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Basin-Scale Geochemical Assessment of Water Quality in the Ganges River during the Dry Season

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Abstract: Identification of sources and transport pathways of heavy metals and major ions is crucial for effective water quality monitoring, particularly in large river systems. The Ganges river basin, the largest and the most populous river basin in India, remains poorly studied in this regard. We conducted a basin-level analysis of major ions, heavy metals, and stable isotopes of nitrate in the Ganges during the pre-monsoon season to constrain the sources and quantify the inorganic chemical composition of the river during its lean flow. Bedrock weathering, anthropogenic interferences, water contribution through tributaries, and surface water-groundwater interaction were identified as the major driver of metal and ion variability in the river. Heavy metals showed the highest concentrations in the upper section of the river, whereas ionic loads were the most variable in the middle. We find a significant impact of tributaries on the metal and ion concentrations of the Ganges in its lower reaches. Isotopic analysis of dissolved nitrate suggested synthetic fertilizers and industrial wastes as the main sources. We find that the otherwise clean waters of the Ganges can show high ionic/metallic concentrations at isolated stretches (As: up to 36 μg/L), suggesting frequent monitoring in the source region to maintain water quality. Except for water collected from the Yamuna and Kannauj in the middle stretch and the Alaknanda and Rishikesh in the upper stretch, the WQI showed acceptable water quality for the sampled stations. These findings provide an insight into the modifications of dissolved inorganic chemical loads and their sources in different sections of the basin, needed for mitigating site-specific pollution in the river, and a roadmap for evaluating chemical loads in other rivers of the world.

Keywords: Ganges; water; stable isotopes; nitrate; heavy metals; major ions

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1. Introduction

The chemical compositions of rivers are very dynamic due to their constant interaction with surrounding atmospheric, lithospheric, hydrospheric, and anthropospheric components. Studying these changes at the basin level helps to identify prominent constituents for river pollution and mitigate potential undesirable changes in the river water quality. Such studies are especially useful in understanding compositional changes in large river systems, such as the Ganges. The Ganges is the longest river in India and the second largest by discharge in the world [1] which flows through densely populated areas with an average population of ~50 million (~520 people per square kilometer; Ministry of Jal Shakti, Govt. of India). The river, initially known as Bhagirathi, originates in the Gangotri Glacier at an altitude of over 4000 m. The Bhagirathi joins another Himalayan river, the Alaknanda (originating from the Bhagirath Satopanth glacier system at an altitude >5000 m), at Devprayag, where it assumes its name, the Ganges/Ganga. The Ganges travels a distance of 2525 km from its origin, flowing through the densely populated Indo-Gangetic plains of south Asia and finally emptying into the Bay of Bengal. The water flow upstream of the Ganges is through groundwater, surface runoff, and glacial melt, where glacial melt contributes up to 40% of water during the melting season [2]. The flow intensifies in its lower stretch due to the inputs through groundwater and tributaries (59,000 million m^3 at Allahabad to 459,000 million m^3 at Farakka; [3]).

The river fulfills the agricultural, domestic, commercial, and industrial demands of the communities residing in the basin. Despite being the most sacred river in the Hindu culture, the Ganges is amongst the most polluted rivers in India as well as the world, mainly due to municipal and industrial wastes causing organic, inorganic and pathogenic pollution in the Ganges [4–8]. Apart from these, geogenic processes can also increase the concentration of certain species beyond the desirable limits and make them a pollutant. For instance, the concentration of Cr can exceed WHO limits (50 μg/L) due to its oxidation state transformation during weathering processes, particularly in regions with ophiolitic rock areas [9], such as the Himalayas. The same applies to U and F [10]. Due to increasing pollution levels in the Ganges, the Indian government launched several programs to protect the river, such as Ganga River Basin Management Plan, National Commission on Integrated Water Resource Development Plan, River Development and Ganga Rejuvenation, and National Mission for Clean Ganga (Namami Gange), with the aims to develop sewerage treatment infrastructure, river-surface cleaning, industrial effluent monitoring, and biodiversity protection. Indeed, these programs have resulted in controlled metal levels [11,12] and improved water quality [13,14]; however, studies reported that inorganic pollution in the Ganges remained ([3,15–17] and references therein). It is noteworthy that most of the work reporting pollution is focused close to the pollution source ([3,11,12] and references therein), biasing the status of the river towards a highly polluted one. The heavy metal pollution index is a common measure to identify the relative contribution of contaminants to water quality [12,18]. However, this has also yielded different and inconsistent representations due to the limited spatial coverage of the river basin. To determine the actual water quality of the Ganges, the basin-scale investigation of the river is required but is challenging due to difficulty in the logistics, sampling, measurement, and conceptual framework for sampling the river at the basin scale [19]. As a result, the basin-scale analysis of heavy metals and major ions is very limited [11,19–21], with no studies documenting co-variations in both. Most basin-level works are done by government agencies where the prime focus lies in measuring fecal coliform counts and physical characteristics (like TDS, pH, DO, and conductivity) of water. This has limited our understanding of the modification in sources, transport and transformation of various inorganic components under changing hydro-geological conditions in the river basin.

In view of the above, our aim for this study is to investigate the variability of heavy/trace metals and major ions and to identify their responsible sources in the Ganges River at the basin level. Among the major ions, we give special emphasis to source identification of dissolved nitrate (NO_3^-) through stable isotope techniques due to its potential to cause algal blooms and eutrophication in the stagnant flow regions during the dry season.

Stable isotope ratios in NO_3^- are powerful tracers for its source apportionment due to unique isotopic fractionation pathways during the formation of NO_3^-. The NO_3^- generated from different sources show distinct $\delta^{15}N$ and $\delta^{18}O$ signatures. For example, $\delta^{15}N$ of NO_3^- present in the non-biological sources, such as precipitation (−10–8‰) and chemical fertilizers (0–3‰), is lower compared to the sources which produce NO_3^- by the biological processes (sewage and manure; ~7–20‰) [22,23]. As $\delta^{15}N$ isotopic signatures of various sources overlap with each other, a combined analysis of $\delta^{18}O$ and $\delta^{15}N$ is often used for better estimation of the NO_3^- sources [24]. The distinct values of $\delta^{18}O$ in different sources, such as precipitation (20–70‰), synthetic NO_3^- fertilizer (22 ± 3‰), and in-situ ammonium nitrification (−5–5‰), helps in partitioning the NO_3^- sources [23,25].

Overall, the present work aims to constrain the sources of inorganic components in the river by measuring both metal and major ion concentrations at 32 selected stations in the Ganges and tributary rivers at the basin scale. We emphasize the identification of water quality in the Ganges during the dry season when the concentrations of the targeted species are high due to reduced water discharge [26]. The volume of water and its flow are the major determinants of water quality and pollution levels [27], with different influences of monsoon and non-monsoon seasons. The river hydrology of the Ganges in the pre-monsoon months or dry season is mostly dictated by the glacial melt runoff [11], where the high water temperature contributes to the dissipation of heavy metals [28]. The depletion in groundwater levels, along with reduced flow during the dry season, can also cause the drying of the river [29], further concentrating inorganic species in the water, making it important to identify the inorganic loads on the river during the dry season. Our work identifies dry season (pre-monsoon) variations in the important heavy metal species (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Sr, U, V, and Zn) which either act as micronutrients in trace quantities but can become toxic at higher concentrations and can potentially impose toxic effects on aquatic life and are extremely hazardous to human health. Concentrations of important anthropogenically alterable major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, $SO_4{}^{2-}$, $NO_3{}^-$, and Cl^-) are also measured. The specific objectives of the work are to (i) evaluate compositional variability of metals and ions under different hydrogeological conditions experienced by Ganges, (ii) determine human interventions to ion and metal concentration in the river, (iii) constrain the sources for $NO_3{}^-$ pollution through its isotopic analysis, and (iv) identify the relative importance of anthropogenic sources, groundwater, and tributary inputs in regulating the metal and ion content in the Ganges during the lean flow. We hypothesize that the metal and ionic contents of Ganges are high in the plains due to increased population loads and can be diluted by addition of discharge from tributaries and groundwater. The impact of lean flow could be observed as high inorganic loads on the river. Our work provides extensive quantification of inorganic species along with the basin-scale evaluation of $NO_3{}^-$ isotopes in Ganges and discusses the modification of inorganic species with the course of the river which is useful for water quality management and comparison with other large rivers of the world.

2. Materials and Methods

Water samples were collected from various locations in the Ganges and its tributaries during June 2019, before the onset of South East Monsoonal precipitation (Figure 1a). The discharge from the Ganges is low from December to June and high from July to November, with a peak in the month of August-September [26]. The geography of the river basin is shown in Figure 1b, whereas land use and geology of the basin are represented in Figure 1c,d, respectively. The sampling locations were chosen around major cities located along the bank of the river and before and after the confluences of major tributaries (Table 1). Care was taken to avoid contamination from the coast by collecting the samples from the center of the stream using a rope and bucket while sampling from bridges or else taking boats into the middle of the flow. We avoided sampling water near the sewage openings, open defecation areas, regions with visible pollution, and stagnant flow, which could bias the results.

The samples were all syringe-filtered (10 mL Dispovan syringe, filter pore size 0.2 µm) and collected in triplicate in pre-cleaned 60 mL polypropylene bottles (Tarsons Products Pvt. Ltd., Kolkata, India). The aliquot for $NO_3{}^-$ isotope analysis was poisoned immediately with a drop of saturated mercuric chloride solution to stop bacterial activity. One aliquot was acidified to pH <2 by adding ultrapure concentrated nitric acid (70% purified by redistillation, ≥99.999% trace metal basis, Sigma Aldrich, Bengaluru, India) for metal analysis. The 3rd was left chemically untreated for major ion determinations. All the samples were stored at 4 °C in the dark until laboratory analysis. Temperature, pH, and conductivity of water were measured on-site using a handheld meter (EcoTestr EC Low, Eutech Instruments, Thermo Scientific, Bermen, Germany).

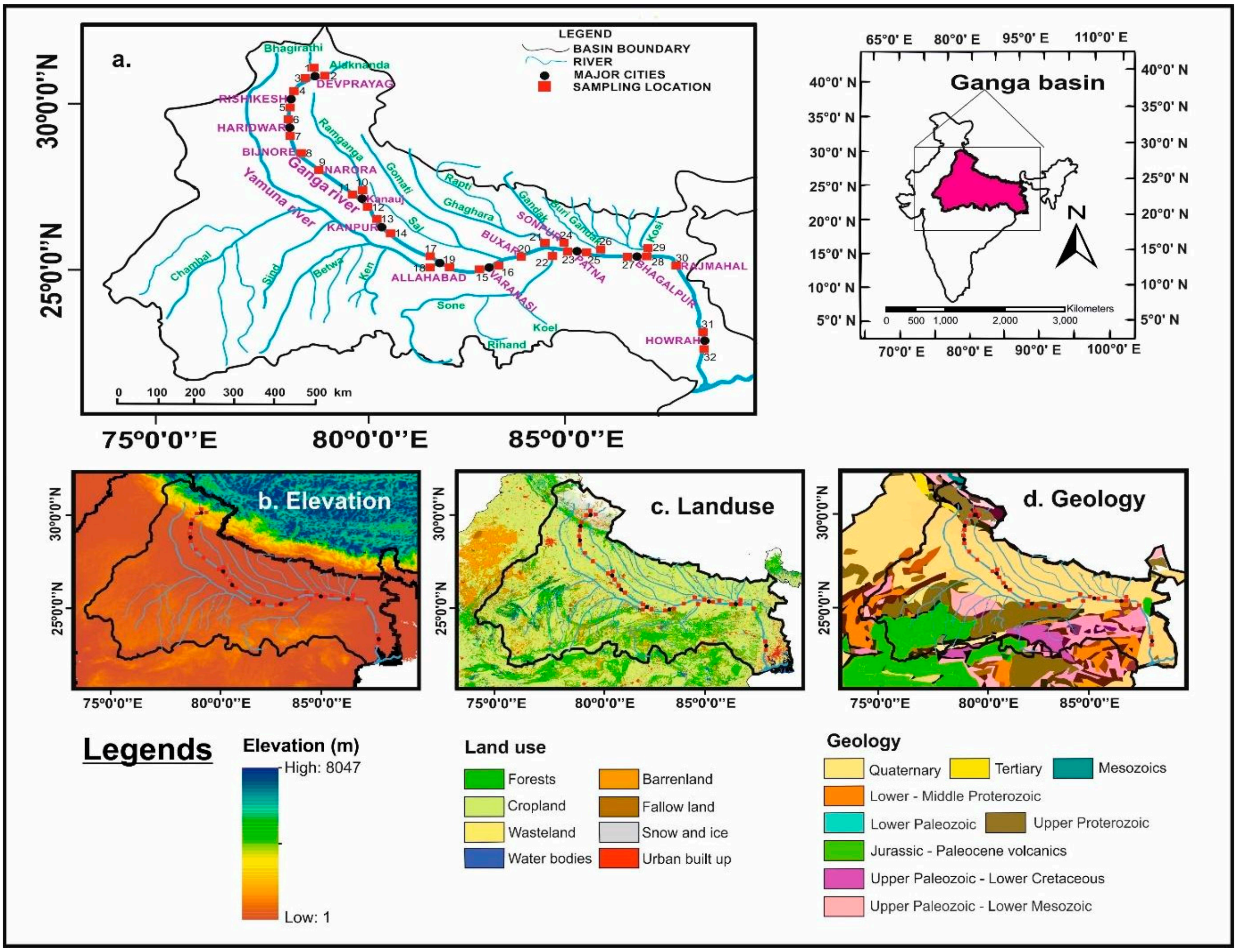

Figure 1. (**a**) Sampling stations, (**b**) digital elevation model, (**c**) land-use pattern, and (**d**) geological characterization of the Ganges river basin.

Analyses of major cations and anions were performed on a high-performance ion chromatography (Dionex ICS-5000$^+$) with a precision better than ±10% (RSD) and a detection limit of 0.1 mg/L. Dionex IonPac AS19 separation column and AG19 guard column were used to analyze Cl^-, NO_3^-, and SO_4^{2-}, whereas Dionex IonPac CS19 separation column and CG19 guard column were used to determine Na^+, K^+, Mg^{2+}, and Ca^{2+} (Detailed data provided in Table S1). The eluents used for anions and cations were 10 mM Na_2CO_3 and 4 mM methanesulfonic acid, respectively. Standard solutions for both anions and cations were prepared separately before analysis, with the calibration range between 0.1 mg/L and 50 mg/L. River water samples were directly diluted with Milli-Q water into the calibration range. The metal concentrations were analyzed using Q-ICP-MS (Agilent 7700X). The instrumental drift and matrix effect were corrected by the internal standards (Sc, Y, Rh, Tb, Lu, and Bi), following the standard method of NIEA M105. The analytical precision was better than 10% (RSD), and the detection limit was 0.05 μg/L. We analyzed 38 metals, including trace elements, heavy metals, and rare earth elements (Supplementary Tables S2 and S3), of which here we will discuss only those metals which show significant variations in different sections of the river.

Table 1. Details of the sampling stations.

Station	Section	Date	Type	Nearby City	pH	Temp (°C)	Conductivity (µS/cm)
St-1	Upper	3 June 2019	Tributary (Bhagirathi)	Devprayag	8.7	19.1	120
St-2		3 June 2019	Tributary (Alaknanda)	Devprayag	8.7	17.9	130
St-3		3 June 2019	Mainstream Ganges	Devprayag	8.8	18.1	130
St-4		3 June 2019	Mainstream Ganges	Rishikesh	8.8	18.3	140
St-5		3 June 2019	Mainstream Ganges	Rishikesh	8.9	19.8	140
St-6		3 June 2019	Mainstream Ganges	Haridwar	9	20.5	150
St-7		3 June 2019	Mainstream Ganges	Haridwar	9	23	160
St-8		4 June 2019	Mainstream Ganges	Bijnore	9	26.2	160
St-9		9 June 2019	Mainstream Ganges	Narora	9	28.5	170
St-10	Middle	8 June 2019	Tributary (Ramganga)	Kannauj	9.8	30.2	190
St-11		8 June 2019	Mainstream Ganges	Kannauj	10.1	31.2	500
St-12		8 June 2019	Mainstream Ganges	Kannauj	10	32.5	350
St-13		7 June 2019	Mainstream Ganges	Kanpur	9.7	32.6	320
St-14		7 June 2019	Mainstream Ganges	Kanpur	9.7	32.8	330
St-15		25 June 2019	Mainstream Ganges	Varanasi	7.8	34	618
St-16		24 June 2019	Mainstream Ganges	Varanasi	8.4	30.3	458
St-17		22 June 2019	Mainstream Ganges	Allahabad	9.2	31	279
St-18		22 June 2019	Tributary (Yamuna)	Allahabad	9.1	32.2	794
St-19		22 June 2019	Mainstream Ganges	Allahabad	9.15	32.9	293
St-20		21 June 2019	Mainstream Ganges	Buxar	8.4	32.1	435
St-21	Lower	27 June 2019	Tributary (Ghaghra)	Chapra	8.5	32.2	184.6
St-22		11 June 2019	Tributary (Sone)	Chapra	7.9	-NA-	-NA-
St-23		11 June 2019	Mainstream Ganges	Patna	8.6	-NA-	-NA-
St-24		11 June 2019	Tributary (Gandak)	Patna	8.4	-NA-	-NA-
St-25		10 June 2019	Mainstream Ganges	Patna	8.7	-NA-	-NA-
St-26		28 June 2019	Tributary (Buri Gandak)		8.8	35.1	296
St-27		13 June 2019	Mainstream Ganges	Bhagalpur	9.2	31.2	470
St-28		13 June 2019	Mainstream Ganges	Bhagalpur	8.75	31.2	315
St-29		13 June 2019	Tributary (Kosi)		8.56	31.2	119.8
St-30		14 June 2019	Mainstream Ganges	Rajmahal	8.5	30.9	252
St-31		16 June 2019	Mainstream Ganges	Howrah	8.2	30.8	281
St-32		15 June 2019	Mainstream Ganges	Howrah	8.15	31.6	334

The water quality index was calculated to assess the station-wise safety of water for different uses. We considered Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}, Al, As, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, U, Zn, pH, and EC for calculating the WQI, following the WHO water quality guidelines. The calculation of WQI was performed by following the 'weighted arithmetic index method' [30] using the following equation:

$$\mathrm{WQI} = \Sigma \mathrm{QnWn}/\Sigma \mathrm{Wn} \quad (1)$$

where Qn is the quality rating, and Wn is the unit weight of the nth water quality parameter. The quality rating Qn is calculated as

$$\mathrm{Qn} = [(\mathrm{Vn} - \mathrm{Vi})/(\mathrm{Vs} - \mathrm{Vi})] \times 100 \quad (2)$$

where Vn is the observed value, Vi is the ideal value, and Vs is the standard permissible value for the nth water quality parameter. Unit weight (Wn) is calculated as

$$\mathrm{Wn} = \mathrm{k}/\mathrm{Vs} \quad (3)$$

where K is the constant of proportionality. The WQI developed by this method classifies water into five major categories based on the index value: excellent (0–25), good/slightly polluted (26–50), poor/moderately polluted (51–75), very poor/polluted (76–100), and unacceptable/extremely polluted (>100).

Isotopic analyses of $\delta^{15}N$ and $\delta^{18}O$ in dissolved NO_3^- in the water samples were conducted following the cadmium-azide reduction method. In this method, the NO_3^- was first reduced to NO_2^- using a cadmium column, followed by a further reduction to N_2O by azide [31–33]. The N_2O produced from the dissolved NO_3^- in the samples were analyzed using an Isotope Ratio Mass Spectrometer (Delta V Plus, Thermo Fisher Scientific Inc.) connected to an in-house PreCon device coupled with a continuous flow device (Con-Flo IV, Thermo Fisher Scientific Inc.). Details of the mass spectrometric analysis are available elsewhere [31,32]. The isotopic compositions were measured for the samples and are reported against atmospheric N_2 for $\delta^{15}N$ and Vienna Standard Mean Oceanic Water (VSMOW) for $\delta^{18}O$. The international reference materials USGS-34 ($\delta^{15}N = -1.8‰$ and $\delta^{18}O = -27.9‰$) and USGS-35 ($\delta^{15}N = 2.7‰$ and $\delta^{18}O = 57.5‰$) along with a 1:1 mixture of the two were used to calibrate the raw values of the samples. The samples were analyzed in triplicate at an averaged analytical precision (1-σ) of 0.4‰ for $\delta^{15}N$ and 0.5‰ for $\delta^{18}O$.

We conducted the data analysis by dividing the samples into 3 groups: the upper stretch- consisting of 2 tributary and 7 mainstream sampling points (Stations 1–9); the middle stretch- consisting of 2 tributary and 9 mainstream sampling points (Stations 10–20); and the lower stretch, consisting of 5 tributary and 7 mainstream sampling points (Stations 21–32; see Table 1 for details). The upper, middle, and lower sections of the Ganges were characterized by steep topography, plain regions with significant groundwater interaction, and a dominant contribution from tributaries, respectively. A 1-way ANOVA was conducted to identify the significant variations ($p < 0.05$) in the elemental concentrations in different sections of Ganges where the unequal N HSD test was applied for post hoc analysis. Major controls on the variability of inorganic species in sampling locations were identified by principal component analysis (PCA) using the singular value decomposition approach to examine covariance between individuals in the prcomp() function of the R software (version 2023.03.0). A KMO (Kaiser–Meyer–Olkin) measure for sampling adequacy was conducted beforehand to check the strength of partial correlations individually for the PCA analysis of ions (0.77) and metals (0.72). An alpha value of less than 0.05 in Bartlett's test of sphericity indicated that the variables do not form an identity matrix. The resulting loadings are orthogonal, and none of the rotation techniques are applied to the loading directions.

3. Results

Water temperature in the Ganges varied between 18 and 34 °C with lower temperatures in the upper stretch which increased gradually on moving downstream (Table 1). The average pH and electrical conductivity (EC) were 8.9 ± 0.6 and 290.0 ± 165.6 µS/cm, respectively. The water was alkaline (pH > 7), and the conductivity of the water was low and uniform in the upper section but high and variable in the lower section (Table 1). Middle Ganges showed a large spread in both pH and conductivity. As conductivity is indicative of ionic concentrations, the overall ionic species were also elevated in the middle stretch of the Ganges (Figure 2a–g). The major ion concentrations were the lowest in the upper section, increased in the middle and decreased again in the lower section (Table 2). Tributaries in the middle Ganges showed large ionic loads compared to that of the lower and upper sections (Figure 2a–g). Among the cations, Na^+ ions exhibited the largest station-wise variability (1.6–121.2 mg/L) with high concentrations in the middle stretch (St-18, the Yamuna, in particular). The concentration variability of Ca^{2+} (15.7–45.9 mg/L) and Mg^{2+} (2.3–27.4 mg/L) followed that of Na^+, whereas K^+ (1.5–24.1 mg/L) was the least variable. The station-wise concentration of anions was the highest for Cl^- (0.4–122.8 mg/L), followed by $SO_4{}^{2-}$ (8.2–60.5 mg/L) and $NO_3{}^-$ (below detection-22.8 mg/L; Supplementary Table S1). In contrast to the major ions, one-way ANOVA of metals showed significantly higher heavy metals in the upper Ganges, followed by middle and lower sections (Table 2, Figure 2h–y). In general, the concentrations of Al, Co, Cr, Fe, Mn, Ni, Pb, Zn, Cu, and Li were higher in the upper section, whereas As, Cd, Sb, Sr, Mo, U, V, and Ba showed high concentrations in the middle sections (Supplementary Table S2). Among these, the concentration of Arsenic showed a significantly higher value in the middle section (Figure 2i, Table 2).

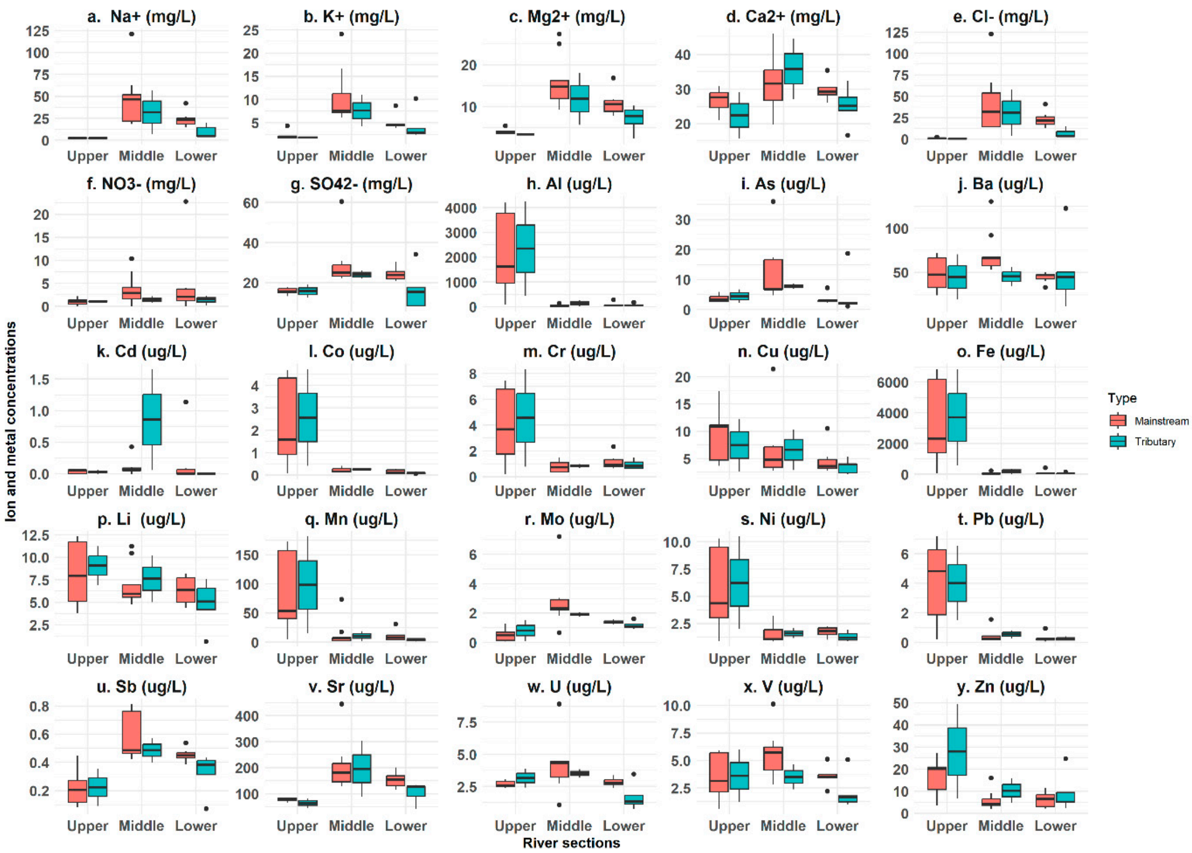

Figure 2. Distribution of (**a**) Na^+, (**b**) K^+, (**c**) Mg^{2+}, (**d**) Ca^{2+},I) Cl^-, (**f**) $NO_3{}^-$, (**g**) $SO_4{}^{2-}$, (**h**) Al. (**i**) As, (**j**) Ba, (**k**) Cd, (**l**) Co, (**m**) Cr, (**n**) Cu, (**o**) Fe, (**p**) Li, (**q**) I (**r**) Mo, (**s**) Ni, (**t**) Pb, (**u**) Sb, (**v**) Sr, (**w**) U, (**x**) V and (**y**) Zn in the three sections of the Ganges River.

Table 2. Comparison of the ions and metals measured in this study to the WHO 2006 drinking water quality standards and global river average concentration. One-way ANOVA for upper, middle, and lower sections of the Ganges with significantly different concentrations ($p < 0.05$) is indicated by different alphabets.

	Present Study				**WHO 2006**	**Global River Average ***
	Range (Min-Max)	**Upper Section ($\mu \pm \sigma$)**	**Middle Section ($\mu \pm \sigma$)**	**Lower Section ($\mu \pm \sigma$)**		
Na^+ (mg/L)	1.6–121.2	2.5 ± 0.7 [b]	43.4 ± 31.7 [a]	17.9 ± 10.9 [b]	200	6.93
K^+ (mg/L)	1.5–24.1	2.10 ± 0.87 [b]	10.0 ± 5.8 [a]	4.74 ± 2.36 [b]	200	1.62
Mg^{2+} (mg/L)	2.3–27.4	3.81 ± 0.66 [c]	15.1 ± 6.6 [a]	9.26 ± 3.50 [b]	600	4.03
Ca^{2+} (mg/L)	15.6–45.9	25.7 ± 4.9	32.6 ± 8.0	27.8 ± 4.7	600	15.68
Cl^- (mg/L)	0.4–122.8	0.88 ± 0.59 [b]	40.6 ± 34.5 [a]	16.2 ± 11.4 [b]	250	8.43
NO_3^- (mg/L)	0–22.8	1.02 ± 0.71	3.11 ± 3.22	3.48 ± 6.20	50	1.16
SO_4^{2-} (mg/L)	8.2–60.5	15.9 ± 2.1 [b]	28.6 ± 11.0 [a]	21.13 ± 7.83 [a/b]	250	12.22
Al (μg/L)	17–4246	2222 ± 1740 [a]	63 ± 71 [b]	83 ± 74 [b]	200	32
As (μg/L)	1.1–36.0	3.82 ± 1.62 [b]	11.9 ± 9.2 [a]	4.15 ± 4.83 [b]	10	0.62
Ba (μg/L)	11.4–130.5	3.8 ± 1.6	11.9 ± 9.2	4.2 ± 4.8	700	23.00
Cd (μg/L)	0–1.66	0.04 ± 0.04	0.24 ± 0.49	0.11 ± 0.33	3	0.08
Co	0.06–4.74	2.44 ± 2.02 [a]	0.23 ± 0.10 [b]	0.13 ± 0.08 [b]	–	0.15
Cr (μg/L)	0.2–8.3	4.17 ± 3.19 [a]	0.78 ± 0.37 [b]	1.07 ± 0.49 [b]	50	0.70
Cu (μg/L)	2.2–21.4	8.73 ± 5.01	6.57 ± 5.45	4.23 ± 2.23	2000	1.48
Fe (μg/L)	21–6851	3531 ± 2897 [a]	84 ± 109 [b]	89 ± 105 [b]	300	66
Li (μg/L)	0.7–12.3	8.4 ± 3.4	7.0 ± 2.4	5.7 ± 2.1	–	1.84
Mn (μg/L)	1.2–181.3	91.4 ± 73.9 [a]	12.9 ± 20.9 [b]	8.10 ± 7.99 [b]	400	34
Mo (μg/L)	0.1–7.2	0.6 ± 0.5 [b]	2.6 ± 1.6 [a]	1.3 ± 0.2 [b]	–	0.42
Ni (μg/L)	0.87–10.5	5.90 ± 3.96 [a]	1.54 ± 0.74 [b]	1.58 ± 0.47 [b]	70	0.80
Pb (μg/L)	0.07–7.17	4.05 ± 2.70 [a]	0.45 ± 0.42 [b]	0.28 ± 0.23 [b]	10	0.08
Sb (μg/L)	0.1–0.8	0.2 ± 0.1 [c]	0.6 ± 0.2 [a]	0.4 ± 0.1 [b]	20	0.07
Sr (μg/L)	42–444	75 ± 13 [b]	204 ± 100 [a]	133 ± 41 [a/b]	–	60.0
U (μg/L)	0.8–8.9	2.8 ± 0.5	4.0 ± 1.9 [a]	2.4 ± 0.9 [b]	30	0.37
V (μg/L)	0.6–10.1	3.6 ± 2.2	5.2 ± 2.1 [a]	3.0 ± 1.4 [b]	–	0.71
Zn (μg/L)	2.0–49.4	18.9 ± 13.9 [a]	6.66 ± 4.95 [b]	7.51 ± 6.20 [b]	3000	0.60

* Global river average values for major ions are after [34], and for heavy metals are after [35].

The PCA loadings for major ions (Supplementary Table S5) showed a close association between Na^+, Cl^-, and SO_4^{2-} and between K^+ and Mg^{2+} (Figure 3a). The NO_3^- behaved differently compared to all other ions (Figure 3a). Most of the middle Ganges samples were characterized by high concentrations of the major ions and formed a distinct cluster from the upper Ganges samples, whereas samples from lower Ganges showed overlap with both upper and middle sections (Figure 3a). The major ion concentrations for Station 11 (Kanauj), 18 (Yamuna), and 25 (Patna) were distinguishable compared to other stations (Figure 3a). Component loadings for heavy metals (Supplementary Table S6) indicated a close association between Al, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, and Zn directed towards stations from upper Ganges that formed a separate cluster (Figure 3b). Loadings for As, Sb, Mo, Sr, Cd and U were directed towards the middle Ganges stations cluster. There was an overlap in the clusters of the middle and lower Ganges stations for heavy metals, where samples from the lower Ganges showed a small spread compared to the middle (Figure 3b). Similar to major ions, Station 18 behaved distinctly for heavy metals as well (Figure 3b).

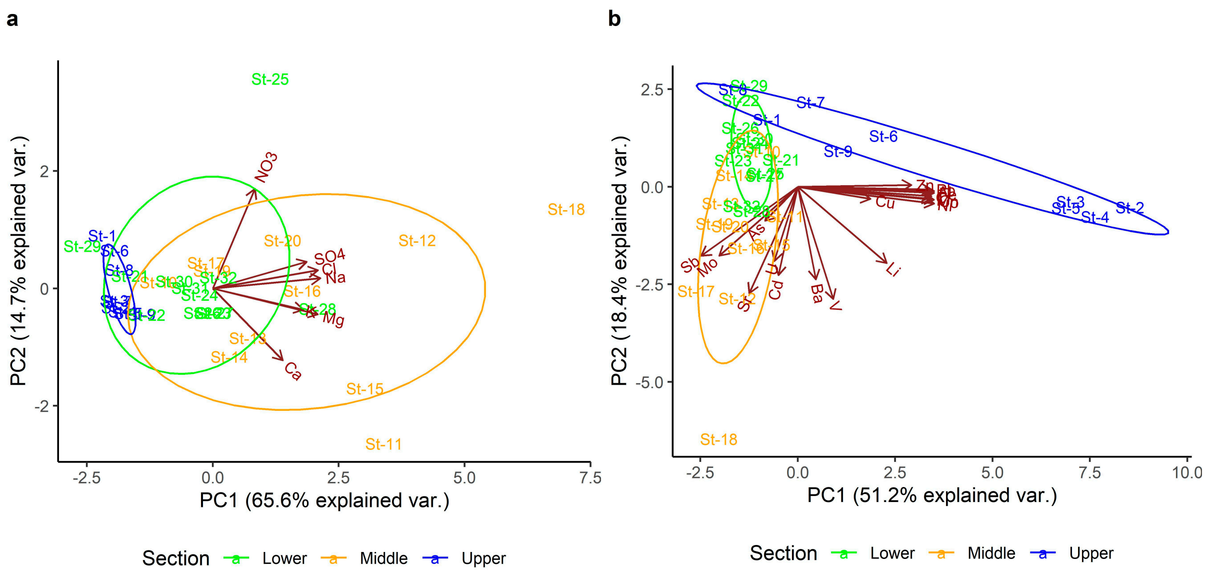

Figure 3. Principal component analysis of (**a**) major ions and (**b**) heavy metals across 32 sampling stations of the Ganges basin. The stations from upper, middle, and lower sections of the basin are shown in blue, yellow, and green ellipse, respectively. The component loadings are shown with brown arrows. Detailed component weights for major ions and metals can be obtained from Supplementary Tables S5 and S6, respectively.

WQI for most of the samples ranged from 25 to 50, indicating these are slightly polluted, categorizing the samples under the 'good' class (Table 3). The water quality of most of the samples in the lower stretch exhibited excellent water quality as per WQI (0–25). The most polluted sample was observed in the middle stretch of the Ganges at Station 11, showing the highest WQI value (77.11), categorizing the water here in the polluted category (Table 3). Samples from the Alaknanda (Station 2) and near Rishikesh (Stations 4–5) also showed moderately polluted water quality (WQI > 50) owing to high concentrations of Al and Fe.

The average concentration of NO_3^- in the Ganges was 2.6 ± 4.2 mg/L, which was comparable to the global average river NO_3^- concentration (1.5 ± 3.8 mg/L; [36]). The $\delta^{15}N$ of NO_3^- varied between -10 and 8.2‰ and $\delta^{18}O$ from -2.7 to 33.8‰ (Supplementary Table S4) with the overall mean of -1.8 ± 3.6‰ for $\delta^{15}N$ and 18.2 ± 8.2‰ for $\delta^{18}O$ (Figure 4). For comparison, the respective global values are 7.1 ± 3.8‰ and 2.3 ± 6.2‰ [36], suggesting different origins of NO_3^- in the Ganges compared to other rivers of the world. None of the metals or ions showed a significant correlation with $\delta^{15}N$ or $\delta^{18}O$ of NO_3^-.

Table 3. Water quality index of the water samples collected from 32 sampling stations across the Ganges river basin.

Station	Type	Nearby City	WQI	Status	Uses
St-1 #	Tributary (Bhagirathi)	Devprayag	29.16	Slightly polluted	Drinking, irrigation, industrial
St-2	Tributary (Alaknanda)	Devprayag	50.91	Moderately polluted	Irrigation, industrial
St-3	Mainstream Ganges	Devprayag	48.10	Slightly polluted	Drinking, irrigation, industrial
St-4	Mainstream Ganges	Rishikesh	52.88	Moderately polluted	Irrigation, industrial
St-5	Mainstream Ganges	Rishikesh	52.30	Moderately polluted	Irrigation, industrial
St-6	Mainstream Ganges	Haridwar	39.36	Slightly polluted	Drinking, irrigation, industrial
St-7 #&	Mainstream Ganges	Haridwar	30.34	Slightly polluted	Drinking, irrigation, industrial
St-8 #	Mainstream Ganges	Bijnore	25.51	Slightly polluted	Drinking, irrigation, industrial
St-9 &	Mainstream Ganges	Narora	35.75	Slightly polluted	Drinking, irrigation, industrial
St-10	Tributary (Ramganga)	Kannauj	39.13	Slightly polluted	Drinking, irrigation, industrial
St-11 &	Mainstream Ganges	Kannauj	77.11	Polluted	Irrigation
St-12	Mainstream Ganges	Kannauj	53.47	Moderately polluted	Irrigation, industrial
St-13 #	Mainstream Ganges	Kanpur	47.79	Slightly polluted	Drinking, irrigation, industrial
St-14 #&	Mainstream Ganges	Kanpur	45.45	Slightly polluted	Drinking, irrigation, industrial
St-15	Mainstream Ganges	Varanasi	16.69	Excellent	Drinking, irrigation, industrial
St-16	Mainstream Ganges	Varanasi	29.11	Slightly polluted	Drinking, irrigation, industrial
St-17	Mainstream Ganges	Allahabad	32.56	Slightly polluted	Drinking, irrigation, industrial
St-18	Tributary (Yamuna)	Allahabad	56.26	Moderately polluted	Irrigation, industrial
St-19	Mainstream Ganges	Allahabad	32.38	Slightly polluted	Drinking, irrigation, industrial
St-20	Mainstream Ganges	Buxar	23.69	Excellent	Drinking, irrigation, industrial
St-21 #	Tributary (Ghaghra)	Chapra	18.08	Excellent	Drinking, irrigation, industrial
St-22 #$	Tributary (Sone)	Chapra	39.75	Slightly polluted	Drinking, irrigation, industrial
St-23 #&$	Mainstream Ganges	Patna	19.86	Excellent	Drinking, irrigation, industrial
St-24 #$	Tributary (Gandak)	Patna	17.61	Excellent	Drinking, irrigation, industrial
St-25 $	Mainstream Ganges	Patna	24.79	Excellent	Drinking, irrigation, industrial
St-26#	Tributary (Buri Gandak)		41.11	Slightly polluted	Drinking, irrigation, industrial
St-27 #	Mainstream Ganges	Bhagalpur	27.29	Slightly polluted	Drinking, irrigation, industrial
St-28 #	Mainstream Ganges	Bhagalpur	27.44	Slightly polluted	Drinking, irrigation, industrial
St-29 #	Tributary (Kosi)		19.19	Excellent	Drinking, irrigation, industrial
St-30	Mainstream Ganges	Rajmahal	18.59	Excellent	Drinking, irrigation, industrial
St-31	Mainstream Ganges	Howrah	16.84	Excellent	Drinking, irrigation, industrial
St-32	Mainstream Ganges	Howrah	31.62	Slightly polluted	Drinking, irrigation, industrial

Cd below detection; & NO_3^- below detection; $ EC not available.

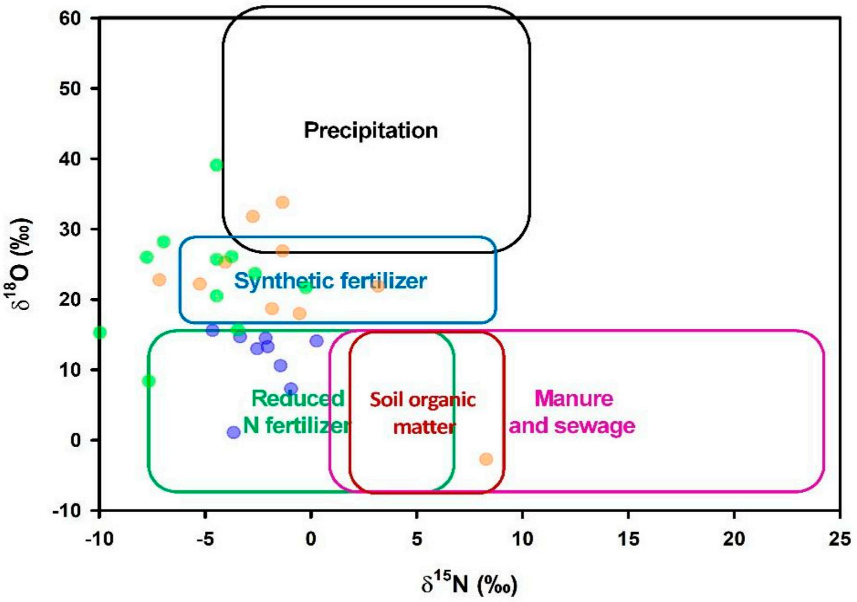

Figure 4. Isotopic analysis of dissolved nitrate in the Ganges for its source apportionment using a dual-isotope cross plot of $\delta^{15}N$ and $\delta^{18}O$ based on [37]. Circles with blue, orange, and green colors indicate stations from the upper, middle, and lower sections of the Ganges, respectively.

4. Discussion

We performed a basin-scale analysis of major ions and various metals in the Ganges River to identify the sources governing their concentrations in the basin. Our results indicate the dominant effect of bedrock weathering, anthropogenic influences, groundwater, and tributary contribution on major ions and heavy metal concentrations in different sections of the Ganges, which are discussed below.

4.1. Major Ions

The origin and variability in major ions are governed by both anthropogenic and natural factors. The anthropogenic sources of major ions include industrial discharge, irrigation return flow, chemical fertilizers, and domestic waste, whereas bedrock weathering, mineral dissolution, and evaporation are among the natural sources [38]. Major ion chemistry has widely been used to identify the nature of weathering for the river basins across the globe, including the Ganges [20,21]. Previous analysis of major ions in the Ganges basin established that the major ion chemistry of the Ganges main channel is controlled by the composition of its tributaries [21]. Analysis of Piper plot and other scatter plots have shown that (Ca^{2+} + Mg^{2+}) and HCO_3^- account for about 80% of the cations and anions in the highland rivers, whereas there is an excess of HCO_3^- than Ca^{2+} + Mg^{2+} along with a relatively high contribution of Na^+ + K^+ to the total cations in the lowland tributaries of Ganges [21]. Based on these observations, it is suggested that carbonate weathering is responsible for ionic concentrations in the upper Ganges, whereas silicate weathering and/or contributions from alkaline soils and groundwater governs ionic composition in the lower section of the river [21].

Due to the already known geogenic origin of major ions in the Ganges, we emphasize our work to identify the anthropogenic perturbations to major ion composition in the Ganges. Unlike previously reported high concentrations of Ca and Mg in the upper Ganges [21], our results showed increased ionic loads in the middle and lower Ganges compared to the upper section, where we find low and uniform ionic concentrations (Figure 3a). The middle section of the Ganges is characterized by a large number of industries and high population loads which could result in the observed variability in ionic concentrations in this region. However, observation of anthropogenic alterations does not deny the dominant contribution of carbonate and silicate weathering in the Ganges major ion chemistry. The two tributaries of the Ganges sampled in the middle section (the Yamuna (Station 18) and the Ramganga (Station 10)) showed the highest ionic loads among all the tributaries (Figure 2a–g, Table S1). Among these, the Yamuna was previously reported as a highly polluted river that deteriorates the water quality of the Ganges downstream of its confluence [39–41]. The EC in the Yamuna was also the highest among all the sampling stations (Table 1), suggesting the external supply of ions to the mainstream Ganges through the Yamuna, making it a potential inorganic load source for the Ganges. The lower section of the Ganges, which is considered highly polluted in terms of organic pathogens due to the release of large quantities of untreated sewage in the river [4], showed relatively lesser ionic loads compared to the middle Ganges (Figure 2a–g). We attribute this lowering in ionic concentrations to the dilution effect caused by a large number of Himalayan tributaries (Gomati, Ghaghra, Gandak and Kosi) joining the mainstream Ganges in this region (Figure 1a, Stations 21–32). Similarly, previous work has also indicated that the contribution from tributaries and their mixing proportions dictate the chemistry of the Ganges and the Yamuna in the lower reaches [21].

Large fluctuations in ionic concentrations, particularly in the middle part of the Ganges, suggested the influence of point sources such as groundwater contribution and/or urban inputs. For example, mineralization of organic matter in wastewater can result in the release of organic-bound chlorine as Cl^-, thereby leading to an increase in Cl^- concentrations [42,43]. The influence of urban wastes on the river water quality in our study was apparent by the shift in the ratio of Na^+ and Cl^- ions. The Na^+/Cl^- molar ratio was higher in the upper section (~5) and gradually reduced to 1 as the stream entered the middle and lower sections (Figure 5), indicating a change in source input for these ions. Higher Na^+ compared to Cl^- in the upstream indicates contribution through silicate weathering [44], whereas the shift of the ratio towards one downstream is attributed to increased Cl^- concentration from sewage discharge [45]. The decrease in Na:Cl is consistent in both the middle and lower sections, suggesting the impact of sewage discharge on major ion concentrations (Figure 5).

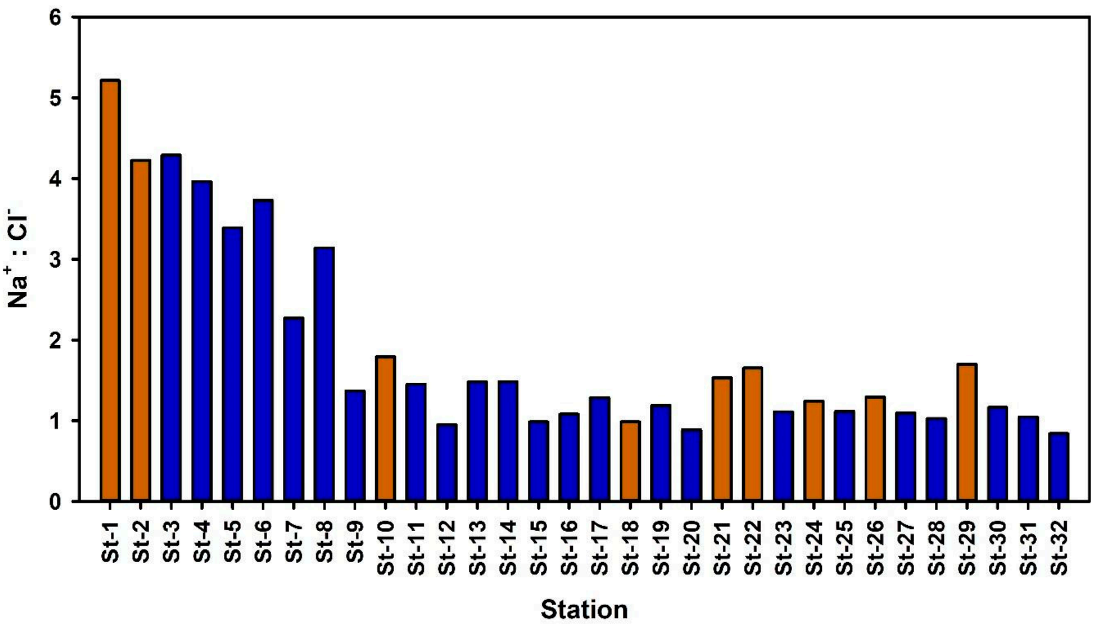

Figure 5. Na^+: Cl^- molar ratio in the Ganges and its tributary rivers. Blue and brown bars indicate the mainstream Ganges and its tributaries, respectively. Tributaries are as follow- St-1: Bhagirathi, St-2: Alaknanda, St-10: Ramganga, St-18: Yamuna, St-21: Ghaghra, St-22: Sone, St-24: Gandak, St-26: Buri Gandak, and St-29: Kosi.

Quantitative source contribution of major ions in the river can be ascertained by estimating the chemical composition of possible ionic sources (such as glacial melt, groundwater, sewage, industrial effluents, and agricultural discharge), which is beyond the scope of this work. Nonetheless, EC, which is a measure of the ionic concentration of water, showed large variability (119.8–794 µS/cm) in the lower and middle sections (Table 1), suggesting large ionic inputs in these sections of the river. The average major ion concentration was comparatively small in the lower section of the Ganges compared to the middle (Figure 2a–g), showing the influence of relatively clean waters from tributaries in the lower Ganges.

4.2. Nitrate Isotopic Composition

Despite being a less abundant ion in the Ganges, we used stable isotope techniques for source apportionment of NO_3^- due to its potential biological impacts on the river water quality, which is particularly important after the recent rises of algal bloom in the Varanasi and nearby regions of the river Ganges [46]. Identifying the sources of NO_3^- in the river could help reduce such instances in the future. Nitrate is one of the important major ions which is introduced to the streams through fertilizer, soil organic matter, atmospheric deposition, manure, and septic wastes [47]. It can easily mobilize into the river water and can lead to harmful algal blooms if present in high concentrations. The average values of δ^{15}N-NO_3^- (-1.8 ± 3.6‰) and δ^{18}O-NO_3^- (18.2 ± 8.2‰) in the Ganges were significantly lower and higher, respectively, compared to the global averages of 7.1 ± 3.8‰ and 2.3 ± 6.2‰ [36], suggesting NO_3^- dynamics in the Ganges to be differently controlled compared to the other rivers of the world, particularly during the summer season. The stable isotope ratios in NO_3^- in the Ganges (-10–8‰ for δ^{15}N and -2.7–33.8‰ for δ^{18}O) broadly overlapped with fertilizer isotopic signature (Figure 4).

A comparison of the isotopic composition of NO_3^- in the Ganges with other rivers (Table 4) showed NO_3^- in most of the rivers results from sewage waste (δ^{15}N-$NO_3^- \approx 7$ to 20‰ and δ^{18}O < 15‰), whereas NO_3^- in Ganges is primarily of fertilizer origin (δ^{15}N-NO_3^- = -1.8 ± 3.6‰, δ^{18}O-NO_3^- = 18.2 ± 8.2‰). Although, several locations in the lower stretch of the Ganges (Station 20, 24, 27, 29, and 31) also showed depleted δ^{15}N-NO_3^- in the range of -7 to -10‰, indicating contribution from industrial wastewater (δ^{15}N-NO_3^- ≈ -8.6‰; [48]). The role of sewage discharge in NO_3^- pollution was small, in contrast to the common notion that sewage is primarily responsible for the pollution of Ganges water. However, sewage could be responsible for increased concentration and the dominant source for other major ions. This is also evident from the absence of correlation between NO_3^- and other major ions in this study which indicates a difference in their origin (Figure 3a).

Table 4. Comparison of the isotopic composition and concentration of NO_3^- in the Ganges River to some of the major rivers of the world (values after Yue et al. (2017) [45]).

River	Length (km)	Basin Area (10^5 km^2)	NO_3^- (mg/L)	δ^{15}N-NO_3 (‰)	δ^{18}O-NO_3 (‰)	Sample Number
Mississippi River	6020	32.2	1.45 ± 0.5	7.7 ± 0.3	4.6 ± 0.3	22
Yellow River	5465	7.95	3.4 ± 0.86	8.4 ± 1.1	1.2 ± 1.3	25
Saint Lawrence River	1287	3.00	0.43 ± 0.08	5.7 ± 0.7	5.4 ± 1.4	41
Rhine River	1320	1.85	2.7 ± 0.7	8.2	0.4	24
Elbe River	1165	1.48	2.6 ± 1.4	8.5	1.3	16
Ganges (present work)	2525	17.3	3.16 ± 4.49	-1.8 ± 3.6	18.2 ± 8.2	32

The dominance of fertilizer-based NO_3^- in the Ganges is apparent from the land-use pattern of the Ganges basin, where more than 90% of the basin is occupied with farming (Figure 1c), and the agricultural sector holds the largest share in the economy of the region and livelihood of the people residing in the basin. PCA loadings also showed that the middle and lower Ganges, which fall under the high-fertility Indo-Gangetic plain region, are characterized by high NO_3^- with distinctive variability from other ions (Figure 3a), thereby imparting NO_3^- through agriculture. Nutrient accumulation through agricultural run-off has previously been suggested as a possible cause of algal bloom developed in the Ganges river [46,49], whereas leaching of agricultural NO_3^- to groundwater of the Ganges basin has already been reported [50,51]. Confirming these suggestions, for the first time, we use stable isotopic techniques to demonstrate that agricultural fertilizers are the most dominant source of NO_3^- in the Ganges during the dry season. Our observations are partly in agreement with a previous study that identified synthetic fertilizers as the second most important source of nitrate during the post-monsoon (wet) season in the Ganges river basin using stable isotopic studies [52]. The absence of significant correlations between δ^{15}N or δ^{18}O of NO_3^- with the analyzed metals and ions suggests the limited influence of agriculture on the river's inorganic chemical composition. Though the concentrations of NO_3^- are within permissible limits during the present study, it might increase in other environmental/seasonal conditions if left unmanaged [53,54]. It is evident from the isotopic signature of NO_3^- that synthetic fertilizers used in agriculture are the major cause of this pollution. Therefore, we suggest minimizing the use of synthetic fertilizers through the promotion of organic farming in the basin to counteract increased fertilizer NO_3^- in the Ganges.

4.3. Metals

Similar to major ions, we observed a large spatial variability in dissolved metal concentrations from the upper to lower section of the Ganges, which indicated the combined effect of weathering processes, the addition of groundwater, surface runoff, and anthropogenic contributions [11]. However, overall metal concentrations were high in the upper and middle Ganges compared to the lower section (Figure 2h–y). A one-way ANOVA for individual metals revealed significantly higher concentrations of most metals in the upper Ganges (Table 2), where the river flows intensely through steep topographic regions, thereby having a high potential to weather the underlying rocks. Our observations were in agreement with previous studies and suggested that the elements are available to the river by weathering of rocks upstream, which reduces considerably downstream due to dilution from the tributaries ([11] and references therein; [20]).

The metal contents in the Ganges have previously been studied for their toxicities and impacts on human and ecosystem health [44,55,56]. However, those studies are limited to regions, providing insight into selected portions of the Ganges. Despite the limited spatial coverage, the concentration of dissolved metals in previous studies ([3] and references therein) broadly agreed with our results which showed the maximum and minimum concentration for Fe and Cd in the basin, respectively. The levels of metals in our study were Fe > Al > Sr > Ba > Mn > Zn > Li > As > Cu > V > U > Ni > Cr > Mo > Pb > Co > Sb > Cd. A similar trend for heavy metal concentration has been reported previously [57]. High Al concentration in the upper Ganges is primarily attributed to weathering of crystalline rock of Higher Himalaya, whereas the high concentration of Fe is derived from lesser Himalayan sedimentary sequences having a large extent of phosphorite and magnesite deposits and black shale, which forms the major lithology of drainage basin for the Alaknanda and tributaries in the upper stretch of Ganges [58]. We attribute the observed high concentrations of Fe and Al to their tendency to get readily affected by chemical weathering and behave as first-order immobile elements during the Himalayan erosion [59]. Similar variations shown by Al, Fe, Co, Cu, Li, Ni, Zn, Cr, Mn, Ni, and Pb through the river suggest similarity in their sources, transformation, and transport across the basin (Figures 2h–y and 3b). The close association of Cu, Zn, Cr and Ni with Al, Fe and Mn in the upper Ganges (Figure 3b) suggests the influence of colloids of Fe-Mn oxides/hydroxides on the metal solubility under different redox conditions [60]. The metals with possible alterations through anthropogenic activities or groundwater and tributary inputs such as As, Cd, Cu, and Zn showed variability along the course of the river. Anthropogenic sources of Cr, Zn, Pb, Ni, Cu, and Cd have been reported previously in the sediments in upper 300 km stretch of Ganges [15]. Arsenic concentrations were much higher than WHO permissible limits at Kanpur and Kannauj (14–36 µg/L; Station 10–14) suggesting anthropogenically generated Arsenic in this industrial region of the Ganges plains. High Arsenic concentrations, as observed around the Kannauj-Kanpur belt, can also be caused by groundwater inputs in this section of the river [61]. It is important to note that groundwater contamination can cause significant health impacts to humans by modifying hydrogeochemistry and heavy metal concentrations through surface water-ground water interactions [10]. High Arsenic concentrations in Ganga compared to various other rivers of the world is also due to the presence of Ganga on a geologically young mountain belt which is predicted as among the favorable areas for As rich groundwater [62]. Similar observations for the absence of metal pollution, except for Arsenic, have previously been reported [20]. Concentrations of certain metals in the dissolved phase could, however, also get modified due to sediment-water interactions and could result in higher concentrations of metals associated with finer particle-size of sediments during long-range transfer [15]. We, therefore, suggest the coevolution of river water and sediments at the basin scale to understand the exchange dynamics.

4.4. Variability in Metals and Ions along the Basin

The variability in the concentration of major ions and metals was controlled by the change in natural, geogenic, and anthropogenic sources along the sampling stations in the basin. The water at the foothills of the Himalayas (Station 1, Station 2) is relatively pristine and little affected by anthropogenic activities. Despite insignificant anthropogenic influences, higher concentrations of major ions and metals were observed in Stations 1–3 (Figure 2). The difference in the concentrations of various metallic and ionic species at Station 2 (Alaknanda) and Station 3 (Bhagirathi) is attributed to the difference in the discharge flux and geology of the two headwater tributaries of the Ganges. The Alaknanda, in which the sampled water flowed through carbonatites, quartzites, slates, phyllites, and greywackes, has higher levels of dissolved ions (1.80×10^6 tons year^{-1} compared to the Bhagirathi (0.34×10^6 tons year^{-1}) [61], resulting in overall high dissolved loads in the Ganges at Devprayag (Station 3) where the two tributaries meet to form the river Ganges.

Samples from the upper Ganges showed high concentrations of metals, particularly at Stations 2, 3, 4, and 5, which indicated similar origin and transport of metals in the upper stretch of the river (Figure 3b). Similar observations for increased metal concentrations in this portion of the Ganges compared to its upstream have been reported previously [18]. Similar lithology of the stations lying in proximal geological settings resulted in parallel variations of most of the metals across these stations. The concentration of metals further dropped till Bijnor (Station 8), after which a sharp peak was observed at Narora (Station 9; see Figure 2). The presence of a nuclear power plant at Narora could result in a sudden rise in the heavy metal concentration. Downstream Narora, major ions and metals increased in Kannauj (Station 11), which is known for high industrial pollution due to heavy tannery effluents [63,64]. The inorganic pollution in the Ramganga (Station 10), a tributary that joins the mainstream Ganges at Kannauj, was relatively low, thereby diluting the major ion and metal concentrations downstream the industrial zone of Kannauj-Kanpur belt (Stations 12–14). It is important to note that the Ramganga is considered among the polluted tributaries of the Ganges, particularly in the industrial regions located upstream of the confluence with the Ganges. However, we observed lower pollution in the Ramganga compared to the mainstream Ganges, which could be due to the location of our sampling site, which was just before the confluence of the Ramganga with the Ganges. A two-component mixing model using $\delta^{18}O$ of river water during the same sampling period estimated ~40% contribution of the Ramganga to the mainstream Ganga at this location [65], which would have diluted the effect of pollution in the mainstream Ganges after the confluence.

The Yamuna River (Station 18), another major tributary of the Ganges, showed elevated loads of metals and ions (Figure 2). The component loadings in PCA showed that the Yamuna was distinct compared to all other stations (Figure 3a) due to the very high inorganic content in the Yamuna. Different origins of pollution in the Ganges and the Yamuna have been previously reported where the Ganges was polluted due to natural, anthropogenic, and organic sources; the Yamuna was polluted primarily due to anthropogenic sources from industrial, agricultural, and domestic sectors [41]. The water contribution of the Yamuna to the mainstream Ganges was only ~5% during the study period [65], and, therefore, its influence on the pollution in the Ganges was insignificant. Additionally, groundwater contribution at Allahabad (Stations 17–19), where the Yamuna meets the Ganges, is estimated to be ~25% [65], which can result in the dilution of metals brought by the Yamuna. However, the scenario may change in other seasons when the water flow in the mainstream Ganges and its tributaries intensifies compared to the summers. A significant change in the concentration of pollutants in the middle stretch of the Ganges has previously been attributed to groundwater contributions, particularly in the regions where the Ganges behaves as a gaining river [66]. Downstream of Varanasi, there was a large fluctuation in the concentrations of the ions and metals, which was associated with a large number of tributaries joining the mainstream Ganges in its lower stretch (Figure 1a).

The metals and ions showed variability in the lower stretch of the Ganges depending on their concentrations and water contribution by the tributaries. Tributaries like Ghaghra (Station 21) and Gandak (Station 24) contributed to more than 55% of water in the Ganges, whereas the contributions from Sone (Station 22) and Buri Gandak (Station 26) were insignificant due to the drying of the rivers in the summer season [65]. Our results indicate that the Ganges is unpolluted in terms of heavy metals or major ions at the basin level. The water quality index calculations also revealed the quality of most of the sampling stations as good or slightly polluted and usable for drinking, irrigation, and industrial purposes (Table 3). Water sampled from the Alaknanda (Station 2), near Rishikesh (Stations 4–5), near Kannauj (Stations 11–12) and the Yamuna (Station 18) showed high WQI compared to all other locations suggesting relatively high pollution levels at these stations. Of these, water from Station 11 was the most polluted and can be used for irrigation purposes only. Samples from the Alaknanda (Station 2) and Rishikesh (Stations 4–5) showed a WQI > 50 due to the presence of high concentrations of Al and Fe originating from geogenic processes. Samples from Kannauj and the Yamuna showed the influence of high Arsenic concentrations in increasing the WQI values. The tributaries in the lower Ganges showed excellent water quality, whereas the Yamuna was the most polluted tributary according to the WQI classification. None of the samples fell in the extremely polluted category. Similar to our observations, assessing the heavy metal pollution index along the course of the Ganges identified very little contamination in the water of the Ganges and qualified it as fit for direct drinking purposes [12]. Nonetheless, we suggest the treatment of Ganges water before consumption despite its qualification in terms of heavy metal and major ion concentrations due to very high loads of fecal coliform carried by the river [67].

Except for some localized points, the ion and metal contents in the Ganges were within the permissible limit for the drinking water standards based on the WHO 2006 guidelines (Table 2) despite sampling performed in the pre-monsoon dry season with expected increased pollution during lean river flow. These findings agree with a previous work in that low dissolved trace metal concentrations in the Ganges were observed compared to the existing dataset [11]. The metal and ion concentrations in the Ganges, although within WHO standards, surpassed the global average concentrations at most of the sampling locations (Table 2), suggesting the potential of the Ganges to get inorganically polluted faster than other rivers of the world. Our work presently finds that the water quality of the Ganges is usable in terms of major ion and metal concentrations at the basin scale, even in the pre-monsoon dry season, which tends to have higher concentrations compared to the wet season. This is due to the discharge-concentration relationship where pre-monsoon months are expected to show high concentrations due to low discharge, and the monsoon months show low concentrations due to high discharge [11,44]. Nonetheless, the predicted increase in population loads for the Ganges river basin makes its water susceptible to contamination through increased urbanization, agriculture, livestock farming, and sewage discharge [68]. We suggest seasonal studies of the Ganges river basin for accurate estimation of inorganic species and their sources and to quantify water contribution from groundwater and tributaries in the Ganges to mitigate future projections for river pollution. Combining geochemical characterization, geochemical modeling, and isotopic characterization of the river waters can provide deeper insights into the evolution of water chemistry during rock-water interaction, sources of various ions/metals, hydrogeochemical processes affecting the composition of water, and reconstructing geological conceptual models [69]. Further, the adaptation of advanced water treatment techniques for specific metals and ions [9] can help mitigate both the overall and site-specific declines in the water quality in the basin.

5. Conclusions

The basin-scale assessment of inorganic species in the Ganges suggests that the major ion and heavy metal concentrations in the river are governed by four major factors during the dry summer season: bedrock weathering, groundwater interactions, tributary inputs, and anthropogenic interferences. Among these, weathering is responsible for elevating metal concentrations at upper sections of the Ganges, whereas tributaries and groundwater show significant impact in lower reaches with a dilution effect on the inorganic loads of the river. We report a dominating impact of anthropogenic activities on major ion concentrations in the middle portion of the river. These activities include agriculture which imparted a significantly large share of dissolved NO_3^- in the river through the use of synthetic fertilizers, as evident from the basin-level isotopic signature of dissolved NO_3^- in the Ganges ($\delta^{15}N = -1.8 \pm 3.6‰$, $\delta^{18}O = 18.2 \pm 8.2‰$). This observation is uncommon compared to the major rivers in the world where sewage ($\delta^{15}N \approx 7$ to 20‰ and $\delta^{18}O < 15‰$) is the primary source [23]. The efficient and planned execution of fertilizer management policies is needed for the Ganges basin to reduce NO_3^- pollution and harmful algal blooms in the river. The basin level concentrations of all the measured elements (except Arsenic: 1–36 μg/L, Fe > 6800 μg/L and Al > 4200 μg/L) were within desirable limits during the lean flow when concentrations are expected to be high. However, metals and major ion concentrations in the Ganges were high compared to the global average indicating high vulnerability of the river to further anthropogenic or natural disturbances. The water quality index also suggested degraded water quality at certain sampling stations owing to high weathering input of Fe and Al and possible anthropogenic inputs. High pollution at isolated stretches can be managed by constructing more efficient sewage treatment plants for urban and industrial wastewaters and by promoting organic farming, particularly under the predictions of a large population increase for the Ganges River basin. We suggest long-term basin-level geochemical and isotopic investigations of Ganges waters along with inorganic speciation of sources such as glacial melt, groundwater, sewage, industrial effluents, and agricultural discharge to get clearer insights into the source input and modification of inorganic species in this vulnerable river system.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w15112026/s1. Table S1: Major ion concentrations (mg/L) of selected ionic species at 32 sampling locations of the Ganga river basin; Table S2: Heavy and trace metal concentration (μg/L) of selected metal species at 32 sampling locations of the Ganga river basin; Table S3: Rare earth elements concentrations at 32 sampling locations of the Ganga river basin; Table S4: Dissolved nitrate isotopic composition at 32 sampling locations of the Ganga river basin; Table S5: Weight/loading of each major ion on the principal components; Table S6: Weight/loading of the analyzed metals on the principal components.

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