Bulletin of Environmental Contamination and Toxicology (2023) 111:7
https://doi.org/10.1007/s00128-023-03747-z

Distribution, Source Identification, and Output flux of Barium in Surface Waters in the Sanjiangyuan Region and Qilian Mountain Region of Tibetan Plateau

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Received: 29 March 2023 / Accepted: 19 May 2023 / Published online: 24 June 2023

Abstract

Water safety concerning Barium (Ba) has become a public issue worldwide. As the "Asian water tower", Tibetan Plateau is the birthplace of many rivers. However, the distribution, source, and output flux of Ba are largely unknown. In this study, surface water samples were collected from different catchments in the Sanjiangyuan Region (SJY) and the Qilian Mountain Region (QLM) in Tibetan Plateau. The concentration of Ba was determined by inductively coupled plasma optical emission spectroscopy, the source of Ba was discussed by a Gibbs diagram, and the output flux of Ba was estimated using the observation data from different hydrological stations. The results showed that the Ba concentrations were less than 160 µg/L, which is much lower than the guideline value of 700 µg/L for surface waters. The main sources of Ba were rock weathering and evaporation concentration. The total Ba output flux from SJY and QLM to downstream waters was 1,240 t/yr, which accounts for about 0.01% of the global freshwater Ba output flux to the ocean. The Ba production rate in Tibetan Plateau was comparable with that in the Arctic rivers. Under the scenario of global warming, water safety issues concerning Ba will be more serious since the output flux of Ba to downstream waters will be increased by intensified rock weathering, evaporation concentration, glacial retreat, and permafrost thawing. This study reveals the Ba flux and production rate in Tibetan Plateau, which will provide important information for evaluating the environmental impact of global warming on public health.

Keywords Tibetan Plateau · Freshwater · Barium · Climate change · Output flux

Introduction

As an alkaline earth metal, Barium (Ba) usually occurs in nature as minerals, including barite ($BaSO_4$) and carbonates ($Ca(Ba)CO_3$) (Lu et al. 2018). It is typically enriched in volcanic products and sedimentary volcanic by-products (Cuoco et al. 2013; Kravchenko et al. 2014). Ba and its compounds have many industrial and commercial applications, including in the production of glass, ceramics, paints, and rubber (Emsley 2011). However, the potential exposure to high levels of Ba can be harmful to human health and has caused public concerns (Quiriny et al. 2017).

The Ba in natural waters can be from natural and anthropogenic sources. The natural sources of Ba include soil erosion, atmospheric deposition, rock weathering, hydrothermal and glacial melting, and permafrost thawing (Dalai et al. 2002; Das and Krishnaswami 2006; Paudyal et al. 2016). The anthropogenic Ba sources include wastewater

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discharged from industrial activities and agricultural fertilizers, etc. (Franciskovic-Bilinski 2006; Sebesta et al. 1981). Dissolved Ba mainly comes from runoff erosion and rock weathering effect, then participates in the geochemical cycle on the surface earth (Taylor et al. 1983). These physical and chemical processes play a vital role in controlling the concentration of Ba in natural water. In particular, the Ba stored in glaciers and permafrost is also a possible source of Ba in water (St Pierre et al. 2018). Therefore, understanding the sources of Ba in natural waters is important for predicting and handling related public health issues.

Tibetan Plateau is called the "Asian water tower" because it is the origin of many large rivers, including the Indus River, the Brahmaputra River, the Ganges River, the Salween River, the Mekong River, the Yangtze River, and the Yellow River. Water from Tibetan Plateau is relatively clean. Accompanied by global warming (IPCC, 2014), the melting of glaciers and permafrost accelerates the water cycle in Tibetan Plateau, intensifies the erosion of the crust surface, and potentially increases heavy metals including Ba in the surface runoff (Jiao et al. 2021). Therefore, knowledge of the concentration of Ba in Tibetan Plateau helps to understand the baseline level of Ba in river waters and will be informative for heavy metal monitoring and management under climate change. However, little information has been revealed so far concerning the Ba in the headwater regions of Tibetan Plateau.

This work selected the Sanjiangyuan Region (SJY) and Qilian Mountain Region (QLM) as study areas because they are representative mountainous areas with glaciers in Tibetan Plateau. The concentration of Ba and other hydrochemical parameters in the surface runoff from SJY and QLM were determined, aiming to (1) investigate the spatial patterns of Ba in Tibetan Plateau, (2) identify the source of

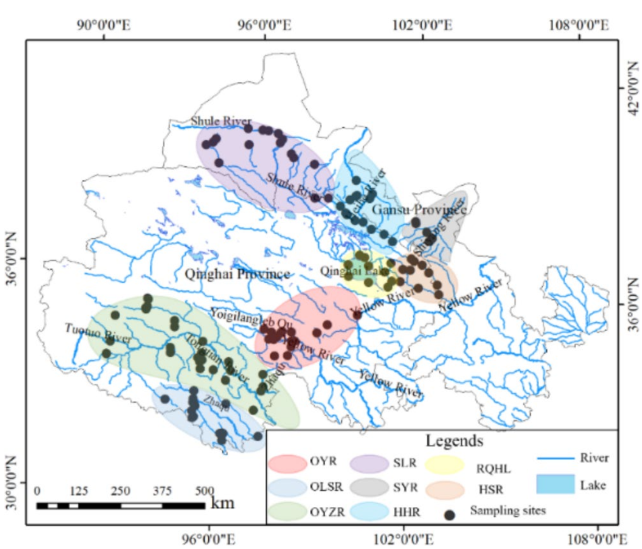

Fig. 1 The map of the study area with sampling sites

Ba in the river waters, and (3) estimate the Ba output flux from Tibetan Plateau to the downstream waters.

Materials and Methods

Description of the Study area

The Sanjiangyuan Region (SJY) and Qilian Mountain Region (QLM) are located in the central and northern parts of Tibetan Plateau, respectively (Fig. 1). SJY is also called the Three-River Headwater Region, including the origin areas of the Yangtze River, Yellow River, and Lantsang River. The average altitude of SJY is above 4,400 m a.s.l., and the area is about 302,000 km^2 (Xu et al. 2018). The QLM is at the northern edge of Tibetan Plateau, with an average altitude of 2,298.36 m a.s.l. and an area of 26,500 km^2. It is also a part of the boundary between the Arid zone and Semi-Arid zone with a typical continental alpine semi-humid mountain climate. There are three inland rivers in QLM, named Heihe River, the Shule River, and the Shiyang River, all of which are less than 1,000 km in length.

Sample Collection

Surface water samples were collected in the SJY and QLM from August to October 2019 (Fig. 1). Sampling sites were distributed in 5×5 grids (less than 50 km × 50 km) from the mainstreams to tributaries of the rivers. We collected water samples in mainstreams, tributaries, lake inlets, and near hydrological stations to best represent the dendrogram structures of the waterways. There were 68 sites in the SJY, including the origin of the Yangtze River (OYZR), the origin of the Yellow River (OYR), and the origin of the Lantsang River (OLSR). There were 76 sites in the QLM, including the Shule River (SLR), the Heihe River (HHR), the Shiyang River (SYR), the Huangshui River (HSR), and the rivers flowing into the Qinghai Lake (RQHL). The parallel samples were collected as less than 10% of total sampling sites, which were 7 and 8 parallel samples in SJY and QLM, respectively.

Sample Analysis

Water quality parameters, including pH, oxidation reduction potential (ORP), electrical conductivity (EC), salinity (Sal), total dissolved solids (TDS), and dissolved oxygen (DO), were measured in situ with a portable water quality instrument (ODEN, PONSEL, France) during field sampling. The water samples were filtered by a 0.45 µm membrane (MF-Millipore®, Millipore Sigma, USA). The filtered samples were then kept in Teflon bottles and transferred to the laboratory with cooling systems with a temperature of around 4 ℃.

The concentrations of Ba, Na, Ca, and Mg in water samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian ICP735-ES) in ALS Minerals-ALS Chemex (Guangzhou). The relative standard deviation was less than 4%. The recovery of standard material (ALSWAT01) was 102 ± 5% and the blank value was less than 20 μg/L. The concentrations of major anions (Cl^-, F^-, NO_3^-, SO_4^{2-}) were measured by ion chromatograph (ICS-90) with a relative standard deviation of less than 0.5% and a spike recovery between 90% and 110%.

Gibbs Distribution Model of Hydrochemistry

The ions in natural water mainly come from three natural sources, including atmospheric deposition, rock weathering, and evaporation concentration (Qu et al. 2019). The Gibbs diagram was applied to investigate the sources of Ba in natural waters (Gibbs 1970). The Gibbs diagram takes TDS as the y-axis and the molar concentration ratio of $Na^+/(Na^++Ca^{2+})$ or $Cl^-/(Cl^-+ HCO_3^-)$ as the x-axis. The ratio diagram of TDS to $Na^+/(Na^++Ca^{2+})$ was used to determine the main sources of ions in the water samples.

Output Fluxes of Ba

The output flux of Ba from the rivers in SJY and QLM to the downstream was calculated according to traditional methods as follows (Samanta and Dalai 2016; Zhang et al. 2013):

$$W = C \times Q \times 10^{-6} \tag{1}$$

$$F = \frac{W}{S} \tag{2}$$

where *W* indicates the annual Ba output flux (kg/yr), C is the concentration of Ba (μg/L), Q is the runoff of the river (m^3), S is the catchment area, and F is the mass of Ba per unit area ($kg/km^2/yr$). The value of F evaluates the Ba yield from the different drainage areas (Alexander et al. 2008).

The discharge data in SJY were acquired from three hydrological stations, including the Zhimenda Hydrological Station, the Tangnaihai Hydrological Station, and the Qamdo Hydrological Station in Qinghai Province (Zhang et al. 2013). The discharge data in QLM was extracted from real-time data released by the Gansu Provincial Water Resources Bureau. The discharge data of HSR, HHR, SLR, and SYR were acquired from the Liancheng Hydrological Station, Yingluoxia Hydrological Station, Changmabao Hydrological Station, and Zamusi Hydrological Sation (He et al. 2011). The RQHL was calculated as a simple sum of the output flux of Ba from the rivers flowing into it. The production rate was calculated based on the Ba flux against the watershed area to evaluate the potential of the Ba yield in the drainage area. When comparing the output flux of Ba in Tibetan Plateau with that of the global rivers to the ocean, we have deducted the output flux of inland rivers.

Statistical Analysis

One-way ANOVA was applied as the main statistical technique to compare the concentrations of Ba in different catchments. Principal component analysis was used to evaluate the potential sources of trace elements in the catchment. Pearson correlation coefficient was used to determine the correlation between Ba and other hydrochemical parameters. All statistical analyses were performed by SPSS V26.

Results and Discussion

The Physicochemical Parameters in River Waters

As shown in Table S1 in Supplementary material, the surface water in SJY and QLM was alkaline. The salinity in SJY was higher than that in QLM. The DO in the QLM was higher than that of SJY, which may be due to the lower altitude in QLM than that in the SJY. The ORP in the water in SJY was higher than the water in QLM. According to the EC and TDS, the ion concentration in the samples in YZR was significantly higher than the samples in the rest of the regions.

In SJY, the temperature, pH, EC, and DO showed no significant difference among OYR, OYZR, and OLSR. The ORP in LSR was higher than OYR and OYZR. The TDS and Sal in OYZR were higher than OYR and OLSR, this may indicate that there exists strong evaporation and concentration in OYZR. In QLM, the pH and Sal showed no significant difference among the five study regions. The ORP in HSR and HHR was relatively low. The EC and TDS in HSR and RQHL were lower than SYR, HHR, and SLR, which may be influenced by rock weathering.

Ba in River Waters

The mean Ba concentration in the water of SJY and QLM were 60.8 ± 29.9 μg/L and 59.8 ± 15.9 μg/L (Fig. 2). Specifically, the mean Ba concentration in water from OYR, OYZR, and the OLSR was 63.8 ± 14.1 μg/L, 61.7 ± 44.8 μg/L, and 62.5 ± 23.8 μg/L, respectively. As a tributary of the Yellow River, HSR showed a mean Ba concentration of 75.0 ± 7.6 μg/L. The SLR, HHR, and SYR are three inland rivers with an average

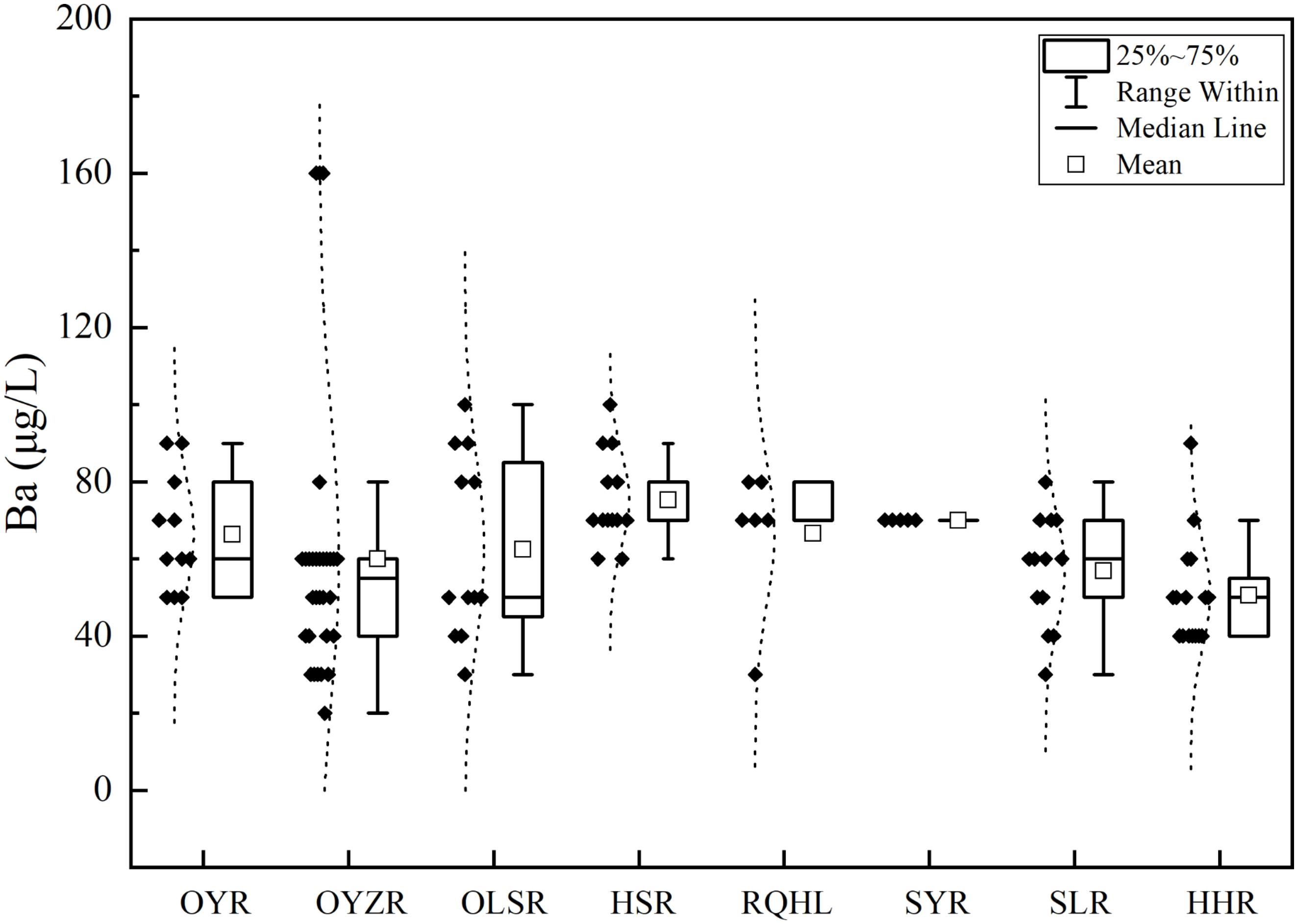

Fig. 2 The Ba concentration characteristics in different river water samples from SJY and QLM.

Ba concentration of 55.9 ± 14.2 μg/L. The mean Ba concentration in RQHL was 66.7 ± 17.0 μg/L (Fig. 2).

One-way ANOVA tests indicated that the Ba concentration in SJY and QLM were not significantly different ($p > 0.05$). On the whole, the Ba concentration in the study regions was less than 700 μg/L (the guideline value for Ba in surface water by World Health Organization (World Health Organization 2004) and the government of China (Ministry of Environmental Protection of China, 2002)), which indicated the surface water had no direct threat to human health.

The spatial variability of Ba concentration in water samples can be shown in Fig S1. The largest Ba variation was shown in OYZR, with the highest Ba concentration in the Tuotuo River and the Tongtian River, and with the lowest Ba concentration downstream of the OYZR. In SLR and HHR, higher Ba concentration in the downstream was shown than in the upstream. There exists spatial variability in the study region. In OYZR, the Ba concentration upstream is higher than downstream, and that is the opposite in QLM.

Origins of Ba in River Waters in Tibetan Plateau

The correlation analysis shows that Ba was significantly correlated with Ca^{2+}, K^+, $Na^{+,}$ and Sr^{2+} ($p < 0.01$) (Table S2), which indicated that the sources of Ba in the water should be the same as the Ca^{2+}, K^+, $Na^{+,}$ and Sr^{2+} in water. Principal component analysis was also applied to analyze the source of Ba in water (Fig S2) and two components were found. PC1 is related to the Ca^{2+}, Na^+, and K^+, and it can explain 71.48% of Ba in water. PC2 is related to Si, and it can explain 10.93% of Ba in water. The principal component analysis results confirmed that the sources of Ba in the water should be the same as the major ions in water.

To further trace the source of ions in the river water, the Gibbs diagram was employed. Based on the TDS to $Na^+/(Na^+ + Ca^{2+})$ in the river water of SJY and QLM, the Gibbs diagram was plotted as shown in Fig. 3. The results showed that the ions in the river water of the two regions mainly fall in the region of rock dominance end-member and evaporation and precipitation end-member. It can be inferred that rock weathering in the watershed and the evaporation

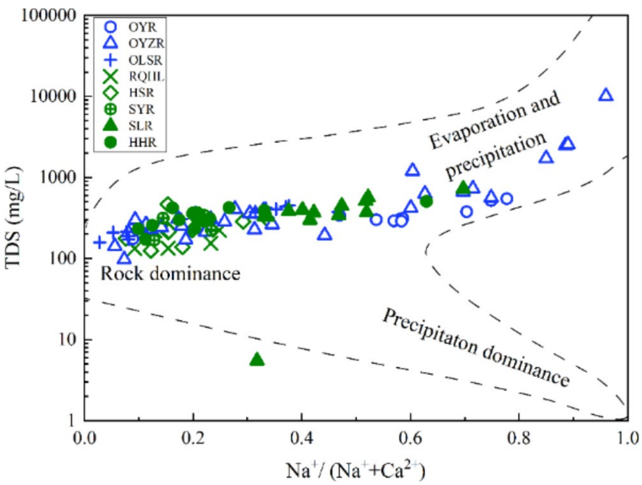

Fig. 3 The Gibbs diagram of the SJY and the QLM.

crystallization process controlled the composition of ions in the water of the rivers. The ions in the river water of the SJY mainly fall in the rock weathering and the evaporation concentration end-member on an average basis, while QLM mostly falls in the rock dominance end-member, and just a small part falls in the evaporation concentration area. The results are compliant with the significant difference of annual evaporation in SJY (~1400.9 mm) and QLM (~800.0 mm) (Jia et al. 2009; Qi et al. 2015) In addition, In SJY, the ions in OYR are mainly affected by rock weathering and evaporation, LSR is mainly affected by rock weathering, and OYZR is affected by the two mechanisms, rock weathering, and evaporating. In QLM, the RQHL, HSR, SYR, and HHR are mainly affected by rock weathering in basins, while SLR was also affected by evaporation and concentration besides rock weathering. Furthermore, based on the significant positive correlation between Ba and ions in river water, the Ba in the water can be from the same sources as the main ions, which are mainly controlled by rock weathering and evaporation.

The different compositions of ions in the river are the result of the weathering of the combinations of the rocks (carbonates, silicates, and evaporites) in the watershed (Chen et al. 2002; Hu et al. 1982). Ca^{2+} and Mg^{2+} are mainly derived from weathering and dissolution of carbonate rocks, silicate rocks, and hydrogenic rocks, while Na^{+} and K^{+} are mainly derived from the weathering of hydrogenic and silicate rocks, Si is mainly derived from silicates (Gaillardet et al. 1999). In the OYZR, silicate, and carbonate are the main rocks (Wu et al. 2008), which are easy to be weathered. This is consistent with the highest concentration of Ba in OYZR. Above all, the river Ba was mainly controlled by rock weathering and evaporation in SJY and QLM.

Ba Output flux

The Ba output flux and production rate were estimated according to the flow rate and the Ba concentration in the rivers (Table S3). Due to the variance of the flow rate, Ba concentration, and the watershed area, the Ba output flux in the eight catchments varied from 18 to 399 t/yr. The average Ba output flux in inland rivers in Tibetan Plateau was significantly lower than that of the global rivers to the ocean ($p < 0.001$). The Ba output flux in SJY was higher than QLM. The Ba output flux from the OYR was highest to be 399 t/yr. While the two inland rivers (HHR and SYR) showed the lowest Ba output flux at 18 t/yr. The total flux of riverine Ba in SJY (in OYR, OYZR, and OLSR) and QLM (in HSR) downstream was 240 t/yr. It accounted for approximately 0.01% of the output Ba flux of the global rivers to the Ocean (Rahman et al. 2022). The Ba fluxes from RQHL to the Qinghai Lake were 89 t/yr and will be enriched in the lake because of Ba precipitation.

The production rate of Ba in SJY and QLM was much lower than that of the large rivers around the world (Table S3), possibly because that less water pollution occurred in Tibetan Plateau. The average Ba production rate in SJY and QLM was 7.38 $kg/km^2/yr$, ranging from 1.69 to 21.1 $kg/km^2/yr$. The Ba production rates in SJY were lower than QLM, which was compliant with the SJY being the headwater region. In General, the Ba production rates in the large rivers with typical strong human activities were high. And the Ba production rates in SJY were comparable with the Yenisey River, which is an Arctic river in Siberia with the typical low human activity as Tibetan Plateau. Under the global warming scenario, high runoff and high erosion resulting from the glaciers retreating and permafrost melting will lead to an increase of the output flux of Ba in the river in Tibetan Plateau. The illustration of the Ba flux and production rate in Tibetan Plateau will aid to evaluate the environmental impact of global warming.

Conclusions

There was generally low and safe Ba concentration in the surface water with no significant difference between SJY and QLM. A large variation of Ba concentration was in the OYZR and the highest Ba concentration was the upstream of Tuotuo River and Tongtian River. The sources of Ba in SJY and QLM were mainly rock weathering and evaporation. The total Ba output flux from SJY and QLM to downstream was 1,240 t/yr which accounts for ~0.01% of the output Ba flux from global rivers to the ocean. The Ba production rates in Tibetan Plateau were comparable with that in the Arctic River. This study illustrates the Ba flux and production rate in Tibetan Plateau which will be important to evaluate the environmental impact of global warming.

Acknowledgements This study was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No.: XDB40020400), the Strategic Priority Research Program of the Chinese Academy of Sciences, Pan-Third Pole Environment Study for a Green Silk Road (Pan-TPE) (Grant No.: XDA20040502), and National Natural Science Foundation of China (Grant No.: 41877405).

Declarations

Competing Interests The authors have no competing interests to declare that are relevant to the content of this article.

References

Alexander RB, Smith RA, Schwarz GE et al (2008) Differences in phosphorus and nitrogen delivery to the gulf of Mexico from the Mississippi river basin. Environ Sci Technol 42(3):822–830
Chen JS, Wang FY, Xia XH et al (2002) Major element chemistry of the Changjiang (Yangtze River). Chem Geol 187(3–4):231–255
Cuoco E, Tedesco D, Poreda RJ et al (2013) Impact of volcanic plume emissions on rain water chemistry during the January 2010 Nyamuragira eruptive event: implications for essential potable water resources. J Hazard Mater 244–245:570–581
Dalai TK, Krishnaswami S, Sarin MM (2002) Barium in the Yamuna River System in the Himalaya: sources, fluxes, and its behavior during weathering and transport. Geochem Geophy Geosy. 3https://doi.org/10.1029/2002gc000381
Das A, Krishnaswami S (2006) Barium in Deccan basalt rivers: its abundance, relative mobility and flux. Aquat Geochem 12(3):221–238
Emsley J (2011) Nature's building blocks: an AZ guide to the elements. Oxford University Press
Franciskovic-Bilinski S (2006) Barium anomaly in Kupa River drainage basin. J Geochem Explor 88(1–3):106–109
Gaillardet J, Dupre B, Louvat P et al (1999) Global silicate weathering and CO2 consumption rates deduced from the chemistry of large rivers. Chem Geol 159(1–4):3–30
Gibbs RJ (1970) Mechanisms controlling world water chemistry. Science 170(3962):1088–1090
He B, Zhang Y, Zhu J, Wei S et al (2011) Analysis of the features of the mountainous runoff in three inland river basins of Qilian mountain during recent 50 years. J Water Res Plan Man 22(5):11–15
Hu MH, Stallard RF, Edmond JM (1982) Major ion chemistry of some large chinese rivers. Nature 298(5874):550–553
Jia WX, He YQ, Wang XF et al (2009) Temporal and spatial change of the potential evaporation over Qilian mountains and Hexi corridor from 1960 to 2006. Adv Water Resour 20(2):159–167
Jiao X, Dong Z, Kang S et al (2021) New insights into heavy metal elements deposition in the snowpacks of mountain glaciers in the eastern tibetan Plateau. Ecotox Environ Safe, 207
Kravchenko J, Darrah TH, Miller RK et al (2014) A review of the health impacts of barium from natural and anthropogenic exposure. Environ Geochem Health 36(4):797–814
Lu Q, Xu X, Xu Z et al (2018) Barium concentrations and speciation in surface waters collected from an active barium mining area in Guizhou Province, southwestern China. Environ Sci Pollut R 25(8):7608–7617
Ministry of Environmental Protection of China (2002) Environmental quality standards for surface water (GB 3838 – 2002)
Paudyal R, Kang S, Sharma CM et al (2016) Major ions and trace elements of two selected rivers near Everest region, southern Himalayas, Nepal. Environ Earth Sci, 75(1)
Qi D, Li X, Xiao H et al (2015) Study on changing characteristics and impact factor of evaporation over three-river source area in recent 50 years. Resour and Environ in the Yangtze Basin 24(9):1613–1620
Qu B, Zhang Y, Kang S et al (2019) Water quality in the Tibetan Plateau: major ions and trace elements in rivers of the "Water Tower of Asia. Sci Total Environ 649:571–581
Quiriny M, Dekeyser C, Moreau M et al (2017) Benign tumors of the parotid gland: a retrospective study of 339 patients. Acta Chir Belg 117(4):227–231
Rahman S, Shiller AM, Anderson RF et al (2022) Dissolved and particulate barium distributions along the US GEOTRACES North Atlantic and East Pacific zonal transects (GA03 and GP16): global implications for the marine barium cycle. Global Biogeochem Cy, 36(6)
Samanta S, Dalai TK (2016) Dissolved and particulate barium in the Ganga (Hooghly) River estuary, India: Solute-particle interactions and the enhanced dissolved flux to the oceans. Geochim Cosmochim Ac 195:1–28. https://doi.org/10.1016/j.gca.2016.09.005
Sebesta F, Benes P, Sedlacek J et al (1981) Behavior of radium and barium in a system including uranium-mine waste-waters and adjacent surface waters. Environ Sci Technol 15(1):71–75
St Pierre KA, Zolkos S, Shakil S et al (2018) Unprecedented increases in total and methyl mercury concentrations downstream of retrogressive thaw slumps in the western canadian Arctic. Environ Sci Technol 52(24):14099–14109
Taylor SR, McLennan SM, McCulloch MT (1983) Geochemistry of loess, continental crustal composition and crustal model ages. Geochim Cosmochim Ac 47(11):1897–1905
World Health Organization (2004) Guidelines for drinking-water quality, vol 1. World Health Organization
Wu W, Yang J, Xu S et al (2008) Geochemistry of the headwaters of the Yangtze River, Tongtian he and Jinsha Jiang: Silicate weathering and CO_2 consumption. Appl Geochem 23(12):3712–3727
Xu M, Kang S, Chen X et al (2018) Detection of hydrological variations and their impacts on vegetation from multiple satellite observations in the three-river source region of the Tibetan Plateau. Sci Total Environ 639:1220–1232
Zhang X, Chen H, Yao Q et al (2013) The seasonal changes and flux of trace elements in the lower reaches of Yellow River. Periodical of Ocean University of China 43(8):69–75