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Determination of 47 Elements in River Water Samples from the Himalayan Region by Tandem inductively Coupled Plasma Mass Spectrometry (ICP-MS/MS)

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Abstract

To understand the effect of water quality by the complex interaction of geogenic factors such as rock-water interactions, natural weathering, climate change-related processes such as glacier melt, altered precipitation, and anthropogenic contamination by industrial effluents, agricultural runoff, and urban waste, the water samples of some Himalayan rivers were analysed by a tandem ICP-MS (ICP-MS/MS) for 47 major, minor, and trace elements, including rare earth elements (REE). The water samples collected were from seven rivers, namely, Alaknanda, Bhagirathi, Ganga, Kaudiyala, Shivpuri, Rishikesh, and Haridwar Rivers in the Himalayan region of India. In addition, spring, tap water, and commercial mineral water samples in Dehradun City were also analysed to see if the water quality conforms to the international acceptable standards for drinking. Tandem ICP-MS provides significant advantages for drinking water quality monitoring by offering high sensitivity with detection limits for several elements across the periodic table, in the pg/ml range, multi-element capability, and superior control over spectral interferences. The water samples were found to be safe when compared to the safe limits proposed by the World Health Organisation (WHO). In addition, the established baseline concentrations of different trace and ultra-trace elements will be useful for future water pollution studies in this area.

Keywords: ICP-MS/MS, Himalayan Rivers, drinking water, rare earth elements, toxic metals

1. Introduction

Groundwater and rivers are critical sources of drinking water for a significant portion of the world's population, with some estimates suggesting that around half of all drinking water comes from these sources. Specifically, groundwater supplies nearly half of the world's drinking water, while rivers serve as a direct source for billions of people globally[1-3]. The surrounding geology is a fundamental control on river water chemistry and quality, acting as the primary source of most dissolved and particulate materials[4]. At some places, natural geological processes release harmful elements like arsenic, fluoride, uranium, iron, and manganese from rocks and sediments into the water, often intensified by human activities like mining or altered river flows[5.6]. Geogenic arsenic pollution in river water and particularly groundwater of the Himalayan mega-river basins (Indus, Ganges, and Brahmaputra) is a widespread environmental crisis affecting millions of people[7]. The Himalaya region is a young, dynamic mountain range formed by the ongoing collision of the Indian and Eurasian tectonic plates, resulting in continuous uplift, deep crustal stresses, and significant seismic activity, making it both majestic and delicate[8]. This contamination happens when water-rock interactions, weathering, and evaporation concentrate naturally occurring minerals/metals, creating significant health risks, especially in developing regions relying on groundwater or river sources for drinking. While climate, vegetation, and human activities modify this chemistry, geology sets the baseline concentrations of different elements in river water. Understanding local geology is the first and most critical step in predicting river chemistry, assessing pollution, managing water resources, and protecting aquatic ecosystems. Climate change and related extreme weather events, such as droughts, heatwaves, rainstorms, and floods, are influencing river water quality through a complex web of interconnected physical, chemical, and biological processes. These impacts are not uniform and can vary significantly by region, but the significant trends are concerning[9]. As a result, rivers are becoming warmer, more turbid, more nutrient-rich, more saline, and more prone to toxic algal blooms[2]. Implementing adaptive monitoring to safeguard these critical freshwater resources is important.

Hence, monitoring of the quality of river water becomes necessary to understand the water treatment requirements to ensure the supply of safe drinking water. A comprehensive monitoring of river water includes: i) the determination of major, minor, and trace elements which include toxic chemicals like heavy metals (e.g., lead, chromium, and mercury) from industrial discharges which can cause a variety of health problems like cancer, neurological damage, and organ failure ii) organic pollutant like pesticides from agriculture run off, and iii) pathogens such as, E. coli bacteria, viruses, and parasites, that cause human health problems such as diseases like cholera, typhoid, and dysentery. In addition, such monitoring efforts help us to understand the riverine fluxes as well as the identification of anthropogenic or natural element cycles[10-12]. In addition, people swim, go boating, and fish in rivers. People eat fish and shellfish that live in river systems. Monitoring for pathogens like E. coli and toxic metals like lead helps prevent outbreaks of illness and issues public advisories when water quality is poor. A healthy river is an economic asset, and a polluted one is a massive liability to any nation. In addition, rivers are highly sensitive to climate change because warming temperatures increase water temperatures, elevate flood risk with intense storms, decrease water availability through drought and reduced snowmelt, and alter ecosystems by stressing aquatic species and promoting erosion[2,6,13]. Monitoring can track changes in water temperature, composition, and flow patterns to enable us to understand how ecosystems are responding. Surface and groundwaters are indeed continuously degraded by a wide range of pollutants, a critical environmental issue driven by human activities. These contaminants pose significant threats to aquatic ecosystems and human health through mechanisms like the disruption of food chains, oxygen depletion, and the introduction of toxic substances. [2,14-16]. There is a great need for varied water quality standards across different applications, highlighting the critical importance of effective water pollution and resource management. This practice is essential for safeguarding public health, ensuring ecosystem vitality, and facilitating sustainable economic development at both national and international levels

Water analysis is required for an early-warning system for human health threats and environmental damage, which highlights that ensuring clean water is not just a technical problem, but a profound management, political, and ethical challenge. In river water, major elements are the most abundant ions like Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, and Cl^{-}; minor elements are next, including Si, Al, Fe, and P, while trace elements are present in very small amounts like Zn, Cu, Pb, and As in µg/ml range, and ultra-trace elements like rare earth elements (REE) which will be present in ng/ml or pg/ml range, often monitored for pollution or as indicators of geological sources. These boundaries are not rigid but are widely accepted conventions[17]. Analysing this spectrum from major to ultra-trace elements allows hydrologists or environmental scientists to understand the complete history of a water sample. This requires that the water samples are analysed by highly sensitive multielement analytical techniques such as inductively coupled plasma optical emission spectrometry (ICP-OES), microwave plasma atomic emission spectrometry (MP-AES), neutron activation analysis, and different forms of inductively plasma mass spectrometry (ICP-MS), such as tandem-ICP-MS (ICP-MS/MS), ICP-time of flight mass spectrometry (ICP-TOF-MS) and high resolution mass spectrometry (HR-ICP-MS)[18-24]. While ICP-OES and MP-AES are powerful multi-element techniques for detailed water analysis for measuring major, minor, and trace metals, for the accurate measurement of ultra-trace metals like REE, tedious ion-exchange separation and preconcentration procedures have to be adopted. The INAA technique is also tedious as it requires the sample to be irradiated in a nuclear reactor and a cooling time, and some REE are not practically measurable because of shorter half-lives[25]. In this context, tandem ICP-MS has recently emerged as a technique of choice for water quality monitoring[12]. Tandem ICP-MS offers a significant advantage over conventional quadrupole ICP-MS by providing superior control over spectral interferences, which leads to lower detection limits and more accurate results for challenging analyses. Here, we aim to provide a methodology for the accurate measurement of several major, minor, trace, and ultra-trace elements in seven Himalayan rivers, namely Alaknanda, Bhagirathi, Ganga, Kaudiyala, Shivpuri, Rishikesh, and Haridwar, using ICP-MS/MS. In addition, spring water nearer to Dehradun city, tap water, and some commercial mineral water samples in and around the Dehradun city market, Uttarakhand State, are also analysed to find their suitability for drinking purposes. Though there were some studies earlier on the quality of river water in the Himalayan region, they were not comprehensive, and many elements were not analysed, and the latest analytical tool, tandem ICP-MS, was not utilised[8,26]. Hence, this comprehensive study was undertaken with the major objectives of understanding: i) how the surrounding geology is affecting the river water quality. ii) the effects of ongoing climate change and related activities in the Himalayan region, iii) the geogenic or anthropogenic contamination of the river water, iv) safety of drinking water and to protect public health in the area, and v) the baseline concentrations of different trace and ultra-trace elements for future water pollution studies in this area.

2. Study area

In general, drinking water is sourced from surface water (rivers, lakes, reservoirs) and groundwater (aquifers, wells) after it undergoes treatment to ensure safety. Large cities typically rely on surface water, while smaller communities may use groundwater, though many systems use a mix of both. It is true even in the case of Dehradun city. The Alaknanda, Bhagirathi rivers meet at Devprayag and form the Ganga River. The Alaknanda River originates in the Higher Himalaya, drains through carbonates, massive quartzite, slates, phyllites, and greywackes, while the Bhagirathi River originates from the higher Himalaya and drains through quartzites, dolomitic limestone, and metabasaltic rocks. The Head Ganga River flows through quartzites, limestone, and phyllites up to Rishikesh. In general, concentrations of toxic elements in water resources are indeed heavily influenced by both the natural underlying geology and a variety of anthropogenic activities. The natural weathering of rocks and soils

Table 1 Drinking water quality criteria in different countries and national and international regulatory limits in ng/ml levels for some elements (Modified after[2, 37])

Element	WHO	India	USA	EU	Canada	China	South Africa
Ag	-	100	100	-	-	50	-
Al	100	30	200	200	100*	200	150
As	10	10	10	10	10	10	10
B	2400	500	-	1000	5000	1000	-
Ba	1300	700	2000	-	1000	700	-
Be	-	-	4	-	-	2	-
Ca	-	75,000	-	-	-	-	32,000
Cd	3	3	5	5	5	5	5
Cr	50	50	100	50	50	50	50
Cu	2000	50	1300	2000	1000	1000	1000
Fe	-	300	300	200	300*	300	100
Hg	6	1	2	1	1	1	1
Li*	-		10	--	-	-	-
Mg	-	30,000	-	-	-	-	-
Mn	-	100	50	50	50*	100	50

Mo	-	70	-	-	-	70	-
Na	-	-	-	200,000	200,000*	200,000	100,000
Ni	70	20	-	20	-	20	-
Pb	10	10	15	10	10	10	10
Sb	20	-	6	5	6	5	-
Se	40	10	50	10	50	10	20
Tl	-	-	2	-	-	0.1	-
U	30	-	30	-	20	30	70
V	-	-	-	-	-	10	100
Zn	-	5000	5000	-	5000*	1000	3000
Li*	-		10	--	-	-	-
Mg	-	30,000	-	-	-	-	-
Mn	-	100	50	50	50*	100	50
Mo	-	70	-	-	-	70	-
Na	-	-	-	200,000	200,000*	200,000	100,000
Ni	70	20	-	20	-	20	-
Pb	10	10	15	10	10	10	10
Sb	20	-	6	5	6	5	-
Se	40	10	50	10	50	10	20
Tl	-	-	2	-	-	0.1	-
U	30	-	30	-	20	30	70
V	-	-	-	-	-	10	100
Zn	-	5000	5000	-	5000*	1000	3000

* There is no clear indication of permissible lithium concentration levels in drinking water by environmental protection agencies like the WHO

determines the baseline levels of elements like arsenic, lead, and mercury present in a catchment area. Human activities such as industrial, mining activities, and farming practices significantly increase these concentrations above natural levels. These inputs combined lead to the contamination of fresh water, posing potential health risks to ecosystems and human populations. International regulatory authorities such as the World Health Organisation (WHO) and different national and international regulatory bodies provide permissible concentrations of certain toxic metals/elements in drinking water (Table 1).

In this study, water samples from seven rivers in the Uttarakhand State in the Himalayan Region, India, were collected. These rivers are where the numerous tributaries merge with the Ganga River. The Alaknanda, Bhagirathi rivers at Devprayag form the Ganga River. The Alaknanda River originates in the Higher Himalaya, drains through carbonates, massive quartzite, slates, phyllites,

and greywackes, while the Bhagirathi River originates from the higher Himalaya and drains through the quartzites, dolomitic limestone, and metabasaltic rocks. The Head Ganga River flows through quartzites, limestone, and phyllites up to Rishikesh.

Table 2 Sample locations and physical parameters of different Himalayan River water Samples

S. No	River	Latitude	Longitude	pH	TDS (mg/L)	Tem (^oC)	Electrical conductivity (µg/cm)	
01.	Alaknanda	30^{o}08’734 N	78^{o}35’876 E	9.7	81	20	151.6	
02.	Bhagirathi	30^{o}08’807 N	78^{o}35’851 E	9.1	57	18	104.1	
03.	Ganga	30^{o}08’355 N	78^{o}35’821 E	8.9	72	20	133.2	
04.	Kaudiyala	30^{o}04’560 N	78^{o}29’857 E	9.3	74	21	145.8	
05.	Shivpuri	30^{o}08’071 N	78^{o}23’433 E	9.3	71	22	141.0	
06.	Rishikesh	30^{o}07’183 N	78^{o}18’481 E	9.3	69	21	142.9	
07.	Haridwar	29^{o}56’580 N	78^{o}10’157 E	9.4	82	26	175.7	

3. **Instrumentation and the analytical protocol**

In this study, seven river water samples were collected at Devprayag, Kaudiayala, Shivpuri, Rishikesh, and Haridwar Alaknanda, Bhagirathi, where the numerous tributaries merge with the Ganga River. Sample locations and physical parameters of different Himalayan River water Samples are provided in Table 2.

A sample location map of the rivers selected in the Uttarakhand State in the Himalayan Region, India, is shown in Figure 1. The pre-cleaned polypropylene (PP) bottles were dipped at a few feet depth, collected the water samples, and sealed immediately. The water temperature, pH, total dissolved solids, and electrical conductivity (EC) were recorded using a portable multi-parameter instrument of

water quality meter (Model: HQ2200, Hach, USA). The Global Positioning System (GPS; Garmin Etrex 10x) was used to record the sampling locations (Table 2). The samples were filtered into 50 ml pre-cleaned centrifuge vials using 0.22 µm cellulose membrane filters to prevent suspended particulate matter. The filtered samples

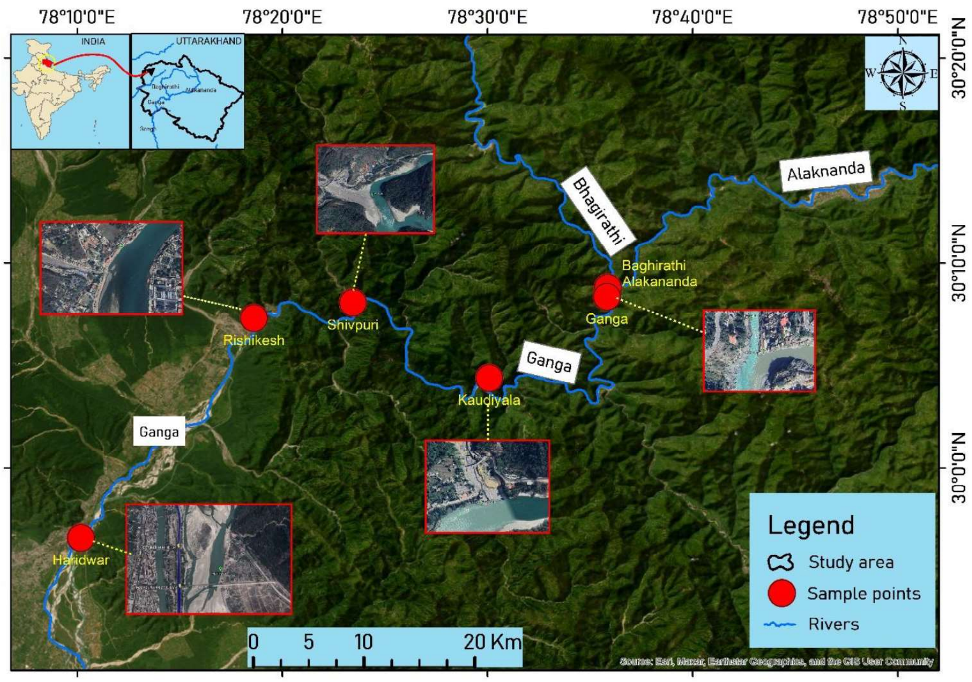

Fig. 1. Sample location map of different rivers in the Uttarakhand State in the Himalayan Region, India

were acidified with an overall acidity of 2% HNO_3 and were used for the measurement of the major, minor, trace, and ultra-trace elements using ICP-MS/MS (8900 ICP-MS/MS Agilent

Technologies) at Wadia Institute of Himalayan Geology (WIHG), Dehradun (India). Acidified samples were analysed within a week. Usually, the acidified samples, when stored in a refrigerator, will be stable for at least six months. The tandem ICP-MS was used in "no-gas mode" to measure major, minor, trace, and REE in water samples. In this mode, no collision or reaction gas (like helium, oxygen, or ammonia) is admitted into the collision/reaction cell (CRC). A tandem ICP-MS can be operated in a "no gas" mode, essentially mimicking a single-quadrupole ICP-MS by using the first quadrupole (Q1) as an ion guide. This operation allows for high sensitivity and improved backgrounds for certain masses because it minimizes scattering losses and avoids the introduction of unwanted interferences from reaction gases, though it does not offer the interference removal capabilities of MS/MS mode, and Q2 acts as only the mass analyser[12]. For example, when analysing very dilute solutions like river water samples with minimal interferences, using ICP-MS/MS in no gas mode is beneficial because it provides the highest sensitivity. Lighter elements such as Li, Be, and B generally do not suffer from significant polyatomic interferences in standard ICP-MS operation because common matrix and plasma ions (like those involving Ar, O, H, N, C, Cl, S, F) do not readily form stable molecular ions at these very low masses. But elements like Mg, Co, Cu, Cs, and Rb often have at least one isotope that is free from severe common polyatomic interferences like ArO, ArH, and ClO, in a relatively clean river water matrix compared to highly complex samples like geological rock digests or high-salinity brines. Thus, the combination of the specific elemental masses and the clean nature of the river water matrix allow for accurate and sensitive analysis in standard 'no gas mode' using ICP-MS/MS. Figure 2 presents a schematic representation of a typical ICP-MS/MS instrument and its operating principle, leading to an interference-free determination of different analytes.

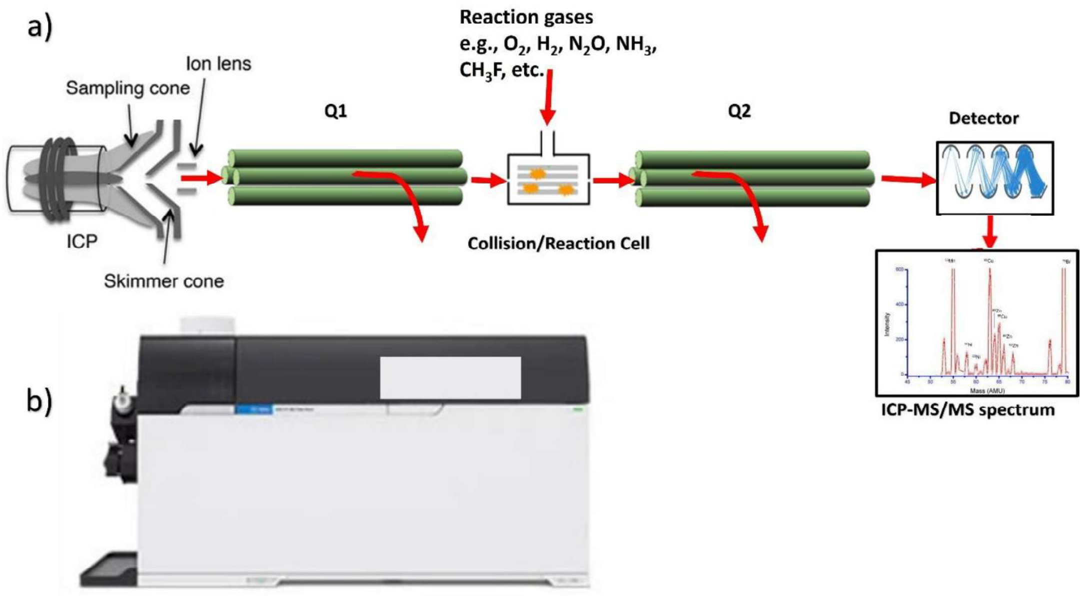

Fig. 2. Tandem ICP-MS: a) Schematic representation of a typical ICP-MS/MS instrument and its operating principle leading to an interference-free determination of different analytes, b) a commercial ninstrument (modified after Balaram[12])

The sample introduction system for the ICP-MS/MS instrument comprises an SPS-4 auto-sampler, a micro mist nebulizer, a 12-roller peristaltic pump, a Peltier-cooled double-pass Scott-type quartz spray chamber, and nickel sampler and skimmer cones. The multi-element standard solutions were used for external calibration (Agilent Technologies and Merck). The rhodium (^{103}Rh) at 5 ng/ml was used as an internal blank standard to minimize the instrument drift and other effects[13]. All these water samples were analysed for 47 major, minor, trace, and ultratrace element concentrations in no gas mode using ICP MS/MS at WIHG, Dehradun, India, using the analytical protocol described by Balaram and Satyanarayanan[27]. Synthetic multi-element mixtures at ng/ml levels were used for calibration, and SLRS-6 was used for data validation. SLRS-6, is a natural River Water Certified Reference Material (CRM) from the National Research Council Canada (NRC-CNRC) with certified values for several elements and extended data for others such as REE. It is valuable for calibrating analytical instruments and developing quality control protocols in water analysis[28]. Mercury was not determined due to the non-availability of a cold vapour accessory. A comparison of the results of trace element data of both reported values and the values obtained for SLR-6 in this study (Table 3) reveals that the quality of the data obtained by tandem ICP-MS is very high.

Table 3 ICP-MS/MS Measured major, minor, trace and ultra-trace elemental concentrations (ng/ml) for Himalayan Head Rivers, spring and packed drinking water samples

Loc.		Devprayag		Kaudiyala	Shivpuri	Rhishikesh	Haridwar	Sahastradhara	Dehradun	Packed Drinking Water (P.W.D)			SLRS-6	SLRS-6
Anal.	**Alak.**	**Bhagi.**	**Ganga**			**Ganga River**		**Spring Water**	**Tap water**	**P.W.D1**	**P.W.D2**	**P.W.D3**	**R.V**	**M.V**
Li	6.095 ± 0.002	4.570 ± 0.004	5.576 ± 0.002	5.792 ± 0.002	5.540 ± 0.002	5.375 ± 0.001	5.710 ± 0.003	16.247 ± 0.005	2.149 ± 0.007	2.572 ± 0.003	0.557 ± 0.003	0.522 ± 0.009	0.53	0.539 ± 0.003
Be	0.01 ± 0.001	0.004 ± 0.001	0.004 ± 0.001	0.004 ± 0.001	0.004 ± 0.001	0.003 ± 0.001	0.003 ± 0.001	0.086 ± 0.001	0.062 ± 0.001	0.012 ± 0.001	0.005 ± 0.001	0.004 ± 0.001	0.0066	0.007 ± 0.001
B	29.916 ± 0.003	23.215 ± 0.002	25.762 ± 0.003	27.809 ± 0.003	27.828 ± 0.004	24.642 ± 0.001	27.360 ± 0.002	36.72 ± 0.003	14.20 ± 0.001	229.14 ± 0.005	14.40 ± 0.005	9.633 ± 0.001	7.39	7.021 ± 0.001
Na	4.1E^{+3} ± 0.002	3.2E^{+3} ± 0.003	3.8E^{+3} ± 0.005	4.2E^{+3} ± 0.003	4.1E^{+3} ± 0.008	4.0E^{+3} ± 0.004	5.3E^{+3} ± 0.005	4.3E^{+3} ± 0.004	1.8E^{+4} ± 0.008	OR	2.3E^{+3} ± 0.005	OR	2.70E^{+0}3	3.2E^{+3} ± 0.006
Mg	6.6E^{+3} ± 0.005	3.8E^{+3} ± 0.005	5.8E^{+3} ± 0.004	6E^{+3} ± 0.006	5.5E^{+3} ± 0.004	5.3E^{+3} ± 0.004	7.2E^{+3} ± 0.006	OR	OR	5.6E^{+3} ± 0.006	6.6E^{+3} ± 0.006	1.1E^{+4} ± 0.001	2.1E^{+3}	2.5E^{+3} ± 0.007
Al	43.41 ± 0.007	48.86 ± 0.001	176.98 ± 0.007	76.14 ± 0.008	46.95 ± 0.009	49.61 ± 0.001	32.70 ± 0.009	4.321 ± 0.007	7.257 ± 0.008	3.920 ± 0.005	1.596 ± 0.001	6.891 ± 0.001	33.8	41.06 ± 0.005
K	2.9E^{+3} ± 0.001	2.4E^{+3} ± 0.008	2.8E^{+3} ± 0.005	2.8E^{+3} ± 0.003	2.8E^{+3} ± 0.007	2.7E^{+3} ± 0.003	3.3E^{+3} ± 0.004	1.2E^{+3} ± 0.006	1.1E^{+3} ± 0.005	6.4E^{+2} ± 0.004	9.6E^{+3} ± 0.007	3.5E^{+2} ± 0.001	6.51E^{+0}2	7.1E^{+2}± 0.005
Ca	1.2E^{+4} ± 0.004	7.8E^{+3} ± 0.004	1.1E^{+4} ± 0.003	1.1E^{+4} ± 0.002	1.1E^{+4} ± 0.002	1.1E^{+4} ± 0.003	1.3E^{+4} ± 0.004	2.8E^{+5} ± 0.003	8.8E^{+4} ± 0.006	1.4E^{+4} ± 0005	1.3E^{+4} ± 0.007	1.4E^{+4} ± 0.001	8.70E+03	6.1E^{+3} ± 0.004
Sc	0.597 ± 0.005	0.596 ± 0.004	0.592 ± 0.002	0.633 ± 0.006	0.632 ± 0.007	0.613 ± 0.003	0.672 ± 0.002	0.635 ± 0.002	1.982 ± 0.004	0.1175 ± 0.004	0.274 ± 0.006	0.060 ± 0.001	0.333	0.454 ± 0.004
V	1.395 ± 0.08	0.982 ± 0.003	0.695 ± 0.002	0.695 ± 0.002	0.936 ± 0.003	0.842 ± 0.002	1.579 ± 0.002	0.104 ± 0.009	0.708 ± 0.006	0.275 ± 0.002	0.217 ± 0.003	0.182 ± 0.001	0.351	0.406 ± 0.003
Cr	1.041 ± 0.002	0.614 ± 0.005	0.393 ± 0.001	0.810 ± 0.006	0.887 ± 0.005	0.762 ± 0.005	1.065 ± 0.004	1.040 ± 0.005	2.800 ± 0.002	1.031 ± 0.002	8.834 ± 0.002	0.601 ± 0.001	0.252	0.399 ± 0.007
Mn	0.879 ± 0.001	1.666 ± 0.003	1.173 ± 0.002	1.156 ± 0.002	1.036 ± 0.002	0.929 ± 0.002	0.671 ± 0.003	4.120 ± 0.003	3.917 ± 0.004	0.883 ± 0.002	2.750 ± 0.002	2.442 ± 0.009	2.12	2.057 ± 0.002
Fe	35.96 ± 0.009	27.63 ± 0.001	1.73 ± 0.001	7.00 ± 0.001	0.485 ± 0.009	20.50 ± 0.009	59.85 ± 0.008	17.30 ± 0.009	3.471 ± 0.001	OR	26.53 ± 0.001	8.402 ± 0.009	84.3	83.30 ± 0.001
Co	0.066 ± 0.003	0.061 ± 0.003	0.070 ± 0.003	0.067 ± 0.003	0.052 ± 0.004	0.051 ± 0.003	0.063 ± 0.004	0.647 ± 0.003	0.240 ± 0.009	0.041 ± 0.001	0.045 ± 0.005	0.034 ± 0.001	0.053	0.058 ± 0.005
Ni	1.864 ± 0.001	4.403 ± 0.003	1.305 ± 0.004	3.435 ± 0.002	0.832 ± 0.003	1.234 ± 0.002	2.285 ± 0.002	6.468 ± 0.002	3.964 ± 0.004	1.793 ± 0.07	2.462 ± 0.003	0.994 ± 0.009	0.616	0.650 ± 0.003
Cu	[illegible] ± 0.002	[illegible] ± 0.002	[illegible] ± 0.003	[illegible] ± 0.002	[illegible] ± 0.002	[illegible] ± 0.002	[illegible] ± 0.003	[illegible] ± 0.003	[illegible] ± 0.004	[illegible] ± 0.004	[illegible] ± 0.002	[illegible] ± 0.001	23.9	[illegible] ± 0.002
Zn	11.677 ± 0.001	13.656 ± 0.002	7.901 ± 0.003	37.588 ± 0.004	2.817 ± 0.002	3.738 ± 0.002	22.502 ± 0.002	7.066 ± 0.002	62.997 ± 0.005	14.339 ± 0.003	6.746 ± 0.003	22.741 ± 0.008	1.76	1.446 ± 0.005
Ga	0.043 ± 0.008	0.037 ± 0.006	0.044 ± 0.005	0.039 ± 0.004	0.035 ± 0.007	0.041 ± 0.001	0.049 ± 0.005	0.053 ± 0.008	0.029 ± 0.001	0.006 ± 0.001	0.004 ± 0.007	0.002 ± 0.001	0.0011	0.009 ± 0.004
As	14.618 ± 0.001	7.476 ± 0.002	7.140 ± 0.003	6.884 ± 0.002	6.499 ± 0.001	5.755 ± 0.001	16.664 ± 0.003	0.092 ± 0.001	0.357 ± 0.008	0.209 ± 0.002	0.077 ± 0.001	0.080 ± 0.001	0.57	0.609 ± 0.003
Se	0.436 ± 0.009	0.316 ± 0.001	0.357 ± 0.008	0.379 ± 0.008	0.354 ± 0.001	0.273 ± 0.001	0.758 ± 0.005	0.755 ± 0.007	1.355 ± 0.004	0.203 ± 0.009	0.081 ± 0.001	0.065 ± 0.009	0.072	0.170 ± 0.004
Rb	11.771 ± 0.004	7.162 ± 0.004	9.532 ± 0.005	7.469 ± 0.004	7.591 ± 0.004	7.343 ± 0.004	8.424 ± 0.005	4.700 ± 0.003	2.208 ± 0.004	0.467 ± 0.008	1.300 ± 0.002	0.218 ± 0.009	1.41	1.469 ± 0.004
Sr	102.2 ± 0.2	53.649 ± 0.5	88.19 ± 0.2	92.30 ± 0.03	87.87 ± 0.04	86.93 ± 0.03	113.39 ± 0.05	5394.5 ± 0.3	306.4 ± 0.3	58.11 ± 0.4	46.18 ± 0.004	38.48 ± 0.001	40.66	41.32 ± 0.003
Ag	0.014 ± 0.001	0.005 ± 0.001	BDL	BDL	BDL	BDL	BDL	0.062 ± 0.003	0.057 ± 0.001	0.009 ± 0.009	0.002 ± 0.009	<0.000 ± 0.0	-	<0.000.(0
Cd	0.016 ± 0.001	0.018 ± 0.005	0.011± 0.001	0.013 ± 0.001	0.008 ± 0.001	0.008 ± 0.001	0.025 ± 0.004	0.059 ± 0.001	0.124 ± 0.007	0.024 ± 0.008	0.014 ± 0.001	0.011 ± 0.002	0.063	0.007± 0.001
In	0.018 ± 0.004	0.005 ± 0.007	0.001 ± 0.001	0.001 ± 0.001	0.001 ± 0.002	0.001 ± 0.009	0.030 ± 0.004	0.066 ± 0.001	0.066 ± 0.001	0.012 ± 0.009	0.004 ± 0.001	0.003 ± 0.001	-	0.001 ± 0.001
Te	0.009 ± 0.001	0.003 ± 0.001	0.002 ± 0.001	0.002 ± 0.001	0.002 ± 0.001	0.002 ± 0.001	0.018 ± 0.001	0.055 ± 0.001	0.029 ± 0.001	0.006 ± 0.001	0.005 ± 0.001	0.002 ± 0.001	-	0.002 ± 0.001
Cs	0.959 ± 0.002	0.182 ± 0.004	0.429 ± 0.003	0.378 ± 0.01	0.313 ± 0.002	0.263 ± 0.003	0.344 ± 0.002	0.217 ± 0.007	1.883 ± 0.004	0.043 ± 0.008	0.008 ± 0.001	0.012 ± 0.007	0.0046	0.010 ± 0.006
Ba	21.89 ± 0.002	12.808 ± 0.003	19.058 ± 0.002	19.518 ± 0.002	18.899 ± 0.003	19.437 ± 0.002	28.535 ± 0.003	13.661 ± 0.002	183.65 ± 0.004	3.929 ± 0.003	12.95 ± 0.002	4.87 ± 0.008	14.28	14.06 ± 0.003
La	0.068 ± 0.001	0.074 ± 0.003	0.712 ± 0.002	0.013 ± 0.008	0.072 ± 0.004	0.256 ± 0.003	0.008 ± 0.009	0.075 ± 0.003	0.034 ± 0.001	0.021 ± 0.001	0.009 ± 0.001	0.008 ± 0.009	0.248	0.264 ± 0.003
Ce	0.378 ± 0.001	0.088 ± 0.002	1.215 ± 0.003	0.019 ± 0.001	0.117 ± 0.007	0.492 ± 0.003	0.011 ± 0.007	0.080 ± 0.002	0.033 ± 0.002	0.014 ± 0.009	0.007 ± 0.001	0.008 ± 0.009	0.293	0.328 ± 0.001
Pr	0.028 ± 0.001	0.012 ± 0.001	0.115 ± 0.003	0.004 ± 0.001	0.011 ± 0.001	0.052 ± 0.002	0.003 ± 0.001	0.055 ± 0.002	0.021 ± 0.001	0.015 ± 0.001	0.006 ± 0.001	0.004 ± 0.001	0.059	0.067 ± 0.005
Nd	0.041 ± 0.002	0.036 ± 0.002	0.367 ± 0.002	0.011 ± 0.001	0.036 ± 0.003	0.158 ± 0.004	0.008 ± 0.001	0.050 ± 0.003	0.013 ± 0.001	0.005 ± 0.001	BDL	BDL	0.228	0.234 ± 0.001
Sm	0.025 ± 0.002	0.008 ± 0.001	0.061 ± 0.005	0.004 ± 0.001	0.007 ± 0.001	0.016 ± 0.001	0.002 ± 0.001	0.057 ± 0.003	0.023 ± 0.003	0.017 ± 0.002	0.007 ± 0.001	0.004 ± 0.001	0.040	0.046 ± 0.002
Eu	0.025 ± 0.002	0.005 ± 0.001	0.015 ± 0.001	0.005 ± 0.001	0.005 ± 0.001	0.007 ± 0.001	0.005 ± 0.001	0.056 ± 0.004	0.057 ± 0.005	0.014 ± 0.001	0.008 ± 0.001	0.005 ± 0.001	0.007	0.012 ± 0.001

Gd	0.027 ± 0.001	0.008 ± 0.001	0.051 ± 0.001	0.004 ± 0.001	0.008 ± 0.001	0.013 ± 0.001	0.002 ± 0.001	0.055 ± 0.003	.023 ± 0.001	0.016 ± 0.001	0.006 ± 0.001	0.004 ± 0.001	0.032	0.039 ± 0.007
Tb	0.020 ± 0.003	0.002 ± 0.001	0.006 ± 0.001	BDL	0.002 ± 0.001	BDL	BDL	0.051 ± 0.002	0.019 ± 0.001	0.013 ± 0.001	0.006 ± 0.001	0.003 ± 0.001	0.004	0.006 ± 0.008
Dy	0.020 ± 0.001	0.006 ± 0.001	0.023 ± 0.001	0.003 ± 0.001	0.007 ± 0.001	0.004 ± 0.001	0.002 ± 0.001	0.050 ± 0.004	0.021 ± 0.002	0.014 ± 0.002	0.006 ± 0.001	0.004 ± 0.001	0.022	0.026 ± 0.002
Ho$_3$	0.018 ± 0.005	0.002 ± 0.009	0.005 ± 0.007	0.001 ± 0.003	0.002 ± 0.009	0.001 ± 0.001	0.001 ± 0.009	0.048 ± 0.005	0.019 ± 0.001	0.013 ± 0.008	0.005 ± 0.007	0.003 ± 0.009	0.004	0.006 ± 0.009
Er	0.017 ± 0.001	0.003 ± 0.001	0.012 ± 0.001	0.002 ± 0.001	0.006 ± 0.001	0.003 ± 0.001	BDL	0.049 ± 0.003	0.020 ± 0.001	0.014 ± 0.001	0.006 ± 0.001	0.003 ± 0.001	0.012	0.015 ± 0.001
Tm	0.015 ± 0.005	0.001 ± 0.004	0.004 ± 0.007	0.001 ± 0.001	0.002 ± 0.001	0.001 ± 0.009	0.001 ± 0.005	0.047 ± 0.005	0.019 ± 0.001	0.013 ± 0.009	0.006 ± 0.006	0.003 ± 0.001	0.002	0.063 ± 0.001
Yb	0.016 ± 0.001	0.003 ± 0.001	0.010 ± 0.001	0.002 ± 0.001	0.008 ± 0.001	0.003 ± 0.001	BDL	0.045 ± 0.002	0.020 ± 0.001	0.013 ± 0.002	0.006 ± 0.001	0.003 ± 0.001	0.011	0.013 ± 0.001
Lu	0.013 ± 0.001	BDL	0.002 ± 0.001	BDL	0.002 ± 0.001	BDL	BDL	0.045 ± 0.001	0.019 ± 0.001	0.013 ± 0.001	0.006 ± 0.001	0.003 ± 0.001	0.002	0.003 ± 0.008
Tl$_2$	0.200 ± 0.002	0.036 ± 0.006	0.016 ± 0.007	0.011 ± 0.008	0.015 ± 0.001	0.011 ± 0.001	0.083 ± 0.002	0.101 ± 0.001	0.091 ± 0.009	0.013 ± 0.001	0.002 ± 0.001	0.001 ± 0.008	0.0085	0.007 ± 0.001
Pb	9.952 ± 0.002	0.654 ± 0.005	0.170 ± 0.003	0.179 ± 0.004	0.172 ± 0.003	0.136 ± 0.005	0.597 ± 0.003	0.073 ± 0.009	0.189 ± 0.006	0.008 ± 0.001	BDL	BDL	0.17	0.128 ± 0.004
Bi	0.187 ± 0.002	0.073 ± 0.006	BDL	BDL	BDL	BDL	0.549 ± 0.002	0.100 ± 0.009	0.016 ± 0.002	BDL	BDL	BDL	0.0013	BDL
Th	0.537 ± 0.008	0.099 ± 0.008	0.055 ± 0.002	0.006 ± 0.001	0.014 ± 0.001	0.007 ± 0.001	0.424 ± 0.001	0.905 ± 0.005	0.048 ± 0.001	0.022 ± 0.002	0.009 ± 0.002	0.008 ± 0.002	0.016	0.030 ± 0.003
U	2.544 ± 0.002	1.997 ± 0.003	2.594 ± 0.002	3.036 ± 0.004	2.809 ± 0.002	2.698 ± 0.004	2.802 ± 0.001	2.240 ± 0.002	2.571 ± 0.002	0.097 ± 0.004	0.216 ± 0.005	0.052 ± 0.006	0.07	0.061 ± 0.003

***Reported values for GSR-6 from Yeghicheyan et al., 2019**
* OR = Out of Range, BDL= below detection limit
*Alak = Alaknanda, Bhagi = Bhagirathi tributaries;
*R.V = Reported value and M.V = Measured value

4. Results and discussion

The primary source of dissolved solids in a river is the chemical weathering of rocks and minerals in the surrounding basin. As water flows over and through the bedrock, it dissolves some of the minerals and carries the dissolved ions downstream. Thus, the chemical composition of river water is influenced by the regional geology. By analysing the major and minor ions, trace elements, and ultra-trace elements, including REE of the river water, regional geology can be very effectively understood. Even the dominant rock types, the prevailing weathering reactions, and the tectonic activity of the landscape can be identified. The river water is a real-time, integrated signal of the geochemical processes happening throughout its entire basin.

4.1 Regional geology and chemistry of river water

The geology of a river's watershed has a primary influence on its water chemistry, as rock weathering releases minerals and dissolved ions that impart a distinct chemical signature. This geochemical fingerprint is determined by the specific rock types present in the drainage basin. Some minerals are more susceptible to weathering than others. Some rocks, like limestone and dolomite, and evaporites like gypsum and halite, weather quickly, while silicate minerals like feldspars and quartz weather slowly. The following elemental trends in river waters are generally evident from our results. Major cations show a trend of

Ca>Mg>Na>K>Fe, and trace elements show a trend of B>Zn>As>Sr>Ba>Rb due to the chemical weathering of carbonate rocks rather than silicate rocks (dolomitic limestone, metabasaltic rocks, slates, phyllites, and clay minerals in the sediments). More studies are required to understand these behaviours, as these issues are critical for assessing water quality and biogeochemical cycles. Table 1 presents the quality criteria in different countries and national and international regulatory limits in ng/ml levels for some elements. If the data in Table 1 is closely observed, some elemental contents in different countries are widely different. The variation in standards for trace elements in drinking water among different regulatory authorities, including the WHO, US EPA, EU, and India's BIS, is not an indication of scientific disagreement on the core toxicology, but rather a reflection of different mandates, methodologies, and socio-economic contexts. A lower-income country with millions of people exposed to naturally high fluoride may set a less stringent interim standard to protect the most people practically, while aiming for the WHO guideline in the long term. A wealthy country can afford advanced treatment to meet a stricter standard. For example, for arsenic, the WHO guideline value: 10 ng/ml based purely on health evidence, analytical achievability, and treatment performance. Countries like India and Bangladesh set a standard: 50 ng/ml for some time, though India's BIS standard is now 10 ng/ml. This reflects the enormous scale of the arsenic crisis with tens of millions of affected tube wells, the catastrophic cost of declaring all 50 ng/ml wells unsafe immediately, and the need for a phased, manageable remediation approach. Enforcing 10 ng/ml overnight would leave millions with no alternative water source[29]. This layered approach allows a high-income nation with advanced infrastructure to pursue a more stringent standard, while a developing nation tackles its most critical public health threats first, using the WHO guidelines as a long-term target[30]. The variation underscores the complex interplay between science, economics, and governance in protecting public health. Table 3 presents major, minor, and trace elements, and REE data (ng/ml) of all 7 Himalayan rivers, spring water, and tap water from Dehradun City. The three commercial mineral water brands in India, and an international water reference sample, SLR-6, were used. The accuracy of these determinations can be assessed by using the obtained and reported data of SLR-6. The data is extremely accurate with ±5%RSD in the majority of the cases, demonstrating the capability of ICP-MS/MS operating even in standard mode or no gas mode.

4.2 Rare earth elements

Rare earth elements (REE) are a group of 17 chemically similar metallic elements in the Earth's crust, including the 15 lanthanides, plus scandium and yttrium. They are divided into two groups. The lower atomic weight elements from La to Sm, with atomic numbers 57–62, are referred to as light REE (LREE); while Eu to Lu, with atomic numbers 63–71, are known as heavy REE (HREE). Despite their low atomic weights, Y and Sc are included in the HREE subgroup because of their co-occurrence, similar ionic radii, and closer chemical properties[31]. They are a valuable tool for understanding both geological and environmental changes because of their similar chemical properties, but slightly different ionic radii, which cause them to fractionate, or separate, predictably during various geochemical processes[32]. The behaviour of REE in rivers is a dynamic process controlled by natural chemistry and increasingly influenced by human activity[33]. It begins with the underlying geology and is then finely tuned by the river's pH and organic content. In today's world, this natural signal is often overprinted by clear markers of human activity, making REE a valuable tool for understanding both geological and environmental changes. Their concentration and distribution are primarily affected by water chemistry, organic matter, and interaction with particles. The behaviour of trace elements and REE in river waters is indeed dynamic and governed by a complex interplay of geochemical, physical, and biological processes with concentrations influenced by both natural and anthropogenic factors. These dynamics are strongly controlled by several key environmental factors such as pH, organic matter, redox, and colloidal interactions[34]. REE, in particular, show systematic fractionation patterns useful for tracing weathering processes and anthropogenic impacts[35]. Weathering of carbonates and felsic rocks significantly controlled the REE behaviours. The measured REE for the studied upper tributaries, Bhagirathi, Alaknanda and Ganga rivers, were normalised to the upper continental crust (UCC), to understand their hydrogeochemical characterisation (Figure 3). The UCC normalised patterns of Alaknanda, Bhagirathi tributaries display weakly fractionated trends (La_N/Yb_N = 0.31-1.80), moving towards the rightward indicates the slight enrichment of HREE over the LREE. The Ganga River shows a flat to increasing HREE pattern, indicating the enrichment of LREE over HREE. From this view, the dissolved sediments are derived from the dominant silicate weathering of the Lesser Himalayan rocks. This is supported by the high Mg/Na ratios, then Ca/Na reflect the silicate weathering of surrounding rocks than evaporate and carbonate dissolutions (Figure 4). The pronounced high positive Eu/Eu* anomalies (2.93-4.52) for these tributaries and the Ganga River (Eu/Eu* = 1.26-11.7) imply the reduction of Eu^{3+} to Eu^{2+} under reduction conditions and the dissolution of plagioclase-rich surrounding rocks, such as granitoid of the Lesser Himalaya. The minimal Ce/Ce* (0.67-1.97 & 0.51-0.97) for those indicates the least whole rock-water interaction.

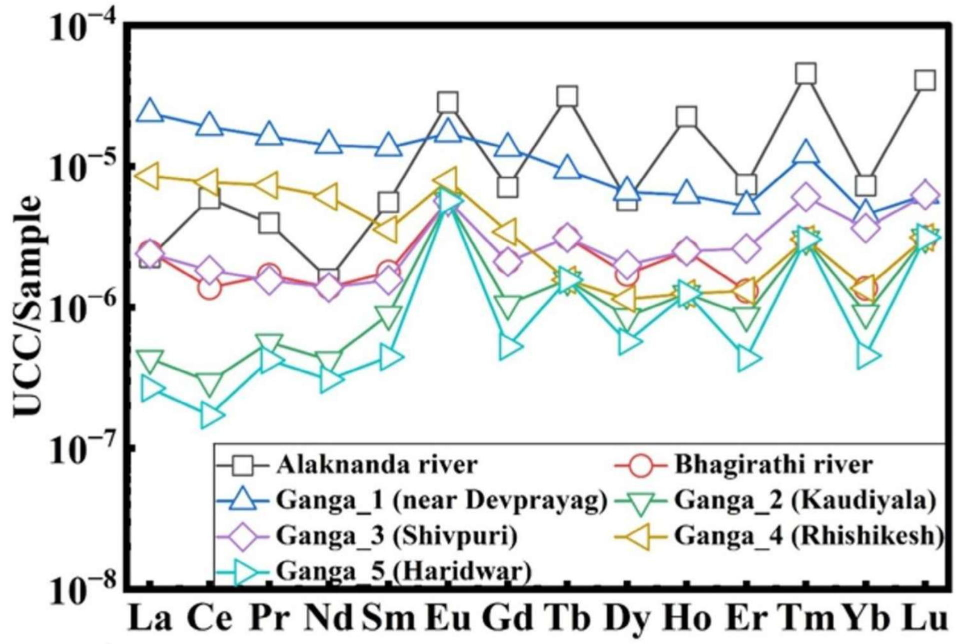

Fig.3. UCC-normalised REE curves of Himalayan River waters[38].

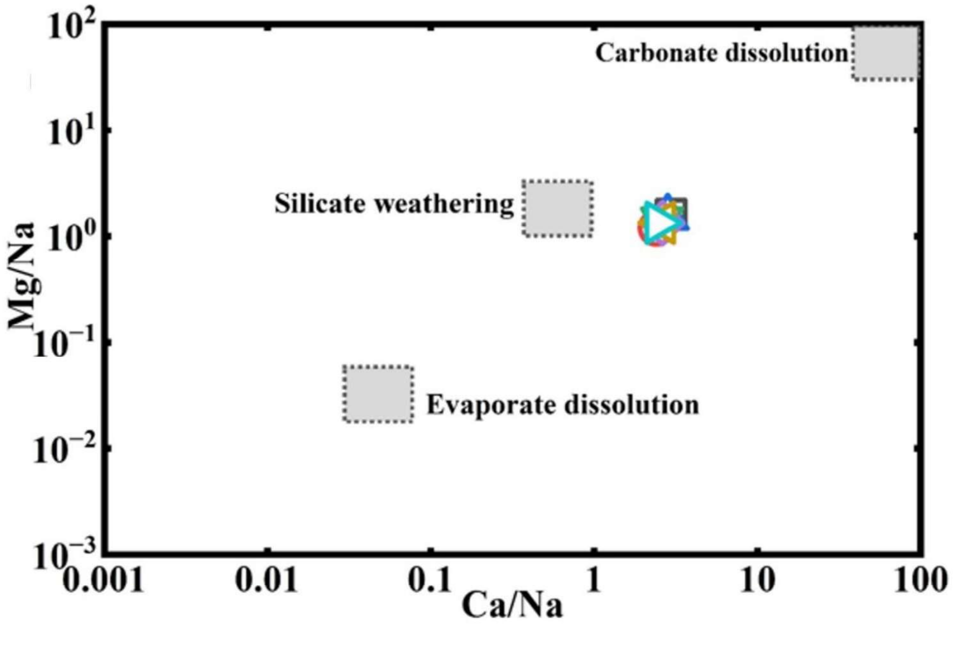

Fig.4. Binary Mg/Na vs Ca/Na diagram, after Dong et al[39].

In pristine river waters where the contamination by human activities is minimal, ∑REE will be present in trace concentrations, typically in the ng/ml to low pg/ml range. The specific total concentration is highly dependent on the local geology and the characteristics of the river basin, and can range from approximately 19.6 pg/ml to a few hundred pg/ml. In the present study, the ∑REE concentration ranged between 0.045 to 2.598 ng/ml (Table 4). Gradwohl et al[36] reported a range of 2.3 to 20 ng/ml for other pristine global rivers, and Brazilian rivers.

Table 4 ∑REE concentrations of different river waters in the studied area

Name of the river/Sampling location	**∑REE (ng/ml)**
Alaknanda/Devprayag	0.676
Bhagirathi/Devprayag	0.245
Ganga/ Outskirts of Devprayag	2.598
Ganga River/Kaudiayala	0.068
Ganga River/Shivpuri	0285
Ganga River/Hrishikesh	0.968
Ganga River/Haridwar	0.045

4.3 Concentrations of toxic metals in river, spring, tap, and bottled waters

The concentrations of toxic metals like As, Pb, Cr, and U are important for assessing the suitability of these waters for human consumption. Ganga River waters have arsenic concentrations slightly higher than the WHO permissible limit. The rest of the waters from all other rivers, spring, tap water, and bottled mineral water conform to the WHO value for arsenic. The concentrations of Cr, Pb, and U are much less than the WHO value in all the samples investigated. Table 5 presents the highest concentration for each element in all the water samples in comparison with the WHO permissible values.

Table 5 the highest concentration (ng.ml) for each element in all the water samples studied in comparison with the WHO permissible values.

Element	WHO permissible values	Highest concentration amongst the samples studied	Nature of sample
Al	100	177	Ganga
As	10	16.66	Ganga river
B	2400	36.72	Spring water
Ba	1300	184	Tap water
Cd	3	0.124	Tap water
Cr	50	8.83	Packed mineral water
Cu	2000	3.72	Tap water
Ni	70	6.5	Spring water
Pb	10	9.95	Alakananda river
Se	40	1.36	Tap water
U	30	3	Kaudiyala river
Ni	70	4.4	Bhagirathi river

Conclusions

Analyses of river, spring, tap water, and mineral waters from the Himalayan region for 47 elements show a wide spread in composition for most of these elements. Most of these river waters, including tap water of Dehradun City, and commercial mineral waters, conform to the quality requirement of the WHO for human consumption. Probably, this situation is possible because there are not many industries in this region, unlike many other areas of the country. The monitoring of drinking water using tandem ICP-MS/MS is a critical diagnostic tool because the technology provides rapid, highly sensitive, and accurate data on a wide range of contaminants. This information is essential for protecting human health, the economy, and the natural environment. Tandem ICP-MS is a powerful tool for ensuring drinking water safety, particularly for quantifying problematic contaminants at ultra-trace levels with high confidence. For understanding the geogenic and the ongoing climate contributions to the river water, some more in-depth studies are required. Anthropogenic contributions look to be minimal in this area. The river water, spring water, and the commercial water marketed in the area were found to be safe from the inorganic content point of view. The baseline concentrations obtained for different trace and ultra-trace elements should be useful for future water pollution studies in this area.

Authors' Contributions

V. Balaram**:** Conceptualization, Validation, Writing—original draft, Writing—review & editing.

C. Perumalsamy; Data generation**,** Writing—original draft, Writing—review & editing

Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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