3.8583273	2.97	0.72513	-32.9	-5
Benasol	Tw/4051	1100	27.1	5.85	1289	2575	909	2853	54	1131	6479	1353	539	9876	10041	1.6592301	7.08	0.72685	-34.2	-5.4
Surda	Tw/4049	240	28	6.5	322	528	366	483	41	1738	614	16	71	2311	2509	8.2223996	1.07	0.74282	-39.5	-6.2
Kendadih	Tw/4048	820	28.2	6.57	1209	1648	564	2893	64	2082	3746	197	772	7379	7569	2.5470409	4.30	0.73859	-31.6	-5.1
Mosabani	Tw/4050	690	28	7.25	863	1708	1337	1301	95	5836	1076	39	258	7485	7467	-0.242523	2.81	0.71839	-30.3	-4.4
Deuli	Tw/4041	910	27.9	6.98	1038	2403	1337	1831	38	5803	2293	377	597	9349	9668	3.3521708	3.72	0.71999	-30.3	-4.5
Sabisa	Tw/4038	1100	28.8	6.15	1113	2550	975	2962	128	4213	5521	50	369	10141	10523	3.7012068	8.33	0.73752	-37.1	-6.1
Amdah	Tw/4035	1010	28	7.01	785	3225	1049	1553	84	4918	3465	655	637	10186	10311	1.2227925	8.78	0.72986	-37.9	-5.9
Narsingharh	Tw/4036	220	28.2	6.82	264	578	296	361	79	2246	62	8	10	2188	2337	6.5793615	1.85	0.73013	-35.7	-5.8
Kesarpur	Tw/4039	235	28.4	6.57	402	440	235	857	28	1885	583	11	5	2234	2490	10.832621	1.61	0.72005	-37.8	-5.8
Bagalkora	Tw/4040	320	29.8	6.41	528	688	230	857	38	2197	676	3	37	2731	2951	7.7352755	1.61	0.72524	-38.6	-6.1
Jarisa	Tw/4052	250	27.8	6.31	352	343	49	800	36	1000	659	3	14	1620	1689	4.2012327	0.75	0.72866	-37.1	-6
Paitalpur	Tw/4043	550	28	6.42	468	1175	362	1992	33	2148	2470	137	268	5100	5292	3.70108	3.65	0.72389	-37.7	-5.8
Galudih	Tw/4042	625	28.9	7.06	507	1158	506	1918	64	1836	2572	834	361	5310	5964	11.609983	3.86	0.72395	-36.2	-5.7

Table 1

mineral	formula	TW	TW	TW	TW	TW	TW	TW	DW	TW	TW
		2022	4033	2018	4039	2012	4035	2016	2017	2020	4052
		Deuli	Deuli	Kesarpur	Kesarpur	Amdah	Amdah	Tentuldenga	Tentuldenga	Jarisa	Jarisa
		DRY	WET	DRY	WET	DRY	WET	DRY	DRY	DRY	WET
Calcite	(CaCO <sub>3</sub> )	-0.17	0.17	-1.32	0.17	0.19	0.15	-0.22	0.43	-3.26	-2.22
Dolomite	(CaMg(CO <sub>3</sub> ) <sub>2</sub> )	0.22	1.14	-1.71	1.14	1.09	1.01	0.28	2.00	-5.57	-4.09
Dolomite-ord	(CaMg(CO <sub>3</sub> ) <sub>2</sub> )	0.23	1.15	-1.70	1.15	1.10	1.02	0.29	2.01	-5.56	-4.08
Gypsum	CaSO <sub>4</sub> :2H <sub>2</sub> O	-3.08	-3.14	-5.03	-3.14	-2.19	-2.17	-1.88	-1.65	-4.45	-4.66
Celestite	(SrSO <sub>4</sub> )	-4.86	-4.57	-6.35	-4.57	-3.65	-3.52	-3.36	-3.15	-5.95	-6.13

Table 2