O, H and Sr isotopes tracing the migration distance of mining, ore processing and metallurgical activities end-products in a river basin (Subarnarekha River, India)

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O, H and Sr isotopes tracing the migration distance of mining, ore processing and metallurgical activities end-products in a river basin (Subarnarekha River, India)

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Abstract

This study reports on the geochemistry of surface- and groundwaters along the Subarnarekha River system (north-eastern India). Multi-isotopic approaches (Sr, O, H) have been applied for tracing the water origin and pathways and investigate how far pollutants released by mining, ore processing and metallurgical activities can migrate at the catchment scale. Results of the Sr isotope systematics did not provide any evidence of mining processes-derived minerals impacts on the water. Pollution from mining activities entering the river are transported to the estuary as non-impacting fine fractions.

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Keywords: river basin, strontium isotopes, weathering, stable isotopes

1. Introduction

Regarding regional-level environmental impact assessment investigation, the extent of polluted areas by industrial activities at river catchment scale is crucial to define[1]. In areas where multiple potential sources are present (mining, metallurgy, industrial activities), metal pollution of water is associated with mine runoff and wastewater discharges. How different migration scales may coexist in a given soil-groundwater-surface water system, according to chemical vector and water flow variations is still a matter of debate[1]. In order to better

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understand the water interactions behind such migration pattern, isotope tracing (O, H, Sr) was applied in the Subarnarekha river system, from the upper part of the catchment towards the estuary. The Subarnarekha river basin is located in north-eastern India, rising in southern Bihar state (Figure 1) and flows eastwards through the Singhbhum copper mining region. Continuing eastwards, it enters the Bay of Bengal after a 470-kilometre course.

Here we investigate, at the river catchment scale, how far pollutants released by mining, ore processing and metallurgical activities can migrate using tracers of the water movements. Strontium isotope ratios are used to trace the degree of water-rock interaction and mixing processes in water[2,3] while stable isotopes provide an insight into the water origin[1,4]. Surface water samples were collected from the Subarnarekha in the area 40 km south-east of Jamshedpur[2] (East Singhbhum district, Jharkhand state). Small or medium-sized tributaries (e.g. nallahs or nalas) were also sampled all along the Subarnarekha River (Dhutra, Garrah, Royam, Sankh, referred in Négrel et al.[1] and Sirsa, Rajghat Jaleswar, Dahi, Sujapur, Dagara from this study) up to the estuary (Dagara estuary).

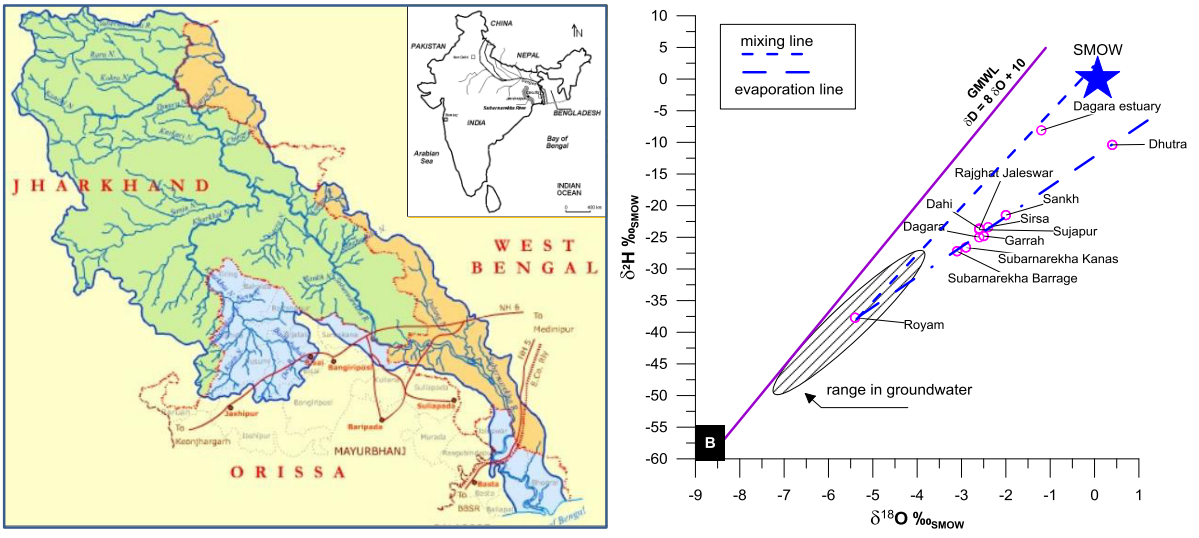

Fig. 1. a) From ref. 1 Location map of the Subarnarekha River basin, from www.dowrorissa.gov.in. b) δ^2H - $\delta^{18}O$ isotope in the Subarnarekha River basin. The range of $d^{18}O$-d^2H in groundwater is from Négrel et al.[2]. SMOW is the Standard Mean Ocean Water.

2. H and 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[4]. The deuterium and oxygen isotopic ratios are reported in figure 1 in per mil deviations from the international SMOW (Standard Mean Ocean Water) following $\delta = [(R_{sample}/R_{standard}) - 1] \times 1000$ 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 analyzed using a Finnigan MAT 252 mass spectrometer with an average precision, based on multiple analyses of various samples and laboratory standards was ± 0.1 ‰ for $\delta^{18}O$ and ± 0.8 ‰ for δ^2H.

The global meteoric water line (GMWL, $\delta^2H = 8 \times \delta^{18}O + 10$) is indicated, reflecting the meteoric input in this area[2]. Groundwater samples, collected from tube wells used for drinking water, are plotted in Figure 1 as a grayed field[2]. The samples plot near the global meteoric water line, with a shift to the right of this line, reflecting mainly a meteoric origin for the water with slight effect of evaporation. This suggests a rapid transfer from rainfall towards groundwater through soils and the unsaturated zone. From the evidence of the meteoric recharge, two trends can be identified. The first relies the groundwater field to the value of the seawater (SMOW in Figure 1b) and only one river water sample plot along this trend (Dagara estuary). This reflects the mixing between seawater (with a SMOW δ^2H - $\delta^{18}O$ signature) and water with a meteoric signature and validates the lack of influence of seawater and/or seasalts on the rest of the surface water samples. The second trend relies all surface water samples, starting with the

Nala Royam and ending with the Nala Duhtra and corresponds to an evaporation line[2,4]. The δ^2H - $\delta^{18}O$ signature of the Nala Royam mimics those of the groundwater, reflecting the meteoric origin of the water and the weak evaporation. Contrary to that, the δ^2H - $\delta^{18}O$ signature of the Nala Duhtra reflects the largest evaporation of the water found in the area. All other surface water samples plot along this evaporation line reflecting the impact of evaporation processes during the flow of water.

3. Upshot of strontium isotopes

A standard procedure was adopted for the chemical separation and mass spectrometry of strontium[3]. After chemical separation, the sample was analyzed using a Finnigan MAT 262 multiple collector mass spectrometer. The $^{87}Sr/^{86}Sr$ ratios were normalized 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 $^{87}Sr/^{86}Sr$ = 0.710227 ± 17. 10^{-6} (2σ, n = 70). Inductively coupled plasma mass spectrometry was used to measure Sr concentration with a precision greater than ± 5%.

Strontium content varies less in surface water samples, between 107 (Subarnarekha Barrage) and 122 µg L^{-1} (Nala Gara) whereas strontium isotopes display a wide variation from 0.71836 (Nala Dhutra) to 0.80518 (Nala Royam). In the Subarnarekha River system, the variations of the $^{87}Sr/^{86}Sr$ 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[2,5]. As stated by Négrel et al.[2], the Sr isotopes in the Subarnarekha River system correspond to three end-members (rainwater input and water-rock interaction but with large anthropogenic inputs, mainly agricultural in origin). A comparison of the $^{87}Sr/^{86}Sr$ versus the 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 (Figure 2a). It is worth noting that (i) the large variation in the $^{87}Sr/^{86}Sr$ ratios corresponds to a relatively restricted range of Sr contents, with the exception of the Dagara estuary sample, and (ii) the highest $^{87}Sr/^{86}Sr$ ratios correspond to relatively low Sr contents.

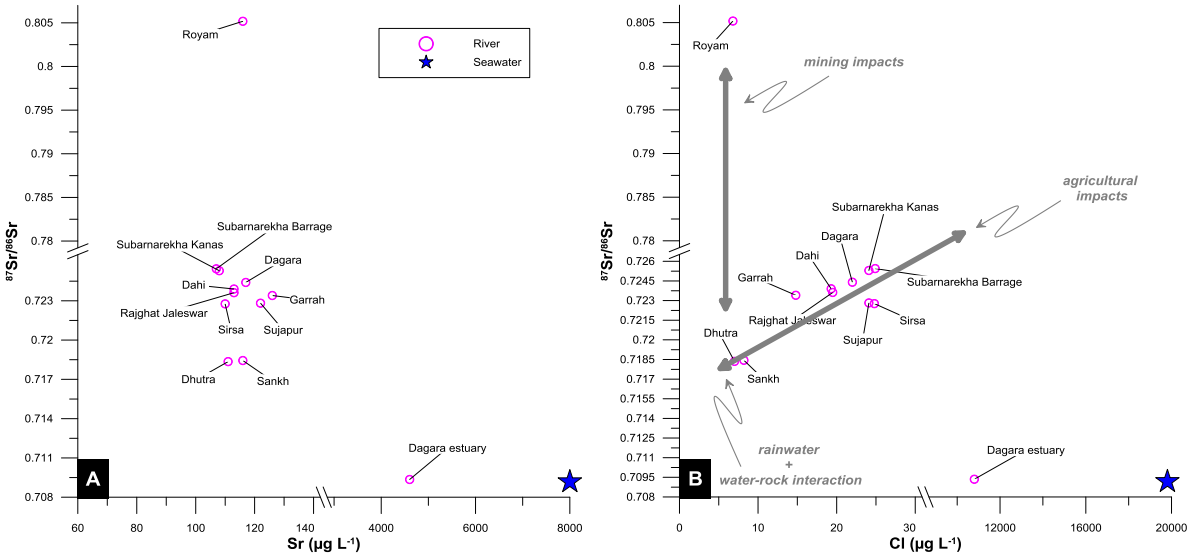

Fig. 1. a) $^{87}Sr/^{86}Sr$ ratios versus the Sr content, b) $^{87}Sr/^{86}Sr$ ratios versus the Cl content in the Subarnarekha River

Within the restricted range of Sr contents, the lowest $^{87}Sr/^{86}Sr$ ratios are from Nala Dhutra and Nala Shankh, while conversely, the highest $^{87}Sr/^{86}Sr$ ratio corresponds to Nala Royam. The sample from the Dagara estuary shows

a high Sr content (around 4.6 mg L^{-1}) and a low $^{87}Sr/^{86}Sr$ ratio (0.70935), reflecting the influence of seawater in the mixing (seawater: Sr content around 8 mg L^{-1} and $^{87}Sr/^{86}Sr$ ratio of 0.70917). Comparing the Sr isotope ratios and the chloride contents (Figure 2b) argues further in favor of these end-members. Rivers marked by rainwater input and water-rock interaction display the lowest Cl contents (7-8 mg L^{-1}) and low $^{87}Sr/^{86}Sr$ ratios (around 0.718) while rivers more marked by anthropogenic inputs show and increase in the Cl contents (up to 25 mg L^{-1}) and in the $^{87}Sr/^{86}Sr$ ratios (up to 0.723-0.725). The natural background, corresponding to Nala Royam which drains a large area of mine tailings[2], has a low Cl content (around 7 mg L-1) and the highest $^{87}Sr/^{86}Sr$ ratio ever measured in river water. 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. Up to the estuary, the rest of the surface waters plot within these end members, e.g. rainwater input and water-rock interaction and agricultural inputs. The Sr isotope data do not provide any insight on slag disposal and deposition along the Subarnarekha. The lack of any accumulation of sediments with mine patterns, and the weakness of the marine Sr isotopic signature suggest that most of the metalliferous load may even be washed out to sea by tidal currents.

4. Summary

Isotope tracing in this hydrosystem highlights the role of evaporation processes in the surface waters along the Subarnarekha River through the O and H tracing. The O and H isotopes also highlight the weak role of the saline water from the estuary. The Sr isotopes demonstrate the role of anthropogenic disturbances on the $^{87}Sr/^{86}Sr$ ratio through its increase at the same level of Sr content. This role is also demonstrated by the comparison with Cl contents as an anthropogenic fingerprint. However, the weathering of mining processes-derived minerals (with a high $^{87}Sr/^{86}Sr$ ratio) does not release Cl to the water as reflected by the plot of the $^{87}Sr/^{86}Sr$ ratio versus Cl contents. Thus the anthropogenic disturbance is more linked to other types of activities such as agriculture and no evidence can be seen through the Sr isotope systematics of mining processes-derived minerals. The lower Subarnarekha Basin does not seem to be significantly contaminated by heavy metals released from the industrial activity of the Cu mining area, despite evidence for significant input (Giri & Singh, 2014). The polluting metals that do enter the river are transported to the estuary within the fine fractions and then randomly disseminated at low levels and no impacts on the water can be evidenced.

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