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Re: **Hydrogeology Journal DOI 10.1007/s10040-007-0227-4**
Hydrogeochemical processes, mixing and isotope tracing in hard rock aquifers and surface waters from the Subarnarekha River Basin, (east Singhbhum District, Jharkhand State, India)
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43	Schedule	Received	11 January 2006
44		Revised	
45		Accepted	20 September 2007

46 Abstract

Geochemical observations, including major ion and trace element analysis, and isotopic tracing have been carried out in the Subarnarekha River system (northeastern India) during a surface-water- and groundwater-monitoring program aimed at evaluating impacts of mining. The aquifer is of fracture type. Groundwater flow conditions and pollutant transfer were observed through a network of 69 wells. $\delta^{18}O$ and $\delta^{2}H$ results suggest that transfer from rainfall towards groundwater storage through soils and the unsaturated zone is fast, without any major transformation like evaporation. The scatter of $^{87}Sr/^{86}Sr$ signatures in surface water and groundwater are explained by three end-members. One is compatible with rainwater inputs. The most mineralised end-member represents anthropogenic inputs (agricultural practices and ore processing). The third end-member, characterised by a high $^{87}Sr/^{86}Sr$ signature, is believed to be controlled by natural geochemical processes, although affected by human activities (e.g. drainage of mine waste). Potential flow paths, investigated north of the area, reveal that all groundwater types seem to evolve more in pockets than along a flow path. The limited extent of transfer and the predominance of natural phenomena help to explain the moderate level of groundwater contamination and the characteristics of surface water contamination by mining and the metallurgy industry.

Résumé: Des études géochimiques dont une analyse des ions majeurs et des éléments en trace, ainsi qu'un traçage isotopique, ont été effectuées sur le système de la rivière Subarnarekha (au nord-est de l'Inde) lors d'un programme de surveillance des eaux de surface et souterraines dont le but était d'évaluer les impacts liés à l'activité minière. L'aquifère est de type aquifère fracturé. Les conditions d'écoulement des eaux souterraines et le transfert de polluant ont été étudiés grâce à un réseau de 69 puits. Les valeurs de $\delta^{18}O$ et $\delta^{2}H$ suggèrent un transfert rapide de la pluie vers la ressource en eau souterraine à travers les sols et la zone non-saturée, sans aucune transformation majeure telle que l'évaporation. La distribution des signatures $^{87}Sr/^{86}Sr$ dans les eaux de surface et souterraines est expliquée par trois pôles. L'un est compatible avec le signal d'entrée des eaux de pluie. Le pôle le plus minéralisé représente le signal d'entrée anthropique (pratiques agricoles et traitements des minerais). Le troisième pôle, caractérisé par une signature de $^{87}Sr/^{86}Sr$ élevée, est supposé être contrôlé par des processus géochimiques naturels, bien qu'affectés par des activités humaines (le drainage de déchets miniers par exemple). Les trajectoires d'écoulement potentiel, étudiées dans le nord de la zone, revèlent que tous les types d'eau souterraine semblent évoluer plus dans des poches que le long de lignes d'écoulement. L'étendue limitée du transfert et la prédominance des phénomènes naturels aident à expliquer le niveau modéré de la contamination de l'eau souterraine et les caractéristiques de la contamination de l'eau de surface par l'industrie minière et métallurgique.

Resumen: En el sistema del Río Subarnarekha (Noreste de la India), se han tomado datos geoquímicos, incluyendo análisis de mayores, elementos traza y trazadores isotópicos dentro de un programa de monitorización de aguas superficiales y subterráneas dedicado a la evaluación del impacto de la minería. El acuífero presenta porosidad por fracturación. Las condiciones de flujo del agua subterránea y la transferencia de contaminantes fueron observados en una red de 69 pozos. Los resultados de $\delta^{18}O$ y $\delta^{2}H$ sugieren que la recarga de la lluvia hacia el almacenamiento de las aguas subterráneas

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		a través de los suelos y la zona no saturada es rápida, sin ninguna transformación importante como evaporación. La dispersión de la relación $^{87}Sr/^{86}Sr$ en las aguas superficiales y subterráneas se explican por la existencia de tres tipos de agua extremos. Uno de ellos es compatible con la entrada de agua de lluvia. El extremo más mineralizado representa las entradas antrópicas (prácticas agrícolas y procesado de minerales). El tercer extremo, caracterizado por valores altos de la relación $^{87}Sr/^{86}Sr$, se piensa que está controlado por procesos geoquímicos naturales, aunque afectados por actividades humanas (por ejemplo, drenaje de residuos mineros). Las líneas de flujo potenciales, investigadas al norte del área, revelan que todos tipos de aguas subterráneas parecen evolucionar más en bolsas que a lo largo de líneas de flujo. El alcance limitado de la transferencia y predominancia de los fenómenos naturales ayuda a explicar el nivel moderado de la contaminación de las aguas subterráneas y las características de la contaminación de las aguas superficiales por la industria minera y metalúrgica.
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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)

P. Négrel · B. Lemière · H. Machard de Grammont · P. Billaud · B. Sengupta

Abstract Geochemical observations, including major ion and trace element analysis, and isotopic tracing have been carried out in the Subarnarekha River system (northeastern India) during a surface-water- and groundwater-monitoring program aimed at evaluating impacts of mining. The aquifer is of fracture type. Groundwater flow conditions and pollutant transfer were observed through a network of 69 wells. $\delta^{18}O$ and $\delta^{2}H$ results suggest that transfer from rainfall towards groundwater storage through soils and the unsaturated zone is fast, without any major transformation like evaporation. The scatter of $^{87}Sr/^{86}Sr$ signatures in surface water and groundwater are explained by three end-members. One is compatible with rainwater inputs. The most mineralised end-member represents anthropogenic inputs (agricultural practices and ore processing). The third end-member, characterised by a high $^{87}Sr/^{86}Sr$ signature, is believed to be controlled by natural geochemical processes, although affected by human activities (e.g. drainage of mine waste). Potential flow paths, investigated north of the area, reveal that all groundwater types seem to evolve more in pockets than along a flow path. The limited extent of transfer and the predominance of natural phenomena help to explain the moderate level of groundwater contamination and the characteristics of surface water contamination by mining and the metallurgy industry.

Received: 11 January 2006 / Accepted: 20 September 2007

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Résumé Des études géochimiques dont une analyse des ions majeurs et des éléments en trace, ainsi qu'un traçage isotopique, ont été effectuées sur le système de la rivière Subarnarekha (au nord-est de l'Inde) lors d'un programme de surveillance des eaux de surface et souterraines dont le but était d'évaluer les impacts liés à l'activité minière. L'aquifère est de type aquifère fracturé. Les conditions d'écoulement des eaux souterraines et le transfert de polluant ont été étudiés grâce à un réseau de 69 puits. Les valeurs de $\delta^{18}O$ et $\delta^{2}H$ suggèrent un transfert rapide de la pluie vers la ressource en eau souterraine à travers les sols et la zone non-saturée, sans aucune transformation majeure telle que l'évaporation. La distribution des signatures $^{87}Sr/^{86}Sr$ dans les eaux de surface et souterraines est expliquée par trois pôles. L'un est compatible avec le signal d'entrée des eaux de pluie. Le pôle le plus minéralisé représente le signal d'entrée anthropique (pratiques agricoles et traitements des minerais). Le troisième pôle, caractérisé par une signature de $^{87}Sr/^{86}Sr$ élevée, est supposé être contrôlé par des processus géochimiques naturels, bien qu'affectés par des activités humaines (le drainage de déchets miniers par exemple). Les trajectoires d'écoulement potentiel, étudiées dans le nord de la zone, revèlent que tous les types d'eau souterraine semblent évoluer plus dans des poches que le long de lignes d'écoulement. L'étendue limitée du transfert et la prédominance des phénomènes naturels aident à expliquer le niveau modéré de la contamination de l'eau souterraine et les caractéristiques de la contamination de l'eau de surface par l'industrie minière et métallurgique.

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Keywords India · Hydrochemistry · Fractured rocks · Strontium isotopes · Stable isotopes

Introduction

The chemical and isotopic compositions of waters reflect the different natural processes, i.e. mainly the weathering of rocks and soils, atmospheric inputs and anthropogenic disturbances (Drever 1988) that contribute chemical elements to the dissolved load. Detailed studies focused on the exogenic cycle of the elements were carried out on large- to medium-size river systems, including the Amazon in South America, the Congo in Africa, the Ganga-Brahmaputra and the Indus in Asia, and the Huanghe in China (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 growing quickly. For example, the number of dug wells increased from around 4 million to 10 million between 1952 and 1992 (Ballukraya and Sakthivadivel 2002). Groundwater resource use needs to be managed. Sustainable use is quantitatively related to such factors as the volume of the existing resource, aquifer recharge and associated environmental factors. From the groundwater quality point of view, sustainability implies the prevention of deterioration of groundwater 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 respect to water quantity (Gupta and Singh 1988) or water quality (Robins and Smedley 1994). The delimitation of resources and aquifers (Singhal et al. 1988) and long-term sustainability (Foster et al. 2000) have also been major issues. Pumping affects groundwater quality through increases in salinity and heavy metal contamination (Kamra et al. 2002; Singh et al. 2002).

Due to strong heterogeneity and anisotropy, these issues are more complex in hard rock terrains with irregular distribution of pathways of groundwater flow. "Groundwater accounts for over 80% of the domestic water supply and 50% of irrigation requirements"; "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." (Morris et al. 2003).

This study uses geochemistry and isotope tracing to determine groundwater characteristics in a copper-mining region located in northeastern India. Data were collected during a large monitoring program involving surface and groundwater sampling, as well as soil and sediment sampling, in the vicinity of mining and metallurgical industries and also within areas of land used for intensive agricultural (P. Billaud, BRGM, unpublished report, 2003).

The recent hydrogeological and hydrogeochemical conditions of the site were investigated through analysis of the isotopic composition of strontium, 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 (Négrel et al. 2001; Négrel and Pauwels 2004) while stable isotopes provide an insight into the water origin (Négrel and Lachassagne 2000).

General features of the catchment

The Subarnarekha River Basin is located in northeastern India, rising in southern Bihar state (Fig. 1). The Subarnarekha river flows eastwards through the Singhbhum copper mining region. Continuing eastwards, it enters the Bay of Bengal after a 470-km course.

The selected area along the Subarnarekha River is about 17 km long and 7 km wide with a mean altitude of 90 m above sea level (m asl). It is located around 40 km southeast 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 shows dominant vertical fracturation. Mineral resources, mainly copper (Cu) but also uranium (U), are associated with a Precambrian shear zone.

Three zones can be identified:

– The south westernmost zone is a hilly area belonging to the Singhbhum belt, reaching an altitude of 450–500 m asl. This area is covered by a fairly dense forest with scattered small settlements in the valleys and small paddy fields close to the settlements

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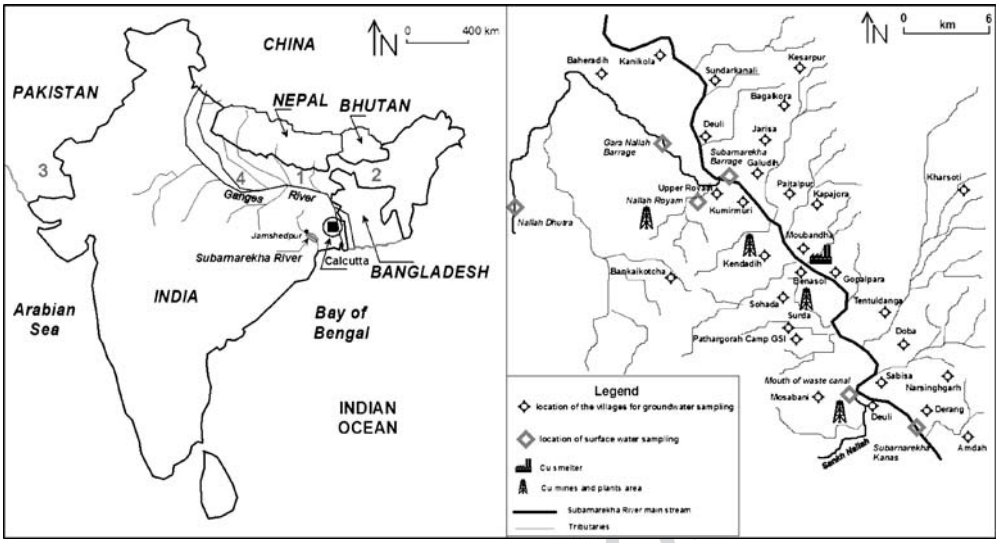


Fig. 1 General setting of the studied site in the Subarnarekha River system. *Nallah* is the local term for tributary .In the general index map of India, numbers refer to the stations of the Global Network for Isotopes in Precipitation (*1* Shiliguri, *2* Schillong, *3* Hyderabad, *4* Allahabad). The *shaded area* refers to the regional map

– The area between the bottom of the hills and the Subarnarekha River on its right bank (e.g. the bank located right downstream) is a strip 17 km long and 1.5 to 3.5 km wide. This area is almost flat with paddy fields, small forested areas, barren land on rock outcrops, and with important settlements in relation to the Cu or U mining sites;
– The left bank (e.g. the bank located left downstream) 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 1,300 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 (increases by 2–3 m). 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 tributary (hereafter referred to as nallah) flow rates, early precipitation being collected and stored in the paddy fields, or recharging the shallow aquifers.

Groundwater occurs under unconfined conditions in the hard rock areas of the district. The potential aquifer comprises 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 reservoir below. Areas with a thick alteration cover have better potential as a groundwater resource than areas with exposed rock outcrops.

The altered layer is rather thin in the study area (usually less than 7 m). Nevertheless, a large number of open dug-wells exist almost everywhere in the valley, with a typical depth of about 10 m; most wells penetrate a few meters inside the fractured rock. Small diameter tube wells are also very frequently found, with a typical depth of about 50 m and usually equipped with 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 one well seems to have little effect on groundwater level in the neighbouring wells, suggesting a poor interconnection within the aquifer. Direct and roughly immediate correlation between rainfall events and rises in groundwater level is observed. Isopotential curves drawn from monthly measurements (P. Billaud, BRGM, unpublished report, 2003) show that there is a complete recovery of the water table from one year to the next. The amount of water abstraction from the monitored wells is not significant 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) in the study area, i.e.

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DOI 10.1007/s10040-007-0227-4

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Subarnarekha Barrage and Subarnarekha Kanas Fig. 2). Small or medium-sized tributaries (nallahs) in the study area were also sampled 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 (Fig. 1). Groundwater data is 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.

Sampling procedure and field measurements

Important water quality variables were measured on site, and results are presented in Table 1. Electrical conductivity (EC) and water temperature were measured using a WTW conductivity meter standardised to 25°C. EC values for the water samples collected during the low water stage were between 115 and ~1,400 µS/cm. The pH was measured on site using a WTW pH-meter calibrated using

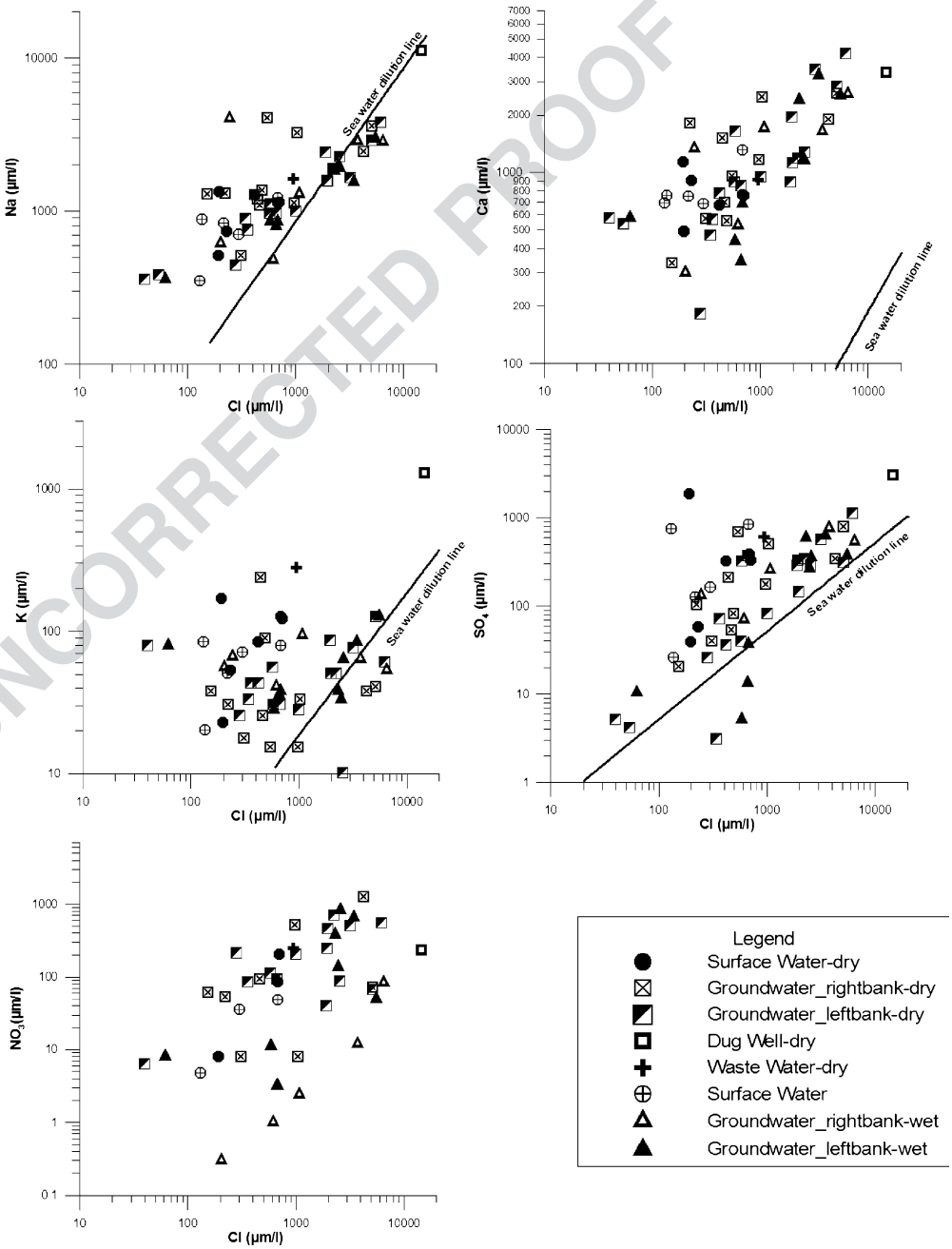


Fig. 2 Plot of major ions (Na, Ca, K, SO_4 and NO_3, all in µmol/l) vs. chloride content from the Subarnarekha River system. Note that contents are represented in log scale

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Table 1 Results of field variables (EC in µS/cm, temperature in °C, pH), TDS (in mg/l, calculated by summing cation and anion contents), major ions (in µmol/l), total cationic and anionic charge (in µeq/l), Normalised Inorganic Charge Balance (NICB), Sr contents, (expressed in µmol/l), Sr isotope values ($^{87}Sr/^{86}Sr$ ratios) and stable isotopes of the water molecule ($\delta^{18}O$ and $\delta^{2}H$) of water samples from the aquifers and surface waters from the Subarnarekha River Basin

Location	Sample ID Code	EC µS/cm (25°C)	T (°C)	pH	TDS mg/l	Ca µmol/l	Mg µmol/l	Na µmol/l	K µmol/l	HCO_3 µmol/l	Cl µmol/l	NO_3 µmol/l	SO_4 µmol/l	Σ+ µeq/l	Σ− µeq/l	NICB %	Sr µmol/l	$^{87}Sr/^{86}Sr$	$\delta^{2}H$ ‰ SMOW	$\delta^{18}O$ ‰ SMOW
Dry period																				
Surface water																				
Nallah Dhutra	SW/2001	310	20.7	8.75	298	495	576	1,348	23	3,230	197	ld	40	3,514	3,506	0	1.27	0.71836	−10.4	0.4
Gara Nallah Barrage	SW/2002	365	21	7.87	305	678	630	1,288	84	2,869	417	ld	326	3,986	3,937	−1	1.44	0.72341	−24.8	−2.5
Nallah Royam	SW/2003	500	22.6	7.4	975	1,140	1,016	513	171	1,082	192	8	1883	4,998	5,048	1	1.32	0.80518	−37.7	−5.4
Subarnarekha Barrage	SW/2008	340	21.5	9.13	276	760	362	1,140	123	1,885	701	208	332	3,507	3,459	−1	1.22	0.72544	−27.2	−3.1
Subarnarekha Kanas	SW/2009	340	21.7	8.52	255	768	379	1,131	128	1,885	679	85	385	3,551	3,420	−4	1.23	0.72530	−26.6	−2.9
Nallah Nala	SW/2023	345	21.9	8.02	334	913	695	739	54	3,590	231	ld	58	4,009	3,938	−2	1.32	0.71844	−21.5	−2
Groundwater																				
Kanikola	TW/2004	210	28.2	6.46	304	338	148	1,292	38	2,016	152	61	21	2,302	2,271	−1	0.84	0.73318	−40	−5.8
Baheradih	TW/2005	270	28.2	6.44	379	703	259	1,100	26	1,984	462	94	54	3,050	2,647	−14	1.88	0.72830	−35.5	−5.2
Pathargorah Camp GSI	TW/2013	325	25.5	6.68	436	560	346	1,366	90	2,639	485	ld	83	3,267	3,290	1	1.03	0.76866	−39.1	−5.8
Deuli	TW/2022	535	28.2	6.83	643	1,813	424	1,318	31	5,525	223	53	104	5,821	6,008	3	1.84	0.72605	−42.8	−6.2
Benasol	TW/2024	875	28	5.93	1,050	1,903	658	2,445	38	1,230	4,254	1,273	347	7,605	7,449	−2	4.83	0.72858	−34.1	−5
Surda	TW/2025	240	28	6.47	294	573	329	513	18	2,148	310	8	41	2,335	2,547	9	1.14	0.75150	−41.7	−6.2
Kumirmuri	TW/2026	880	27.5	7.03	1,004	2,493	609	3,249	33	7,770	1,031	8	510	9,486	9,829	4	4.38	0.72766	−34	−5
Sohada	TW/2027	675	27.6	6.81	724	963	387	4,093	15	5,115	541	ld	700	6,807	7,056	4	2.68	0.73448	−33.2	−4.9
Kendadih	TW/2028	1,125	27.8	6.28	1,495	2,600	988	3,589	41	3,475	5,099	73	803	10,805	10,253	−5	6.69	0.73575	−38.7	−5.6
Upper Royam	TW/2029	420	29	6.49	397	1,165	218	1,135	15	2,197	969	518	176	3,917	4,035	3	2.00	0.73471	−30.2	−4.5
Mosabani	TW/2037	765	27.5	7.12	853	1,518	1,947	1,196	240	8,066	439	ld	211	8,365	8,927	7	2.48	0.75221	−29.5	−4
Sundarkanali	TW/2006	230	27.8	6.17	269	568	235	757	43	1,738	358	85	72	2,404	2,325	−3	1.53	0.72836	−44.4	−6.4
Deuli	TW/2007	520	26.3	6.92	566	1,643	749	1,122	31	4,328	577	113	327	5,936	5,672	−5	1.94	0.72008	−30.6	−4.2
Sabisa	TW/2010	1,085	27.6	6.45	1,059	2,825	1,053	2,897	128	4,393	5,099	68	310	10,782	10,180	−6	7.50	0.73807	−39.2	−5.9
Derang	TW/2011	680	27.9	6.82	833	1,948	877	1,592	87	4,066	1,938	247	330	7,327	6,910	−6	3.49	0.73810	−35.9	−5.4
Amdah	TW/2012	1,005	28.2	6.98	795	3,475	1,132	1,653	77	5,344	3,183	508	575	10,943	10,186	−7	7.42	0.73018	−38.6	−5.7

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DOI 10.1007/s10040-007-0227-4

JrnlID 10040_ArtID 227_Proof# 1 - 08/10/2007

DOI 10.1007/s10040-007-0227-4

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Table 1 (continued)

Location	Sample ID Code	EC µS/cm (25°C)	T (°C)	pH	TDS mg/l	Ca µmol/l	Mg µmol/l	Na µmol/l	K µmol/l	HCO^3 µmol/l	Cl µmol/l	NO^3 µmol/l	SO^4 µmol/l	Σ+ µeq/l	Σ− µeq/l	NICB %	Sr µmol/l	$^{87}Sr/^{86}Sr$	δ^2H ‰ SMOW	$\delta^{18}O$ ‰ SMOW	t1-29
Narsinghgarh	TW/2014	195	27.4	6.68	250	578	296	361	79	2,098	39	6	5	2,188	2,155	−2	1.61	0.73034	−37.4	−5.6	t1.30
Doba	TW/2015	490	27.4	6.3	645	1,130	477	1562	51	1,770	1,972	458	145	4,827	4,490	−7	2.77	0.73261	−41	−6	t1.31
Tentuldanga	TW/2016	1,420	27.3	6.57	1,485	4,200	1,420	3,789	61	4,934	6,169	556	1,134	15,089	13,928	−8	8.70	0.72695	−35	−5.3	t1.32
Kesarpur	TW/2018	230	27.7	6.6	394	473	255	892	33	2,164	341	ld	3	2,380	2,511	5	1.39	0.72000	−38.2	−5.7	t1.33
Bagalkora	TW/2019	340	27.8	6.49	639	895	383	970	56	2,803	569	ld	41	3,582	3,453	−4	1.99	0.72912	−40.3	−6.2	t1.34
Jarisa	TW/2020	115	27	5.63	178	183	107	448	26	541	279	218	26	1,053	1,090	3	0.38	0.73168	−41.3	−6.1	t1.35
Bankaikotcha	TW/2030	300	26.3	6.7	414	538	794	387		3,180	54	ld	4	3,051	3,242	6	0.86	0.72342	−45.5	−6.8	t1.36
Kharsoti	TW/2031	340	26.8	6.6	460	783	420	1,279	43	3,443	417	ld	36	3,727	3,932	5	2.35	0.72941	−28.6	−4	t1.37
Gopalpara	TW/2032	345	26.3	6.92	295	858	329	966	31	1,934	662	95	373	3,370	3,437	2	2.16	0.72506	−28.5	−3.3	t1.38
Moubandha	TW/2033	390	27.4	6.79	508	953	391	1,005	28	2,475	997	208	82	3,720	3,845	3	2.61	0.72498	−37.7	−5.3	t1.39
Kapajora	TW/2034	495	28.1	6.58	503	893	239	2,427		2,148	1,890	40	288	4,690	4,654	−1	2.15	0.72578	−28.9	−4.3	t1.40
Paitalpur	TW/2035	595	28.1	6.51	531	1,280	383	2,271	10	2,344	2,541	87	287	5,606	5,547	−1	3.66	0.72423	−37.6	−5.5	t1.41
Galudih	TW/2036	570	28.2	6.28	479	1,188	498	1,896	51	1,639	2,217	705	341	5,319	5,244	−1	3.57	0.72417	−35.6	−5.4	t1.42
Tentuldanga	DW/2017	2,630	23.5	7.6	1,578	3,350	3,082	11,135	1,307	3,443	14,535	240	3,039	25,307	24,295	−4	6.98	0.73220	−37.4	−5.3	t1.43
Mouth of waste canal	WW/2038	515	23.5	8.08	376	920	527	1,622	279	2,410	946	250	606	4,795	4,818	0	1.44	0.75012	−23.5	−2.2	t1.44
Wet period																					t1.45
Surface water																					t1.46
Nallah Dhutra	SW/4044	333	26.1	8.24	332	763	621	887	20	3,623	135	0	26	3,676	3,810	4	1.57	0.71866	−27	−3.5	t1.47
Gara Nallah Barrage	SW/4045	408	27	8.03	293	750	551	835	51	3,082	217	0	128	3,489	3,555	2	1.50	0.72208	−29.1	−3.9	t1.48
Nallah Royam	SW/4046	324	26.3	7.5	512	695	753	352	84	1,803	130	5	747	3,333	3,432	3	0.89	0.77354	−39	−6	t1.49
Subarnarekha Barrage	SW/4047	491	27.1	8.12	431	1,315	539	1,227	79	2,770	676	48	853	5,014	5,201	4	1.80	0.72785	−29.6	−4	t1.50
Subarnarekha Kanas	SW/4037	280	27.1	8.18	238	688	379	705	72	2,344	299	35	164	2,908	3,007	3	1.26	0.72340	−31.2	−4.3	t1.51
Groundwater																					t1.52
Pathargorah Camp GSI	TW/4034	125	28.6	6.89	459	300	165	618	56	1,459	203	5	0	1,603	1,667	4	0.37	0.75608	−38	−6.1	t1.53
Deuli	TW/4033	710	28.5	7.18	708	1,335	535	4,050	66	7,656	245	0	132	7,856	8,165	4	2.97	0.72513	−32.9	−5	t1.54
Benasol	TW4051	1,100	27.1	5.85	1,289	2,575	909	2,853	54	1,131	6,479	1,353	539	9,876	10,041	2	7.08	0.72685	−34.2	−5.4	t1.55

Surda	TW4049	240	28	6.5	322	528	366	483	41	1,738	614	16	71	2,311	2,509	8	1.07	0.74282	−39.5	−6.2	t1.56
Kendadih	TW/4048	820	28.2	6.57	1,209	1,648	564	2,893	64	2,082	3,746	197	772	7,379	7,569	3	4.30	0.73859	−31.6	−5.1	t1.57
Mosabani	TW/4050	690	28	7.25	863	1,708	1,337	1,301	95	5,836	1,076	39	258	7,485	7,467	0	2.81	0.71839	−30.3	−4.4	t1.58
Deuli	TW/4041	910	27.9	6.98	1,038	2,403	1,337	1,831	38	5,803	2,293	377	597	9,349	9,668	3	3.72	0.71999	−30.3	−4.5	t1.59
Sabisa	TW4038	1,100	28.8	6.15	1,113	2,550	975	2,962	128	4,213	5,521	50	369	10,141	10,523	4	8.33	0.73752	−37.1	−6.1	t1.60
Amdah	TW/4035	1,010	28	7.01	785	3,225	1,049	1,553	84	4,918	3,465	655	637	10,186	10,311	1	8.78	0.72986	−37.9	−5.9	t1.61
Narsinghgarh	TW/4036	220	28.2	6.82	264	578	296	361	79	2,246	62	8	10	2,188	2,337	7	1.85	0.73013	−35.7	−5.8	t1.62
Kesarpur	TW/4039	235	28.4	6.57	402	440	235	857	28	1,885	583	11	5	2,234	2,490	11	1.61	0.72005	−37.8	−5.8	t1.63
Bagalkora	TW/4040	320	29.8	6.41	528	688	230	857	38	2,197	676	3	37	2,731	2,951	8	1.61	0.72524	−38.6	−6.1	t1.64
Jarisa	TW/4052	250	27.8	6.31	352	343	49	800	36	1,000	659	3	14	1,620	1,689	4	0.75	0.72866	−37.1	−6	t1.65
Paitalpur	TW/4043	550	28	6.42	468	1,175	362	1,992	33	2,148	2,470	137	268	5,100	5,292	4	3.65	0.72389	−37.7	−5.8	t1.66
Galudih	TW/4042	625	28.9	7.06	507	1,158	506	1,918	64	1,836	2,572	834	361	5,310	5,964	12	3.86	0.72395	−36.2	−5.7	t1.67

Sample codes: *SW* surface water; *TW* groundwater collected by tube wells; *DW* groundwater collected by dug well t1.68

Low water stage corresponded to February 2001 and high water stage to November 2001. *EC* electrical conductivity of the water; *TDS* the sum of cations and anions; *NICB* normalised inorganic charge balance according to $NICB = 2\xi\{\sum^{-} - \sum^{+}/\sum^{-}+\sum^{+}\} \times 100$ with Σ^{+} and Σ^{-} corresponding to the total cationic and anionic charges

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DOI 10.1007/s10040-007-0227-4

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standard buffers; groundwaters display pH in the range 5.60–7.25, and 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-µm acetate cellulose filters using a precleaned Nalgene filter apparatus. The filtrate was separated into three aliquots: the 100 and 500 ml aliquots were acidified with suprapure nitric acid and stored in precleaned polyethylene bottles for major cations, trace elements analysis and strontium isotope determination, and the 250 ml aliquot was stored in polyethylene bottles, unacidified, for anion determination.

Major- and trace-element determination, and 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_4, NO_3), inductively coupled plasma mass spectrometry (Mg, trace elements), HCl titration and Gran's method (HCO_3). 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 Mean Ocean Water) following $\delta = [(R_{sample}/R_{standard}.R_{standard}) - 1] \times 1000$ where R is the isotopic ratio of the heaviest isotope over the lighter (e.g. $^{18}O/^{16}O$). The deuterium and oxygen isotopic ratios were analysed using a Finnigan MAT 252 mass spectrometer. The average precision, based on multiple analyses of various samples and laboratory standards was ±0.1‰ for $\delta^{18}O$ and ±0.8‰ for $\delta^{2}H$.

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

Results and discussion

Surface water and groundwater 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 stage 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 to 1,485 mg/l, while during the higher water stage, the TDS ranged from 264 to 1,289 mg/l. The average TDS does not vary much between the low and high water seasons despite the extreme discharge variations in the river (615±341 mg/l and 687±343 mg/l, respectively).

The range of total cationic charge ($\Sigma^{+}=Na^{+}+K^{+}+2\,Mg^{++}+2Ca^{++}$, expressed in µeq/l) in surface water samples is 3,500–5,000 µeq/l, clearly higher than the 'world average river water' (1,200 µeq/l, Meybeck 1979). In groundwater, the range of Σ^{+} is large, (1,000–15,000 µeq/l,

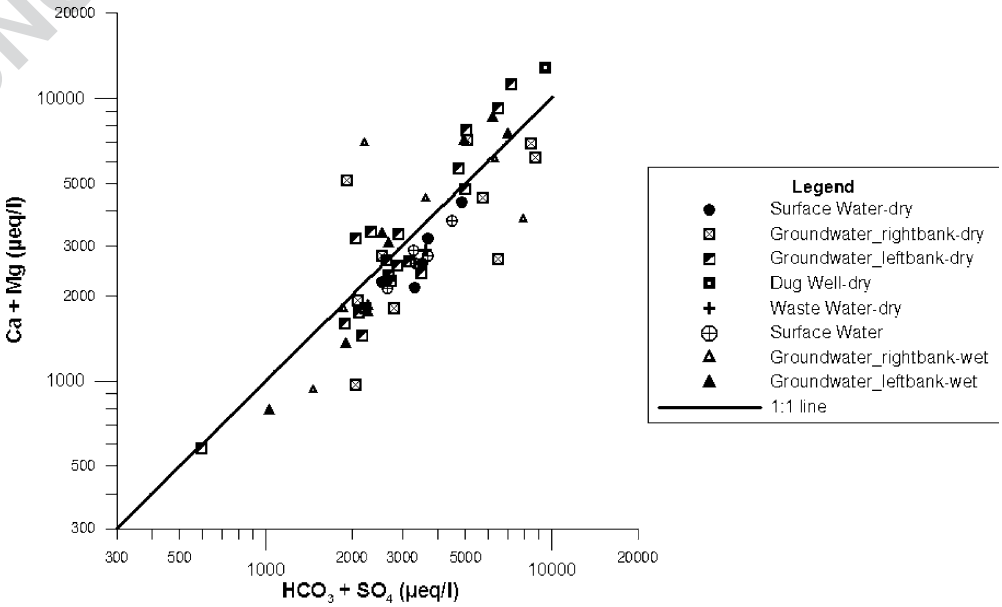


Fig. 3 Plot of Ca+Mg vs. HCO_3+SO_4 (in µeql/l). The 1:1 line is calculated in µeq/l

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without any discrepancy between the right and left banks of the river). The charge imbalance, estimated by the normalised inorganic charge balance ($NICB = 2 \times \{\sum^- - \sum^+ / \sum^- + \sum^+\} \times 100$) 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 Σ^+. 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 Na>Ca or Mg>K during the low water stage and Ca>Na>Mg>K during the higher water stage. For anions, the order is HCO_3>SO_4 or Cl>NO_3 during both the low and higher water stages. In groundwater, the order is Na or Ca>Mg>K and HCO_3 or Cl>SO_4>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 HCO_3–Ca type during both water stages, with the exception of the Royam nallah that plots within the field of Ca–SO_4 water type during the low water stage, and within the field HCO_3–Ca during the higher water stage. Most groundwater samples are of Ca–SO_4 water type and HCO_3–Ca water type, in agreement with the fresh and mined-water types defined by Sikdar et al. (2001) in the Quaternary aquifer near Calcutta (India). However, two samples plot within the field HCO_3–Na (TW/4052 and TW/4033, see Table 1) during the higher water stage and their low water stage equivalents fall within the HCO_3–Ca field, reflecting a higher Ca input during the low water stage.

Inter-element relationships

The chemical composition of the surface waters and groundwaters is efficiently examined through binary diagrams between two chemical species X and Y expressed in µmol/l. The sea-water 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 a 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 (seasalt aerosols) and human activities.

In the Na vs. Cl plot (Fig. 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 Fig. 2, Ca, 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 (Fig. 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 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 SO_4 contents (Fig. 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 (Fig. 3, in log scale) provides evidence of 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 SO_4 (Fig. 2) departs from the results of Leybourne et al. (1998) whom reported low Cl (0.1–10 mg/l) associated with high SO_4 (up to 10–100 mg/l) in groundwater at sulphide deposits. This suggests that fertilisers may be responsible for the correlation between Cl, 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_3, 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 (Figs. 2 and 3). Comparing Ca and SO_4, most points display a Ca/SO_4 mole ratio close to 1.03, lower than that of the gypsum or anhydrite dissolution. Therefore, Ca seems depleted compared to SO_4, suggesting that the additional source of SO_4 did not contribute Ca to the water.

The higher Ca and SO_4 contents in the river sample upstream during the wet period are not accompanied by a significant increase in the NO_3 content. Conversely, the highest NO_3 content is observed during the dry period. It is therefore suggested that the source of Ca and SO_4 in surface waters is independent from that responsible for NO_3 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 salinity 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. Narsinghgarh, Patargorah and Deuli). On the other hand, during the dry period, most elements are almost constant downstream, excepted NO_3 which exhibits a

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DOI 10.1007/s10040-007-0227-4

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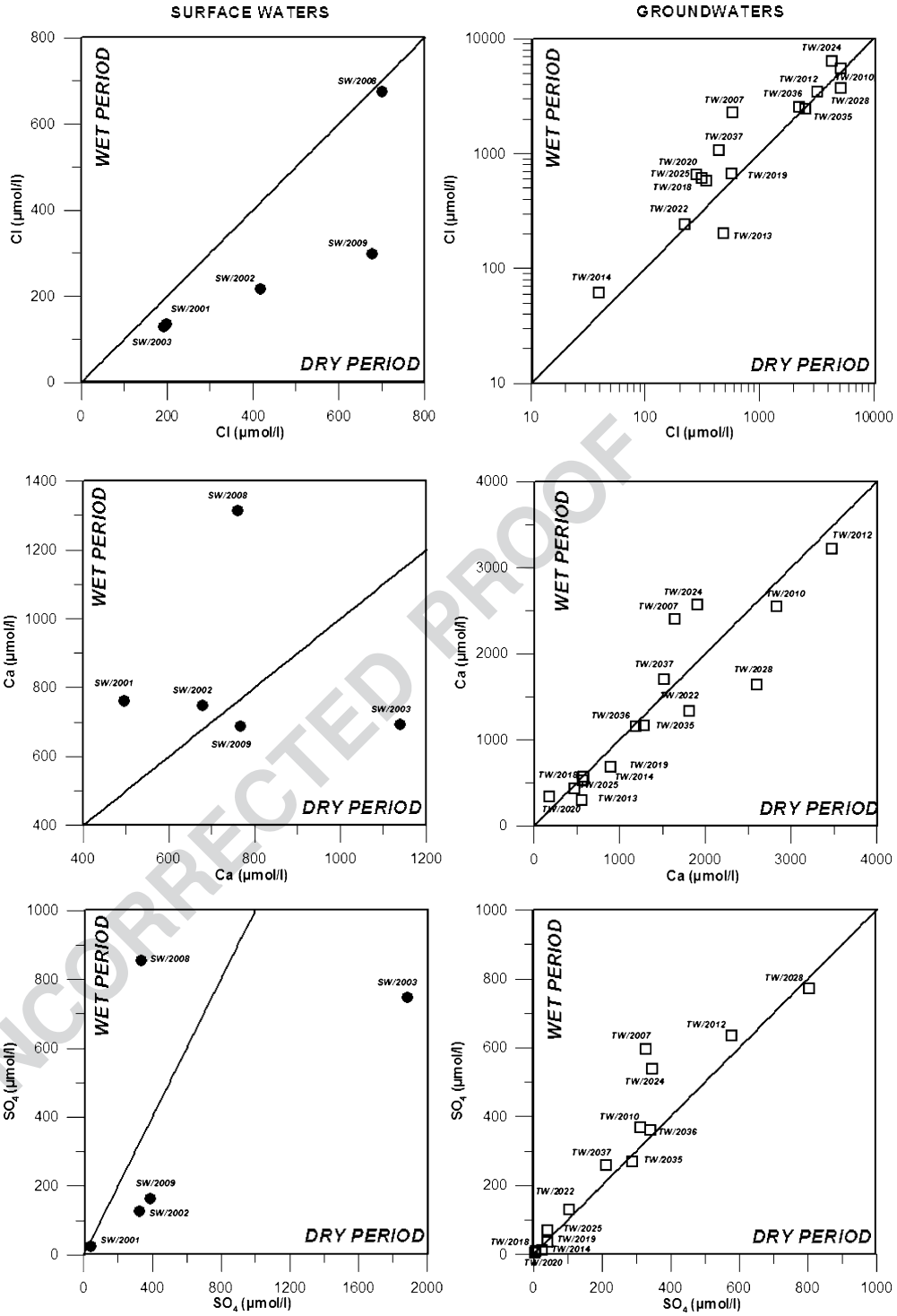


Fig. 4 Plots of Cl, Ca and SO_4 contents (expressed in µmol/l) between the dry and wet periods for surface waters and groundwaters in the Subarnarekha River system. The Cl contents scale is expressed in logarithmic units for the groundwaters for easier viewing

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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_3 enrichment is locally observed during the wet period, but most wells show identical values between the two periods. Much of Ca and SO_4 inputs in groundwater can therefore be related to agricultural practice.

The carbonate system and the origin of Ca and SO_4

The carbonate system in waters can be investigated by using Ca and bicarbonate which are the dominant ions. Samples plot above and below the $Ca=HCO_3$ 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_3+SO_4 (Fig. 4), which shows a better scatter of the points around the 1:1 line (Edmond

DOI 10.1007/s10040-007-0227-4

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t2.1 **Table 2** Saturation indices on selected samples from the aquifers from the Subarnarekha River Basin

t2.2 t2.3 t2.4 Mineral	Formula	Deuli TW 2022 Dry	Deuli TW 4033 Wet	Kesarpur TW 2018 Dry	Kesarpur TW 4039 Wet	Amdah TW 2012 Dry	Amdah TW 4035 Wet	Tentuldenga TW 2016 Dry	Tentuldenga DW 2017 Dry	Jarisa TW 2020 Dry	Jarisa TW 4052 Wet
t2.5 Calcite	$CaCO_3$	−0.17	0.17	−1.32	0.17	0.19	0.15	−0.22	0.43	−3.26	−2.22
t2.6 Dolomite	$CaMg(CO_3)_2$	0.22	1.14	−1.71	1.14	1.09	1.01	0.28	2.00	−5.57	−4.09
t2.7 Dolomite-ordered	$CaMg(CO_3)_2$	0.23	1.15	−1.70	1.15	1.10	1.02	0.29	2.01	−5.56	−4.08
t2.8 Gypsum	$CaSO_4:2H_2O$	−3.08	−3.14	−5.03	−3.14	−2.19	−2.17	−1.88	−1.65	−4.45	−4.66
t2.9 Celestite	$SrSO_4$	−4.86	−4.57	−6.35	−4.57	−3.65	−3.52	−3.36	−3.15	−5.95	−6.13

et al. 1995). This observation highlights the important role of Ca and SO_4 in the Subarnarekha River system and implies that sulphate must be taken into consideration in the carbonate system equilibrium.

The PHREEQC geochemical code (Parkhurst and Appelo 1999) 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_4 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

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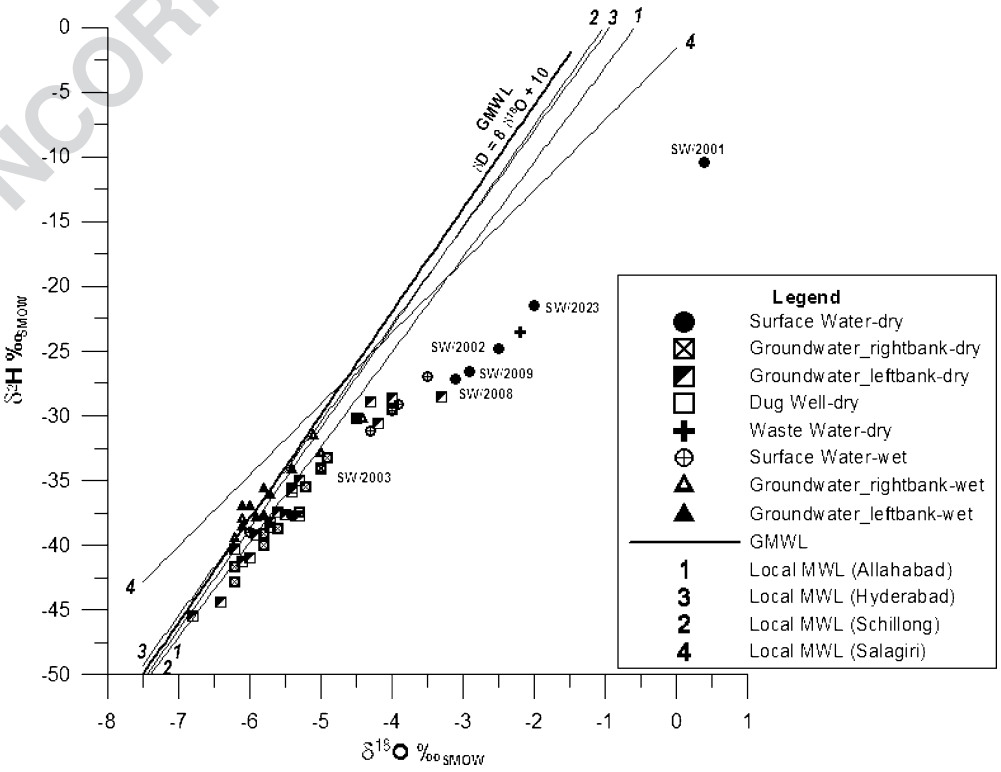


Fig. 5 Plot of the $\delta^{18}O$ vs. the $\delta^{2}H$ in rainwater (data are from the IAEA/WMO, 2001) and in the Subarnarekha River system. GMWL corresponds to the global meteoric water line ($\delta^{2}H=8\ \delta\ ^{18}O+10$)

DOI 10.1007/s10040-007-0227-4

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suggest that part of the Ca depletion compared to SO_4 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_4 plead in favour of a common source for Cl and Ca and a specific one for SO_4. The first source can be related to agricultural practices via fertiliser application and the second one can be related to mining activities.

δ^2H and $\delta^{18}O$ 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 $\delta^{18}O$ and 10.4 to −39.0‰ for δ^2H in surface waters, including sample WW2038 which contains a wastewater component. For groundwaters, the range for $\delta^{18}O$ is −3.3 to −6.8‰ and −28.5 to −45.5‰ for δ^2H, 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 $\delta^{18}O$ vs. δ^2H diagram (Fig. 5). The global meteoric water line (GMWL, $\delta^2H=8\ \delta^{18}O+10$) 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 unsaturated 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 (Fig. 5), the ranges of ^{18}O and ^2H isotopes are narrow, e.g. from −5 to −7‰ for $\delta^{18}O$ and −30 to −45‰ for δ^2H. 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) showed evidence of a geographic distribution of the δ^2H and $\delta^{18}O$ 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. The values derived from this present study 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 $\delta^{18}O$ in groundwater around 1±1‰, but a decrease in $\delta^{18}O$ up to −7‰ towards the northeast of their zone is clearly in evidence. 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 water and groundwater samples show a significant shift of more than 1‰ to the right of the GMWL. Comparison of the $\delta^{18}O$ in the surface waters and groundwaters in the Subarnarekha River system between the wet and dry periods shows that all surface waters display $\delta^{18}O$ enrichment more marked during the dry period (Table 1). These ^{18}O and ^2H enrichments in surface waters may be linked to evaporation processes in soils, to evapotranspiration or sometimes to surface evaporation from the river water masses (Négrel and Lachassagne 2000). Some of the groundwaters are also shifted on the right of the GMWL in relation to either evaporation processes linked with a poor isolation of the tube well or to water return flow with a depleted value as illustrated by Négrel et al. (2007) in the Maheshwaram watershed (Andra Pradesh, India). However, most of the

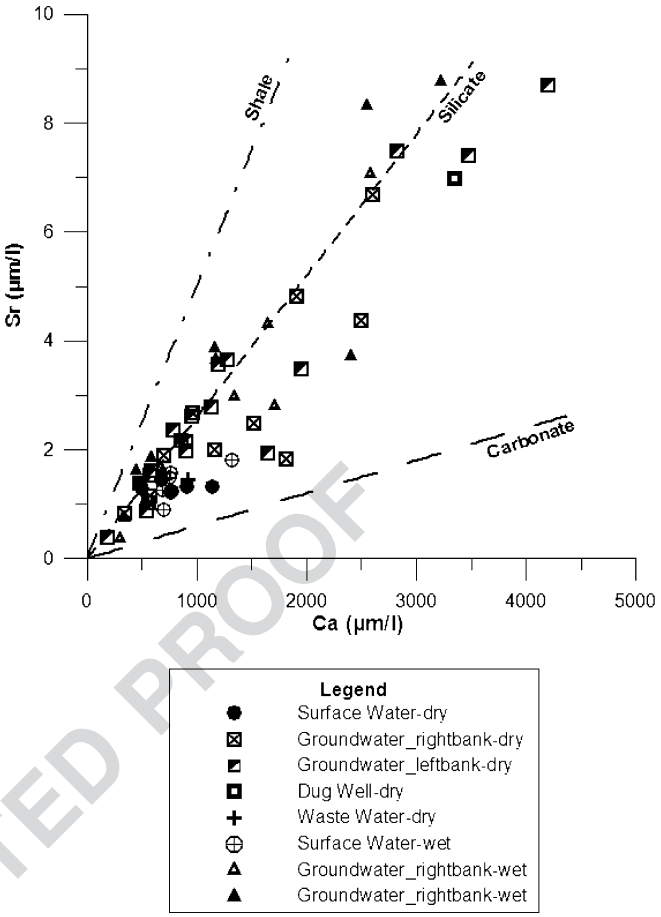


Fig. 6 Plot of strontium vs. calcium contents (expressed in µmol/l) in the Subarnarekha River system. The *dashed lines* correspond to the weathering of shales, silicate and carbonate, respectively

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DOI 10.1007/s10040-007-0227-4

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groundwaters display similar $\delta^{18}O$ 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 µmol/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 orders of magnitude from less than 0.4 up to 10 µmol/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 µmol/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 (Fig. 6) shows different linear relationships, resulting from the weathering of shales, silicate and carbonate. Different Ca/Sr ratios reflect 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 are 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 (1) carbonate amendments used in agriculture and (2) 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 water and groundwater, with relatively high $^{87}Sr/^{86}Sr$ 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 in Russia, Huh and Edmond 1999) and for the Ganga-Brahmaputra-Indus River system in India (Krishnaswami et al. 1992; Pande et al. 1994; Singh et al. 1998). Similar ranges are observed in Himalayan rivers (Galy et al. 1999). The $^{87}Sr/^{86}Sr$ 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

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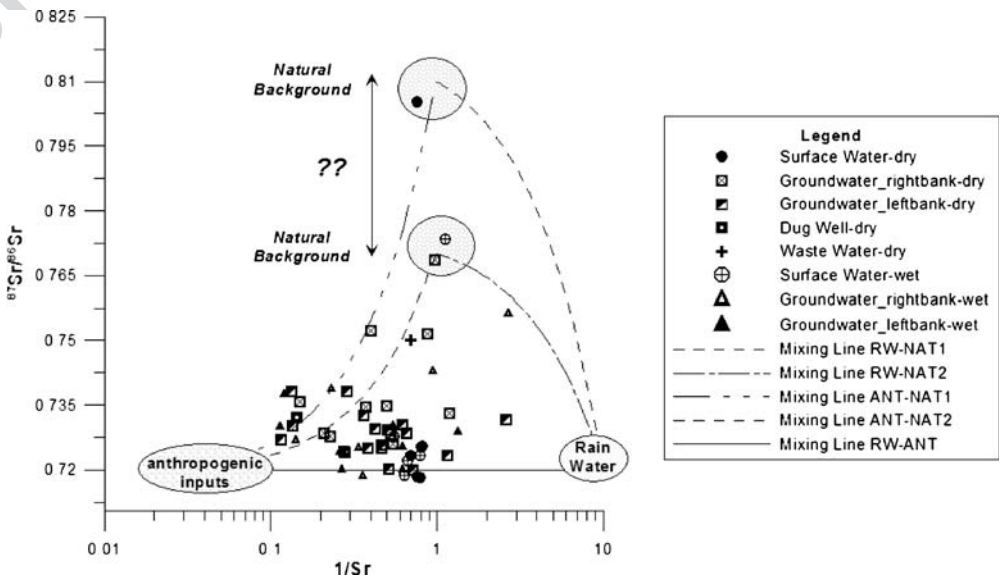


Fig. 7 Plot of $^{87}Sr/^{86}Sr$ vs. 1/Sr (Sr concentration expressed in µmol/l) for the surface waters and groundwaters samples during dry and wet periods in the Subarnarekha River system. The 1/Sr scale is reported in logarithmic units for easier viewing. *Curves* represent calculated mixing lines according to Eq. (1) (see text)

DOI 10.1007/s10040-007-0227-4

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silicate displays $^{87}Sr/^{86}Sr$ ratios between 0.7143 and 0.724 while that draining carbonate displays $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ and Sr contents are caused primarily by mixing of waters of various origins with different $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ 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 (1) the large variation in the Sr contents corresponds to a relatively restricted range of the $^{87}Sr/^{86}Sr$ ratios and (2) the highest $^{87}Sr/^{86}Sr$ ratios correspond to relatively low Sr contents. The $^{87}Sr/^{86}Sr$ ratios vs. 1/Sr diagram (Fig. 7) are classically used to evaluate two-component mixing and

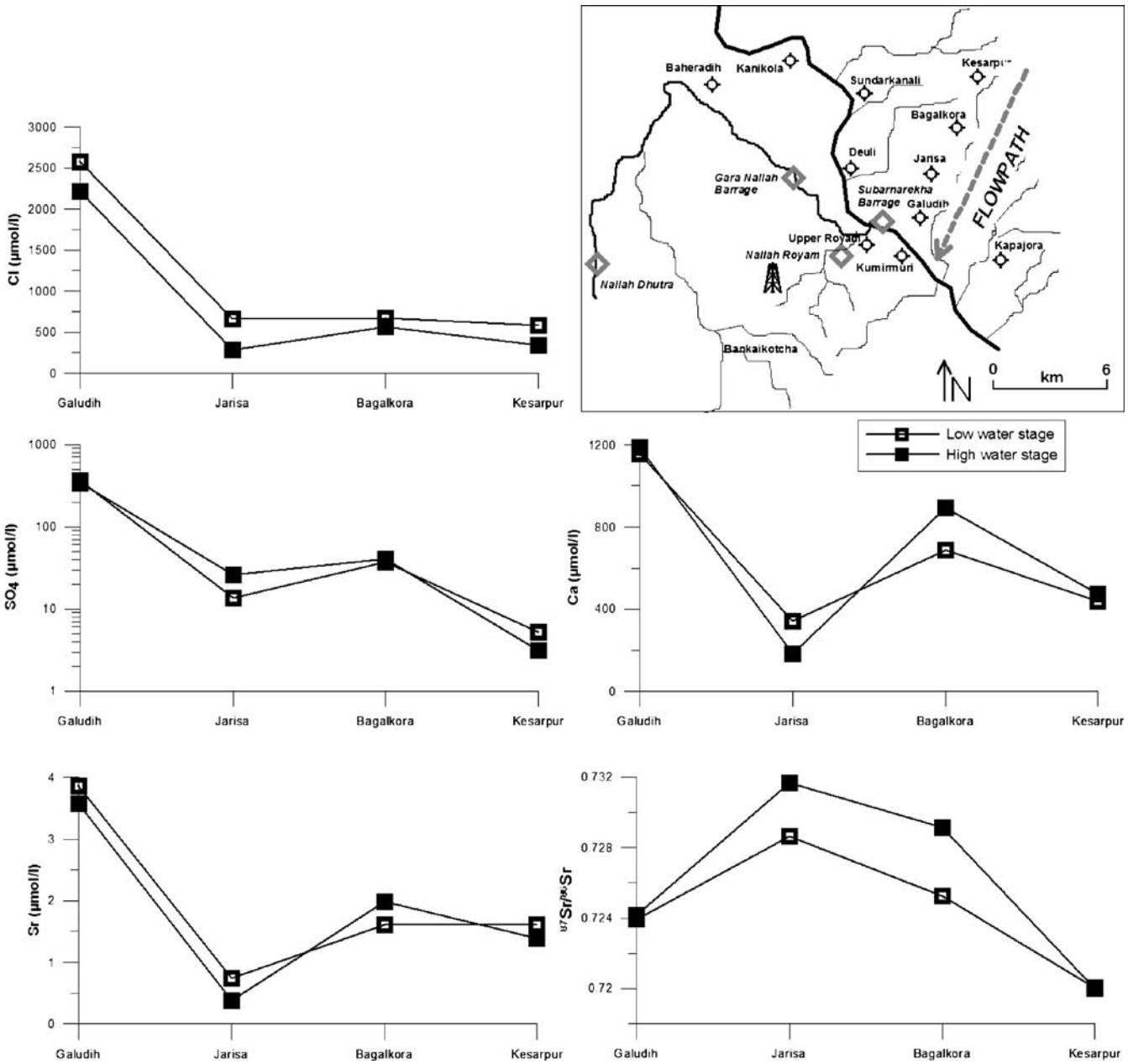


Fig. 8 Plot of selected chemical indicators (Cl, Ca, SO_4, Sr, µmol/l) and Sr isotopes for the groundwaters samples during dry and wet periods in the supposed flowpath between Kesarpur and Galudih (north of the Subarnarekha River system, see Fig. 1 for legend)

DOI 10.1007/s10040-007-0227-4

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end-member water compositions. The 1/Sr logarithmic scale is used for easier viewing (Négrel et al. 2001; Négrel and Casanova 2005). The samples are scattered in three directions, suggesting the existence of at least three end-member compositions (Hogan et al. 2000). The most dilute end-member should be compatible with the rainwater inputs (hereafter referred to as rainwater) for which characteristics are usually $^{87}Sr/^{86}Sr$ close to 0.720, and Sr content around 0.1 µmol/l. The most mineralised end-member has very similar isotopic compositions, and Sr concentrations around 100 µmol/l. It is believed to represent anthropogenic inputs, mainly agricultural in origin. The third end-member is characterised by a Sr content around 1 µmol/l and a more radiogenic signature ($^{87}Sr/^{86}Sr>0.760$). This end-member is represented by Royam nallah, which drains a large area of mine tailings. This very high $^{87}Sr/^{86}Sr$ 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 show the highest Cl contents, and the natural background has a low Cl content (around 100 µmol/l). These three end-members can also be observed by comparing Sr and SO_4 contents, $^{87}Sr/^{86}Sr$ ratios and SO_4 and $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ ratios vs. 1/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:

$$^{87}Sr/^{86}Sr_m \times [Sr]_m = \alpha\left(^{87}Sr/^{86}Sr_1 \times [Sr]_1\right) + (1-\alpha)\left(^{87}Sr/^{86}Sr_2 \times [Sr]_2\right) \quad (1)$$

where $^{87}Sr/^{86}Sr_m$ is the measured isotopic ratio in the mixture, and $^{87}Sr/^{86}Sr_1$, $^{87}Sr/^{86}Sr_2$ represent the isotopic ratios of the first and second end member, respectively. $[Sr]_m$, $[Sr]_1$, $[Sr]_2$ are the Sr content of the mixture, and of the first and second end members, respectively. The mixing parameter α derived from Eq. (1) is represented by $\frac{Sr_1}{Sr_1+Sr_2}$ and $1-\alpha$ by $\frac{Sr_2}{Sr_1+Sr_2}$; α represents the proportion of the two components in the mixture.

Different mixing trends exist between the end-members in Fig. 7. The application of Eq. (1) allows the calculation of the mixing curves RW-NAT1 and RW-NAT2 on Fig. 7 for which end-members are rainwater ($^{87}Sr/^{86}Sr=0.720$; Sr=0.1 µmol/l) and the two natural backgrounds ANT-NAT1, represented by Royam nallah ($^{87}Sr/^{86}Sr=0.80518$; Sr=1 µmol/l) and ANT-NAT2 ($^{87}Sr/^{86}Sr=0.77354$; Sr content=1 µmol/l).

The application of Eq. (1) allows the calculation of the second mixing curve RW-ANT on Fig. 7 for which end-members are rainwater ($^{87}Sr/^{86}Sr=0.720$; Sr=0.1 µmol/l) and the anthropogenic end-member ($^{87}Sr/^{86}Sr=0.720$; Sr=30 µmol/l)., as well as that of the third mixing curves ANT-NAT1 and ANT-NAT2 on Fig. 7 for which end-members are the anthropogenic end-member ($^{87}Sr/^{86}Sr=0.720$; Sr content=30 µmol/l) and the two natural backgrounds NAT1and NAT2.

Considering the mixing diagram in Fig. 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 and flowpaths

According to the piezometric levels, some areas can be the focus for flowpath investigations. Within the studied catchment, the most probable flowpath area to be further detailed is located in the north. This area concerns the samples collected in the villages Kesarpur, Bagalkora, Jarisa and Galudih. 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 Fig. 8. Along this possible flowpath, the chloride contents display a similar behaviour both between the

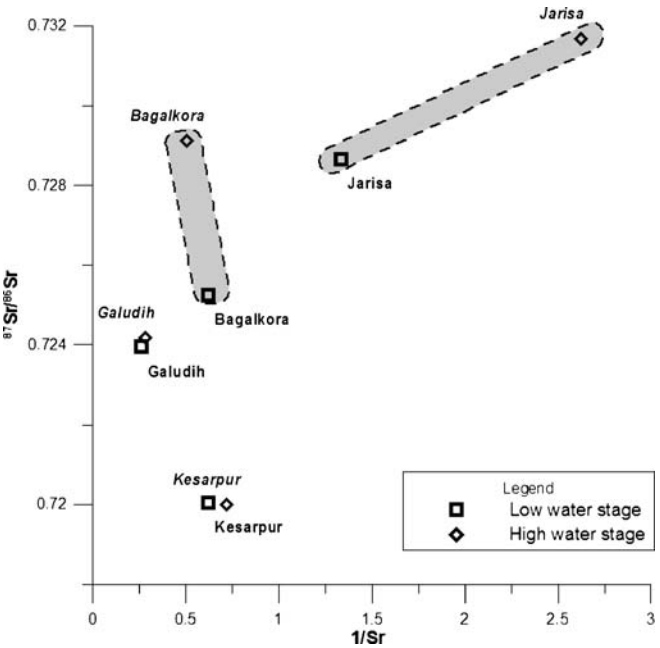


Fig. 9 Plot of $^{87}Sr/^{86}Sr$ vs. 1/Sr contents (Sr concentration expressed in µmol/l) for the ground- waters samples during dry and wet periods in the supposed flowpath between Kesarpur and Galudih (North of the Subarnarekha River system)

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samples and between the dry and wet period. The Cl contents fluctuate between 280 and 680 μmol/l in Kesarpur, Bagalkora and Jarisa and a larger value (up to 2,200–2,600 μmol/l) is observed in Galudih. The large increase in solutes in the Galudih samples in 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 to Galudih, whatever the period is. SO_4 contents, as well as numerous other chemical indicators not shown in Fig. 8 (e.g. K, 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 $^{87}Sr/^{86}Sr$ ratios, several features can be pointed out. First, the $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ 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 not only true for meteoric inputs and for water–rock interactions, but also for anthropogenic activities. The $^{87}Sr/^{86}Sr$ ratios differ in Bagalkora and Jarisa samples between the dry and wet periods, the wet period ratio being higher.

As discussed previously for Fig. 8, and with further evidence on Fig. 9 ($^{87}Sr/^{86}Sr$ vs. 1/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 $^{87}Sr/^{86}Sr$ 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 $^{87}Sr/^{86}Sr$ ratio. The increase of the $^{87}Sr/^{86}Sr$ ratios showed in Fig. 8 between Kesarpur and Jarisa is not supported by a binary mixing trend between two end-members, as illustrated in the plot $^{87}Sr/^{86}Sr$ vs. 1/Sr ratios by the lack of any linear relationship (Fig. 9). This suggests that all groundwaters evolved more as 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 and Sirat 2001).

Conclusions

This study reports on the geochemistry of surface waters 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 waters and groundwaters in the studied catchment.

A large range of salinities in surface waters 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.

Surface water samples are of HCO_3-Ca type during both water stages. Most groundwater samples are of Ca–SO_4 and HCO_3–Ca types, reflecting 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 ($\delta^{18}O$ and $\delta^{2}H$), 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 unsaturated zone.

Sr and Ca show different linear relationships resulting from the weathering of shales, 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 (1) carbonate amendments used in agricultural practice or (2) residues of mining treatment.

The scatter of $^{87}Sr/^{86}Sr$ signatures needs to be explained by at least three 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).

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DOI 10.1007/s10040-007-0227-4

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Potential flow paths were investigated in the north of the area. In the scope of the different geochemical tools used, all groundwaters in this area seem to evolve more 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 (minerals 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.

Acknowledgements This study was carried out in the framework of a cooperation project on environmental technology transfer: the Subarnarekha Project, led in 1999–2003 by BRGM and the Geological Survey of India (GSI) and funded by the Indian and French governments. The isotopic studies were also supported by the research activities of BRGM on behalf of the French Ministry of Education and Research. The study was granted by the total, constant and enthusiastic support of the GSI Eastern Region Project Managers, Officers and by GSI personnel, who ensured that we obtained all the necessary scientific and technical support on time and with quality, as well as hospitality. Most mineralogical, chemical and isotopic analyses were performed in the BRGM Laboratories, France, but analytical results obtained by GSI laboratories, Eastern Region Chemical Division, were continuously available. Field analyses and sampling operations were performed first as teamwork between BRGM and GSI geoscientists, then by GSI teams with BRGM support.

References

Ballukraya PN, Sakthivadivel R (2002) Over exploitation and artificial recharge of hard rock aquifers of south India: issues and options. IWMI-Tata Water Policy Research program, International Water Management Institute, Mumbia, India, 14 pp. http://www.iwmi.org/iwmi-tata. Cited August 2007

Ben Othmann D, Luck JM, Tournoud MG (1997) Geochemistry and water dynamics: application to short time-scale flood phenomena in a small Mediterranean catchment. I: alkalis, alkali-earth and Sr isotopes. Chem Geol 140:9–28

Bullen TD, Krabbenhoft DP, Kendall C (1996) Kinetic and mineralogic controls on the evolution of groundwater chemistry and $^{87}Sr/^{86}Sr$ in a sandy aquifer, northern Wisconsin, USA. Geochim Cosmochim Acta 60:1807–1821

De Silva CS, Weatherhead EK (1997) Optimising the dimensions of agrowells in hard-rock aquifers in Sri Lanka. Agric Water Manage 33:117–126

Deshpande RD, Bhattacharya SK, Jani RA, Gupta SK (2003) Distribution of oxygen and hydrogen isotopes in shallow groundwaters from Southern India: influence of a dual monsoon system. J Hydrol 271:226–239

Dowling CB, Poreda RJ, Basu AR (2003) The groundwater geochemistry of the Bengal Basin: weathering, chemsorption, and trace metal flux to the oceans. Geochim Cosmochim Acta 67:2117–2136

Drever JI (1988) The geochemistry of natural waters, 2nd edn. Prentice Hall, Englewood Cliffs, NJ, 437 pp

Edmond JM, Palmer MR, Measures CI, Grant B, Stallard RF (1995) The fluvial geochemistry and denudation rate of the Guayana shield in Venezuela. Geochim Cosmochim Acta 59:3301–3325

Faure G (1986) Principles of isotope geology. Wiley, New York, 589 pp

Foster SSD, Chilton PJ, Moench M, Cardy F, Schiffler M (2000) Groundwater in rural development: facing the challenges of supply and resource sustainability. World Bank Technical Paper no. 463, World Bank, Washington, DC

Gaillardet J, Dupre B, Allegre CJ, Négrel Ph (1997) Chemical and physical denudation in the Amazon River Basin. Chem Geol 142:141–173

Galy A, France-Lanord C, Derry LA (1999) The strontium isotopic budget of Himalayan rivers in Nepal and Bangladesh. Geochim Cosmochim Acta 63:1905–1925

Ghosh SK, Sengupta S, Dasgupta S (2002) Tectonic deformation of soft-sediment convolute folds. J Struct Geol 24:913–923

Grosbois C, Négrel Ph, Fouillac C, Grimaud D (2001) An overview of dissolved and suspended matter fluxes in the Loire River Basin: natural and anthropogenic inputs. Aquatic Geochem 7:81–105

Gupta CP, Singh VS (1988) Flow regime associated with partially penetrating large-diameter wells in hard rocks. J Hydrol 103:209–217

Gupta SK, Deshpande RD, Bhattacharya SK, Jani RA (2005) Groundwater $\delta^{18}O$ and δD from central Indian Peninsula: influence of the Arabian Sea and the Bay of Bengal branches of the summer monsoon. J Hydrol 303:38–55

Hogan JF, Blum JD, Siegel DI, Glaser PH (2000) $^{87}Sr/^{86}Sr$ as a tracer of groundwater discharge and precipitation recharge in the Glacial Lake Agassiz, Peatlands, northern Minnesota. Water Res Resour 36:3701–3710

Huh Y, Edmond JM (1999) The fluvial geochemistry of the rivers of Eastern Siberia: III. tributaries of the Lena and Anabar draining the basement terrain of the Siberian Craton and the Trans-Baikal Highlands. Geochim Cosmochim Acta 63:967–987

Huh Y, Tsoi MY, Zaitsev A, Edmond JM (1998) The fluvial geochemistry of the rivers of Eastern Siberia: I. tributaries of the Lena River draining the sedimentary platform of the Siberian craton. Geochim Cosmochim Acta 62:1657–1676

IAEA (1981) Stable isotope hydrology: deuterium and oxygen-18 in the water cycle. In: Gat JR, Gonfantini R (eds) Technical Report Series 210, IAEA, Vienna, 339 pp

IAEA/WMO (2001) Global network of isotopes in precipitation: the GNIP database. IAEA, Vienna. http://isohis.iaea.org

Kamra SK, Lal K, Singh OP, Boonstra J (2002) Effect of pumping on temporal changes in groundwater quality. Agric Water Manage 56:169–178

Krishnamurthy J, Mani A, Jayaraman V, Manivel M (2000) Groundwater resources development in hard rock terrain: an approach using remote sensing and GIS techniques. Int J Appl Earth Observ Geoinform 2:204–215

Krishnaswami S, Trivedi JR, Sarin MM, Ramesh R, Sharma KK (1992) Strontium isotopes and rubidium in the Ganga-Brahmaputra river system: weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic $^{87}Sr/^{86}Sr$. Earth Planet Sci Lett 109:243–253

Leybourne MI, Goodfellow WD, Boyle DR (1998) Hydrogeochemical, isotopic, and rare earth element evidence for contrasting water-rock interactions at two undisturbed Zn-Pb massive sulphide deposits, Bathurst Mining Camp, N.B., Canada. J Geochem Exp 64:237–261

Majumdar N, Majumdar RK, Mukherjee AL, Bhattacharya SK, Jani RA (2005) Seasonal variations in the isotopes of oxygen and hydrogen in geothermal waters from Bakreswar and Tantloi, Eastern India: implications for groundwater characterization. J Asian Earth Sci 25:269–278

Meybeck M (1979) Concentrations des eaux fluviales en éléments majeurs et apports en solution aux océans [Major element concentrations in fluvial waters, and dissolved load inputs to the oceans]. Rev Géol Dyn Géog Phys 21:215–246

Meybeck M (1986) Composition chimique des ruisseaux non pollués en France [Chemical composition of unpolluted streams in France]. Sci Géol Bull 39:3–77

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DOI 10.1007/s10040-007-0227-4

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Morris BL, Lawrence ARL, Chilton PJC, Adams B, Calow RC, Klinck BA (2003) Groundwater and its susceptibility to degradation: a global assessment of the problem and options for management. Early Warning and Assessment Report Series, RS. 03-3, United Nations Environment Programme, Nairobi, Kenya

Négrel Ph, Casanova J (2005) Comparison of the Sr isotopic signatures in brines of the Canadian and Fennoscandian Shields. Appl Geochem 20:749–766

Négrel Ph, Deschamps P (1996) Natural and anthropogenic budgets of a small watershed in the Massif Central (France): chemical and strontium isotopic characterization in water and sediments. Aquatic Geochem 2:1–27

Négrel Ph, Lachassagne P (2000) Geochemistry of the Maroni River (French Guyana) during low water stage: implications for water rock interaction and groundwater characteristics. J Hydrol 237:212–233

Négrel Ph, Pauwels H (2004) Interaction between different groundwaters in Brittany catchments (France): characterizing multiple sources through strontium- and sulphur isotope tracing. Water Air Soil Pollut 151:261–285

Négrel Ph, Allègre CJ, Dupré B, Lewin E (1993) Erosion sources determined from inversion of major, trace element ratios and strontium isotopic ratio in riverwater: the Congo Basin case. Earth Planet Sci Lett 120:59–76

Négrel Ph, Casanova J, Aranyossy JF (2001) Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: the Vienne case (France). Chem Geol 177:287–308

Négrel Ph, Petelet-Giraud E, Widory D (2004) Strontium isotope geochemistry of alluvial groundwater: a tracer for groundwater resources characterisation. Hydrol Earth System Sci 8:959– 972

Négrel Ph, Dewandel B, Gandolfi JM, Dayal AM, Pauwels H, Roy S, Flehoc C (2007) Stable isotope hydrogeology of the Maheshwaram watershed (Andra Pradesh, India). 3rd International Groundwater Conference (IGC-2007) on Water, Environment and Agriculture, Combinatore, India, 7–10 Feb. 2007

Neretnieks I (2002) A stochastic multi-channel model for solute transport-analysis of tracer tests in fractured rock. J Contam Hydrol 55:175–211

Pande K, Sarin MM, Trivedi JR, Krishnaswami S, Sharma KK (1994) The Indus river system (India-Pakistan): major ion chemistry, uranium and strontium isotopes. Chem Geol 116:245–259

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2): acomputer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geol Surv Water Resour Invest Rep 99-4259, 312 pp

Pitkänen P, Kaija J, Blomqvist R, Smellie JAT, Frape SK, Laaksoharju M, Négrel Ph, Casanova J, Karhu J (2002) Hydrogeochemical interpretation of groundwater at Palmottu. Paper EUR 19118 EN, European Commission, Brussels, pp 155–167

Robins NS, Smedley PL (1994) Hydrogeology and hydrogeochemistry of a small, hard-rock island: the heavily stressed aquifer of Jersey. J Hydrol 163:249–269

Sarin MM, Krishnaswami S, Dilli K, Somayajulu BL, Moore WS (1989) Major ion chemistry of the Ganga-Brahmaputra river system: weathering processes and fluxes to the Bay of Bengal. Geochim Cosmochim Acta 53:997–1009

Sikdar PK, Sarkar SS, Palchoudhury S (2001) Geochemical evolution of groundwater in the Quaternary aquifer of Calcutta and Howrah, India. J Asian Earth Sci 19:579–594

Singh SK, Trivedi JR, Pande K, Ramesh R, Krishnaswami S (1998) Chemical and strontium, oxygen, and carbon isotopic compositions of carbonates from the Lesser Himalaya: implications to the strontium isotope composition of the source waters of the Ganga, Ghaghara, and the Indus rivers. Geochim Cosmochim Acta 62:743–755

Singh RV, Sinha RM, Bisht BS, Banerjee DC (2002) Hydrogeochemical exploration for unconformity-related uranium mineralization: example from Palnadu sub-basin, Cuddapah Basin, Andhra Pradesh, India. J Geochem Expl 76:71–92

Singhal DC, Niwas S, Singhal BBS (1988) Integrated approach to aquifer delineation in hard rock terrains: a case study from the Banda District, India. J Hydrol 98:165–183

Stüber D, Berner Z, Chandrasekharam D, Karmakar J (2003) Arsenic enrichment in groundwater of west Bengal, India: geochemical evidence for mobilization of As under reducing conditions. Appl Geochem 18:1417–1434

Talbot CJ, Sirat M (2001) Stress control of hydraulic conductivity in fracture-saturated Swedish bedrock. Eng Geol 61:145–153

Zhang J, Huang WW, Liu MG, Zhou Q (1990) Drainage basin weathering and major element transport of two large Chinese rivers (Huanghe and Changjiang). J Geophys Res 95:13277–13288

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