

## Spatial and seasonal variations in nutrient load and trophic status of Ganga and Yamuna rivers in Uttar Pradesh, India

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### ABSTRACT

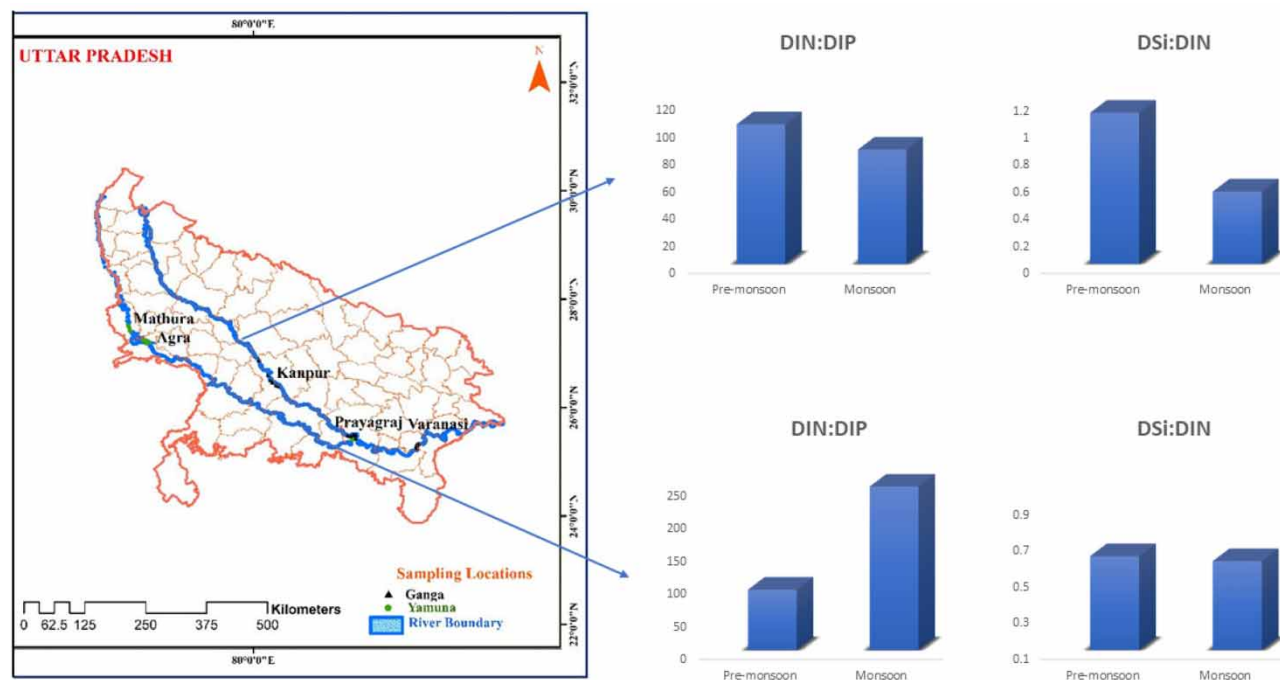
Nutrient loading in aquatic systems from anthropogenic sources is a worldwide concern. The Ganga is the most important river in India, but pollution is currently severely threatening its biodiversity and long-term environmental viability. Water samples were taken from 36 locations along the length of the Ganga and Yamuna rivers in Uttar Pradesh and analysed for nutrient concentration to evaluate the nutrient load, eutrophication danger, and river trophic status. The average concentration of  $\text{NO}_3\text{-N}$ ,  $\text{PO}_4\text{-P}$ ,  $\text{NH}_4\text{-N}$ , and  $\text{SiO}_2\text{-Si}$  exceeded the values in unpolluted rivers, indicating the contribution of anthropogenic sources. The concentration of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  showed significant spatial variation, and  $\text{PO}_4\text{-P}$  showed significant seasonal variation in the study area. The DIN/DIP ratio in the study area exceeded 16:1, indicating a phosphate-limiting condition for phytoplankton development. The DSI/DIN value showed a declining trend in the downstream region of both rivers with average values  $<1$ , indicating nitrate pollution leading to eutrophic conditions. The Indicator for Coastal Eutrophication Potential (ICEP) showed a positive value, indicating that the Ganga and Yamuna rivers in Uttar Pradesh were eutrophic due to nitrogen pollution. Trophic State Index (TSI) values indicated that super-eutrophic conditions existed in the Ganga River (65.62) and hypereutrophic conditions existed in the Yamuna River (75.55) in Uttar Pradesh.

**Key words:** dissolved inorganic nutrients, Ganga River, nutrient load, Trophic State Index, Yamuna River

### HIGHLIGHTS

- The high DIN/DIP ratio indicated phosphate-limiting conditions in both rivers.
- The low DSI/DIN ratio indicated the algal bloom condition in the Yamuna River.
- The positive value of N-ICEP showed eutrophic conditions in both rivers.
- The Yamuna River showed poor quality with hypereutrophic conditions.
- The Ganga River showed high nitrogen loading with super-eutrophic conditions.

## GRAPHICAL ABSTRACT



## INTRODUCTION

The quality of the riverine ecosystem is significantly dependent upon external factors (agricultural, industrial, and municipal waste), apart from natural factors. The source of nutrients in the rivers can either be allochthonous (weathering, precipitation, and domestic and agricultural runoff) or autochthonous (instream production and mineralisation of organic matter) (Sharma *et al.* 2017; Jargal *et al.* 2021). Rapid population growth has enhanced industrialisation and urbanisation due to changes in land use patterns, fossil fuel combustion, and residential runoff, disturbing the river's nutrient balance. Around 10%–90% of the mean annual flow in the rivers is contributed by treatment plants. Modern agricultural practices with high inputs of fertiliser and other agrochemicals have further aggravated the issue of nutrient pollution in the river systems (Bellos *et al.* 2004; Haque 2021). The last two decades have witnessed the unfettered use of pesticides and fertilisers, increasing the river's nutrient content (particularly nitrate, potassium, and phosphate). Phosphorus and nitrogen loading in aquatic systems is a major concern, particularly in areas where heavy urban or agricultural land use leads to contamination through diffuse nutrient inputs. Managing nutrients from diffuse sources in riverine systems is more difficult as it requires a combination of mitigation strategies at both the catchment and reach scales (Weigelhofer *et al.* 2018). This excessive nutrient loading may lead to ecological problems, including nutrient imbalance (C/N/P/Si) and eutrophic conditions and hypoxia zones (Rajmohan & Elango 2005; Ravi *et al.* 2021).

The Ganga and the Yamuna rivers are northern India's two most significant rivers. Along the banks of these rivers are highly populated cities, and the residents of these cities rely on these freshwater sources for their needs, including for household, agricultural, and industrial uses. Ganga is revered as sacred for its purity and capacity for self-cleansing, and the river's water is part of every Hindu tradition and ceremony. However, it was listed as one of the world's top five most polluted rivers due to anthropogenic activities (Kesari *et al.* 2022). The river Yamuna is one of the Ganga's most polluted tributaries and receives over 76% of the nation's total pollution load from Delhi-NCR Press Trust of India (2018), effectively converting the river into a 'sewage drain' (CPCB 2021a, 2021b). There are more than 100 industries situated along the Ganga River, among which 68 are designated as grossly polluting (NMCG-NEERI 2017). Surface waters receive between 3% and 20% of the phosphorus and 18% of the nitrogen applied to croplands. The global load of anthropogenic nitrogen to freshwater systems from agricultural lands, including leaching and runoff, was projected to be  $24.4 \times 10^6$  t N per year (Yadav & Pandey 2017). Most freshwater bodies have P-limited conditions that affect the aquatic balance by disturbing the structure

and diversity of plants and other micro-organisms vital for maintaining a healthy ecosystem (Wade *et al.* 2004). Hence, nutrient pollution remains a significant concern as it can create problems with alterations in the food chain, deterioration of water quality, and deleterious effects on the health of living beings (Bende-Michl & Hairsine 2010). To combat this issue of river pollution, the Indian government has started river protection efforts, including the Ganga Action Plan (GAP), Namami Gange, and Yamuna Action Plan (YAP).

Programmes like GAP I and GAP II were introduced between 1985 and 2015, and a total of Rs. 4,000 crores were provided for these action plans over 30 years. However, a new regeneration strategy was needed to maintain the Ganga River's cleanliness. The Namami Gange Programme was started to view the basin as a whole rather than the Ganga as a separate river. An additional Rs. 30,235 crores budget has been allocated to revitalise this river (Balkrishna *et al.* 2022). Another major river restoration initiative, the YAP, was started to clean the Yamuna River. Action Plans I, II, and III constitute the YAP, a bilateral agreement between the governments of Japan and India. YAP-III is currently being executed with an allocated budget of Rs. 1,656 crores (Srivastava & Prathna 2022) to abate pollution in the river Yamuna. Despite these initiatives, the quality of both these rivers does not seem to have achieved the desired results, as the deterioration of river water quality by nutrient pollution is still a major concern (NMCG-NEERI 2017). It is, therefore, necessary to monitor the nutrient loading of the two major rivers (Ganga and Yamuna) in Uttar Pradesh, has an intensive agricultural region with little information on the trophic condition of river bodies. Most research conducted along the river in Uttar Pradesh has concentrated on the pollution load related to physicochemical parameters, such as DO, BOD, heavy metals, and faecal coliform (NMCG-NEERI 2017; Paul 2017; Singh *et al.* 2022). There is little research in the literature on the relationship between nutrient load and the risk of eutrophication due to nutrient load and trophic status of aquatic systems. This study was carried out to bridge the knowledge gaps with the objective of (1) determining the spatial as well as seasonal variation in the dissolved nutrient concentration in the Ganga and Yamuna rivers; (2) analysing the nutrient chemistry along with the factors influencing it in the Ganga and Yamuna rivers using multivariate statistical analysis; (3) estimating the dissolved nutrient ratios and dissolved nutrient load in the Ganga and Yamuna rivers; and (4) determining the eutrophication potential of the Ganga and Yamuna rivers using the Indicator for Coastal Eutrophication Potential (ICEP) and Trophic State Index (TSI) values.

## MATERIALS AND METHODS

### Study area

The Ganga basin is India's largest river system, covers 26% of the geographical area of India and is home to more than 600 million people, and accounts for more than 40% of the country's GDP (NMCG-NEERI 2017). It originates from the Gangotri glacier as Bhagirathi in Uttarakhand and descends from the mountainous region to the plains at Haridwar. It then turns southeast to Kanpur, the industrial city, and further to Prayagraj, where it is joined by the Yamuna River (Ganga's largest tributary). Here onwards, the river flows in an easterly direction to flow through Varanasi (Garg *et al.* 2020). Several tributaries join it in its 2,525 km-long course before finally draining into the Bay of Bengal (Purushothaman & Chakrapani 2007; Trivedi 2010). The basin is one of the largest alluvial plains formed mostly over the Quaternary period. The Ganga River, together with the Yamuna, erodes Himalayan sedimentary rocks depositing layers of sediment in the plains, creating a wide alluvial plain about a kilometre in thickness. With an erosion rate three times that of the Amazon and three and a half times the global average, the Ganga River comes in third place for sediment transport behind the Yellow and Amazon rivers (Subramanian *et al.* 1987; NMCG-NEERI 2017). Most of the region in this basin falls in the tropical climate zone, and around 85% of the rain is received from June to September (monsoon season). The annual average range of precipitation is from 600 to 1,200 mm, while the maximum temperature ranges from 35 to 40 °C (Sinha *et al.* 2017). The state of Uttar Pradesh contributes 54% of the total wastewater discharged and 76% of the BOD load in the river Ganga (CPCB 2013). Several drains, namely Golaghat Nala, Ranighat Drain, Wazidpur Drain, Sisamau Nala, Permiya Nala, and City Jail Drain join the river Ganga, discharging sewage with high concentrations of nitrate and ammonia into the river (Santy *et al.* 2020). The major drains in Prayagraj include the Arail Drain, Mahewa Drain, Fort Drain, Rasulabad Drain, Sadananda Ashram Drain, Jhusi Drain, and Chhatnag Drain, while in Varanasi, Ramnagar Drain, Varuna Drain, Assi Drain, Rajghat Drain, and Shivala Drain are the major drains that discharge millions of litres of wastewater into the Ganga River along with the nutrients that degrade river water quality (CPCB 2021a, 2021b; Jamal & Sen 2022). The population density of Kanpur is 1,452/km<sup>2</sup> (per sq. km.), Varanasi is 2,395/km<sup>2</sup>, and Prayagraj is 1,087/km<sup>2</sup> (Census of India 2011). The land use of Kanpur mainly includes industrial and public utilities. Agriculture makes up most of the basin's land use, at

65.57%, forest at 16%, and built-up at 4.28% (WRIS 2014). The major portion of Varanasi and Prayagraj was under agricultural use until the last two decades but has recently increased in the built-up area (Jaiswal & Verma 2013; Roustia *et al.* 2018). The sampling sites along the Ganga River were Kanpur (K), Prayagraj (GPY), and Varanasi (V). The water samples at Prayagraj were collected 2 km before the Ganga and Yamuna confluence points for both rivers. In Prayagraj, the water samples collected from the Ganga and Yamuna rivers are represented as GPY and YPY in this study.

The river Yamuna emerges from Yamunotri glacier, Bandarpunch (38°59' N and 78°27' E) in the lower Himalayas (6,320 m above mean sea level). It travels a distance of 1,370 km before meeting the river Ganga at Prayagraj. It accounts for 10.7% of the catchment area in the country and drains an area of 345,848 km<sup>2</sup> (Bawa *et al.* 2014; Joshi *et al.* 2022). The Yamuna basin is underlain by rocks from the Upper Vindhyan Supergroup's Upper Bhandar series. Interbedded sand, silt, and clay layers make up the alluvium. Calcareous concretions are present along with alluvium in certain locations (State Water Resources Agency 2020). The Himalayan region of the river basin has a humid climate, whereas the northwestern and western regions are semi-arid, and the southwestern part is sub-humid. The average annual precipitation ranges from 400 to 1,500 mm (peaking in June to September), while the average maximum and minimum temperatures are, respectively, between 24 and 42.5 °C, and –1 and 11 °C (Sharma *et al.* 2017). The cities chosen for the study along the Yamuna River were Mathura (M), Agra (A), and Prayagraj (YPY). Some of Mathura's most important drains are the Gokul Barrage Drain, Rani Ghat Drain, Gaughat Drain, and Dhruv Ghat Drain. Significant Agra drains include Bhimnagri Drain, Jaganpur Drain, Dhadhupura Drain, and Kalindi Vihar Drain (CPCB 2021a, 2021b). The population density of Mathura is 763/km<sup>2</sup>, while that of Agra is 1,093/km<sup>2</sup>. The cities along the Yamuna River have also seen a drastic shift in land use patterns. The cropland in Mathura has decreased while the urban land has increased from 234 to 332 km<sup>2</sup> (Ahmed *et al.* 2022). Agra, being a tourist spot, has most of the land under hotels and residential blocks (Biswas *et al.* 2017). The study area map is given in Figure 1.

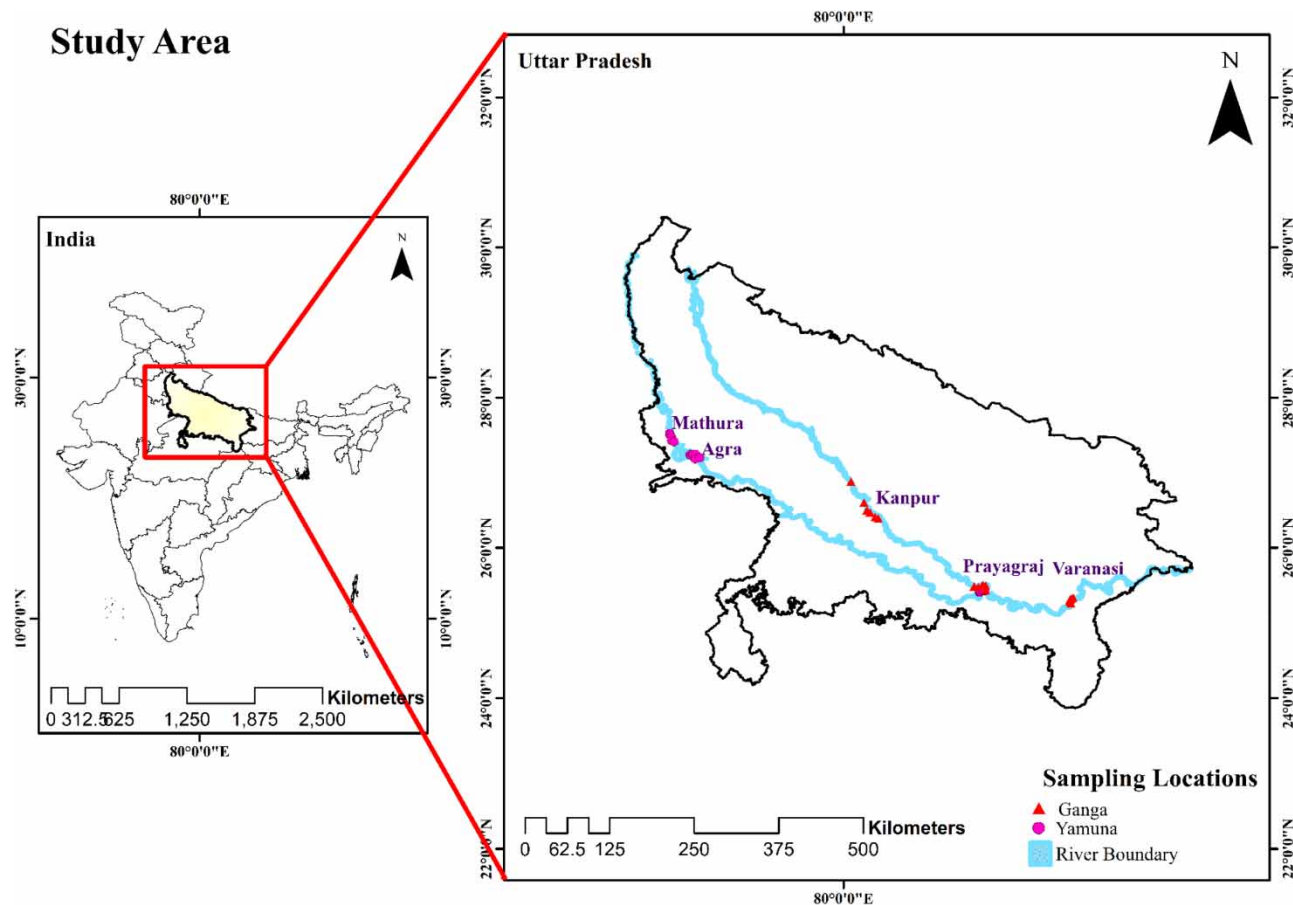
## Analytical methods

Eighteen water samples were taken from the Ganga and the Yamuna rivers ( $n = 36$ ) in acid-cleaned polyethylene bottles during the dry (pre-monsoon, April 2022) and wet (monsoon, August 2021) seasons. BOD (biochemical oxygen demand) analysis samples were collected in stoppered glass bottles. Some of the parameters, such as pH, EC (electrical conductivity), TDS (total dissolved solids), and DO (dissolved oxygen), were analysed on-site by a soil and water analysis kit (Labtronics, model- LT68). All the samples were collected, preserved, and carried to the laboratory according to the protocol given in APHA (2005). Water samples were filtered with a nylon filter paper of 0.45 µm and analysed for NH<sub>4</sub>-N (phenate method), NO<sub>3</sub>-N (brucine method), PO<sub>4</sub>-P (ascorbic acid method), and SiO<sub>2</sub>-Si (molybdosilicate method) by using a Systonics spectrophotometer. BOD was determined as a difference in DO levels over five days (temperature maintained at 20 °C). All the samples were analysed using the protocols given in APHA (2005), and the values were subsequently compared with their standard limits given by the Bureau of Indian Standards (BIS 2012) and World Health Organisation (WHO 2004). MS Excel 2019 was used for One-Way ANOVA (Analysis of Variance) and Pearson's correlation coefficient analysis. ANOVA assessed the variation in dissolved nutrient concentration in the Ganga and Yamuna rivers. The null hypothesis will be rejected if  $F_{\text{calculated}} > F_{\text{critical}}$  and  $p\text{-value} < 0.05$ . The relationship among the water quality parameters was ascertained using Pearson's correlation coefficient based on the correlation coefficient's value ( $r$ ). A correlation value greater than 0.5 indicates a significant relationship and points to a similar source of origin or mode of transit within the watershed (Shrestha 2021). The Statistical Package for Social Sciences (SPSS), version 10.0, was used for the factor analysis.

## RESULTS AND DISCUSSION

### Physicochemical characteristics

The concentration of measured parameters in the Ganga and Yamuna rivers is given in Table 1. In the dry and wet seasons, the water samples in the Ganga River were mostly alkaline, with observed mean values of 8.2 and 8.72, respectively. In the case of the Yamuna River, it was 8.51 and 7.83 in the dry and wet seasons, respectively (Table 1). Around 42% of the samples in the Ganga and 33% in the Yamuna River exceeded the BIS (2012) limit of 8.5 in Uttar Pradesh. Compared with the solids in surface water bodies, the large water supply does not allow pH to fluctuate drastically, maintaining the pH levels between 7 and 9 (Olalekan *et al.* 2023). A study by Maji & Chaudhary (2019) reported pH values between 7.9 and 8.7 for the Ganga River in Allahabad, Uttar Pradesh. The EC values varied from 380 µS cm<sup>-1</sup> (K2) to 560 µS cm<sup>-1</sup> (V5) in the dry period and from 230 µS cm<sup>-1</sup> (K2) to 350 µS cm<sup>-1</sup> (GPY3) in the wet period in the Ganga River. In the Yamuna River, EC varied from 430 µS cm<sup>-1</sup> (YPY2) to 650 µS cm<sup>-1</sup> (A4) in the dry season and from 410 µS cm<sup>-1</sup> (M1) to 960 µS cm<sup>-1</sup>



**Figure 1** | Map of the study area showing sampling sites along the Ganga and the Yamuna rivers.

(YPY1) in the wet season (Table 1). The EC value for collected samples was within the recommended limit of BIS (2012). However, two samples (from Agra and Prayagraj each) exceeded this limit in the Yamuna River wet season, indicating contribution from the weathering process and the anthropogenic input. The conductivity of water depends upon several factors, such as number, type, size, degree of hydration, and mobility of ions. It is directly proportional to the TDS as the higher the TDS, the greater the number of ions available for conductance (Jawad *et al.* 2023). The study assessing the water quality of the Yamuna River in Delhi by Sharma *et al.* (2017) reported EC values of the Yamuna River in the range of 97–2,846  $\mu\text{S cm}^{-1}$  due to increased load from natural as well as anthropogenic sources. The mean value of TDS in the Ganga River was 358.33  $\text{mg L}^{-1}$  in the dry and 170.61  $\text{mg L}^{-1}$  in the wet season. In the Yamuna River, the mean TDS value was 519.44 and 373.33  $\text{mg L}^{-1}$  in dry and wet seasons, respectively (Table 1). All the samples of the Ganga River were under the permissible limit of BIS (2012), but around 36% of the samples of the Yamuna River exceeded the limit of 500  $\text{mg L}^{-1}$ . Rahman *et al.* (2021) reported the average value of TDS in the northern floodplains of the Ganga River to be 587  $\text{mg L}^{-1}$  due to the dissolution of cations and anions from the weathering process as well as anthropogenic inputs.

DO is a significant parameter as it supports aquatic life, which removes organic pollution from surface water. It also plays an important role in determining water's corrosiveness and oxidation of inorganic compounds (Wang *et al.* 2022). The DO concentration was observed to be less than the permissible limit (6  $\text{mg L}^{-1}$ ) in both seasons for both rivers, indicating the deficiency of oxygen, which subsequently negatively affects aquatic life. It showed the minimum value at Kanpur (K5) and maximum value at Prayagraj (GPY6) in both dry and wet seasons in the Ganga River. In the Yamuna River case, the minimum DO concentration was found at Agra and the maximum at Prayagraj in both seasons (Table 1). Kanpur and Agra are the industrial cities of Uttar Pradesh, where most industries are leather-based. These industries, on average, discharge around 22.1 MLD of wastewater into the rivers, reducing the river water quality (CPCB 2009; MSME 2023). BOD is indicative of the amount of oxygen required by microbes for the degradation of organic matter. The concentration of BOD in the



**Table 1** | The concentration of physicochemical parameters in the pre-monsoon and monsoon seasons in the Ganga and Yamuna rivers

Parameter	Ganga				Yamuna				Water Quality Standard	Unpolluted river
	Pre-monsoon		Post-monsoon		Pre-monsoon		Post-monsoon			
	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD	Range	Mean $\pm$ SD		
<b>pH</b>	7.70–8.95	8.20 $\pm$ 0.34	7.10–9.60	8.72 $\pm$ 0.54	7.94–8.90	8.51 $\pm$ 0.30	7.40–8.61	7.83 $\pm$ 0.41	6.5–8.5 <sup>a</sup>	
<b>EC</b>	380–560	492.78 $\pm$ 56.94	230–350	272.78 $\pm$ 32.8	430–650	573.33 $\pm$ 64.12	410–960	578.33 $\pm$ 138.41	750 <sup>a</sup>	
<b>TDS</b>	220–490	358.33 $\pm$ 62.20	14–240	170.61 $\pm$ 24.87	450–670	519.44 $\pm$ 58.45	260–640	373.33 $\pm$ 93.15	500 <sup>a</sup>	
<b>DO</b>	3.60–5.20	4.34 $\pm$ 0.47	4.10–5.80	5.27 $\pm$ 0.45	3.70–4.70	4.16 $\pm$ 0.28	1.20–6.80	4.53 $\pm$ 1.86	>6 <sup>b</sup>	
<b>BOD</b>	2.20–15.60	6.11 $\pm$ 3.49	1.30–8.60	3.38 $\pm$ 2.23	1.40–22.40	9.56 $\pm$ 5.50	3.60–16.80	7.37 $\pm$ 3.65	$\leq$ 2 <sup>b</sup>	
<b>COD</b>	12.80–56	32.71 $\pm$ 11.93	8–32	16.44 $\pm$ 8.63	32–72	50.67 $\pm$ 13.33	24–56	42.31 $\pm$ 11.43	10 <sup>c</sup>	
<b>NO<sub>3</sub>-N</b>	13.60–29.88	20.84 $\pm$ 5.10	1.24–28.64	12.49 $\pm$ 6.85	30.68–63.29	48.56 $\pm$ 9.82	1.79–55.55	22.58 $\pm$ 17.28	45 <sup>c</sup>	0.1 <sup>d</sup>
<b>PO<sub>4</sub>-P</b>	0.02–0.26	0.13 $\pm$ 0.06	0.03–0.46	0.15 $\pm$ 0.12	0.55–1.15	0.88 $\pm$ 0.17	0.06–1.61	0.27 $\pm$ 0.34	5 <sup>c</sup>	0.01 <sup>d</sup>
<b>NH<sub>4</sub>-N</b>	0.21–0.44	0.34 $\pm$ 0.07	0.15–0.38	0.24 $\pm$ 0.08	0.33–0.51	0.43 $\pm$ 0.05	0.29–0.42	0.36 $\pm$ 0.03	0.1 <sup>c</sup>	0.02 <sup>d</sup>
<b>SiO<sub>2</sub>-Si</b>	12.40–29.90	21.56 $\pm$ 4.61	0.67–15.47	6.75 $\pm$ 3.70	16.50–41.30	27.50 $\pm$ 7.83	1.12–34.77	14.13 $\pm$ 10.82	100 <sup>c</sup>	4.85 <sup>d</sup>

<sup>a</sup>Bureau of Indian Standards (2005).<sup>b</sup>CPCB (2013).<sup>c</sup>WHO (2004).<sup>d</sup>Ravi *et al.* (2021).All values in mg L<sup>-1</sup> except pH and EC ( $\mu$ S cm<sup>-1</sup>).

Ganga River was above the permissible limits ( $2 \text{ mg L}^{-1}$ ) in all samples taken during the dry season. In the wet season, about 72% of the samples exceeded the BOD limits, indicating that the organic load from the municipal and agricultural sectors was present in the river system. In the case of the Yamuna River, average BOD values exceeded the permissible limit in both dry and wet seasons (Table 1). BOD values decreased by 2.13 times in the dry and 1.14 times in the wet season in the downstream region of the Yamuna River. This decrease in BOD value indicates a dilution of the Yamuna River water as the Chambal River merges with it at Etawah district (CPCB 2006). The COD values exceeded the permissible limit ( $10 \text{ mg L}^{-1}$ ) given by WHO in the dry season, and 61% of the samples in the wet exceeded the limits in the Ganga River. A rise of around 1.2 times in the COD values was observed in the downstream region of the Ganga River, indicating the contribution from anthropogenic sources in the catchment area (NMCG-NEERI 2017). The COD values showed high concentrations, particularly in the dry season, reaching a maximum value of  $72 \text{ mg L}^{-1}$  at both Mathura (M3) and Agra (A4) (Table 1). Such high COD values indicate high organic load in both rivers from domestic, agricultural, and industrial sectors. Parmar & Singh (2015) reported a BOD value of  $58 \text{ mg L}^{-1}$  (maximum) and a DO value of less than  $4 \text{ mg L}^{-1}$  in the Delhi-NCR stretch of the Yamuna River, indicating unsuitable conditions for aquatic life.

Nitrogen and phosphorus are the two limiting macronutrients responsible for plant and animal cell growth. The Ganga River receives significant nutrients from both point and nonpoint sources. According to studies, point and nonpoint sources, including atmospheric deposition (either direct deposition on the surface of water or indirect through catchment deposition-coupled surface runoff), significantly regulates the input of nutrients like N and P (Pandey & Yadav 2015; Prajapati *et al.* 2020). The aquatic system's dissolved inorganic nitrogen (DIN) mainly comprises  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$ . All the samples of the Ganga River had  $\text{NO}_3\text{-N}$  concentrations within the limits of BIS ( $45 \text{ mg L}^{-1}$ ) in both the dry and wet seasons. The average concentration of  $\text{NO}_3\text{-N}$  in the Yamuna River was significantly higher than in the Ganga River. However, the average  $\text{NO}_3\text{-N}$  concentration in the Ganga River was 208 and 125 times more than the value reported for the unpolluted river in the dry and wet seasons, respectively (Table 1). Kesari *et al.* (2022) reported nitrate concentrations between 2.52 and  $4.92 \text{ mg L}^{-1}$  in the Prayagraj and Varanasi stretch of the Ganga River. Another study by Chaudhary *et al.* (2017) reported nitrate content of 1.8– $15.8 \text{ mg L}^{-1}$  in the upper Ganga stretch (Table 2). This high nitrate content from the upper stretch of the river, along with instream nitrification and runoff from the catchment area, results in increased nitrogen load in the downstream section of the river runoff (Kumar *et al.* 2023). For the Yamuna River, the  $\text{NO}_3\text{-N}$  concentration was 486 and 226 times more than that of the unpolluted river in the dry and wet seasons, respectively. The high nitrate concentration in the dry season compared with the wet season indicates the accumulation of inorganic-N from agricultural sources and its subsequent dilution due to rainfall in the wet season. The high nitrate concentration is mainly derived from organic sources (Kurwadkar *et al.* 2020). Previous studies by Ahmed *et al.* (2020) and CPCB (2006) reported high nitrate concentrations ranging from 0.01 to  $149.32 \text{ mg L}^{-1}$  in Mathura and negligible to  $46.20 \text{ mg L}^{-1}$  from Yamunotri to Prayagraj, respectively (Table 2). The nitrate concentration observed for the Yamuna River in this study was comparable to the results reported in previous studies (Tables 1 and 2). The major sources of nitrate in this stretch include horticultural, sewage, agricultural, and other anthropogenic activities. The concentration of  $\text{NH}_4\text{-N}$  was the main concern as all the sites showed significantly high values exceeding the limit given by WHO ( $0.1 \text{ mg L}^{-1}$ ). The average  $\text{NH}_4$  concentration was 17 and 12 times more than that of the unpolluted river in the dry and wet seasons in the Ganga River. The main reason for such a high concentration was the discharge of untreated sewage from the catchment area (Table 1). The value of  $\text{NH}_4\text{-N}$  obtained in the Ganga River in this study ( $0.15\text{--}0.38 \text{ mg L}^{-1}$ ) was significantly lower than that obtained by Saxena & Singh (2020) ( $0.19\text{--}1.50 \text{ mg L}^{-1}$ ) and Santy *et al.* (2020) ( $1\text{--}6.5 \text{ mg L}^{-1}$ ) in Varanasi and Kanpur, respectively (Table 2). In the Yamuna River,  $\text{NH}_4$  concentration ranged between  $0.29$  and  $0.51 \text{ mg L}^{-1}$ , which was much less as compared with the reports of CPCB (2006) from Yamunotri to Prayagraj ( $\text{trace--}43.34 \text{ mg L}^{-1}$ ) and CPCB (2021a, 2021b) from Agra to Prayagraj ( $0.2\text{--}39.9 \text{ mg L}^{-1}$ ). Both these studies included samples from the Delhi region, where  $\text{NH}_4$  concentration is relatively higher due to sewage pollution than in other parts of the Yamuna River (CPCB 2021a, 2021b). The relatively lower value observed in this study can be due to the instream nitrification of the  $\text{NH}_4$  process, which is also responsible for the high nitrate concentration observed in this study.  $\text{NH}_4\text{-N}$  concentration showed 22- and 18-times higher values than unpolluted rivers in the dry and wet seasons (Table 1). The concentration of  $\text{PO}_4\text{-P}$  ranges from 0.02 to  $0.46 \text{ mg L}^{-1}$  in the Ganga River (Table 1).  $\text{PO}_4\text{-P}$  showed the minimum concentration at Varanasi and maximum concentration at Prayagraj in both the dry and wet seasons in the Ganga River. This value was lower than the value reported by Bowes *et al.* (2020) in the upper Ganga stretch ( $0.310\text{--}0.778 \text{ mg L}^{-1}$ ) and Kesari *et al.* (2022) in Varanasi and Prayagraj ( $0.92\text{--}1.82 \text{ mg L}^{-1}$ ). The major sources of  $\text{PO}_4\text{-P}$  reported in these studies were untreated sewage and agricultural and urban runoff in the Ganga River (Table 2). The concentration of  $\text{PO}_4\text{-P}$  ranges from 0.06 to  $1.61 \text{ mg L}^{-1}$  in the

**Table 2** | Comparative data of other studies showing nutrient concentration in the Ganga and Yamuna rivers

Nutrient	Ganga				Yamuna			
	Range	Source	Region	Reference	Range	Source	Region	Reference
NO <sub>3</sub> -N	1.8–15.8	Untreated wastewater	Haridwar to Garh	Chaudhary <i>et al.</i> (2017)	0.01–149.32	Horticulture and sewage	Mathura	Ahmed <i>et al.</i> (2020)
	2.52–4.92	Domestic and agricultural waste	Varanasi and Prayagraj	Kesari <i>et al.</i> (2022)	BDL – 46.20	Agriculture and anthropogenic activities	Yamunotri to Prayagraj	CPCB (2006)
PO <sub>4</sub> -P	0.310–0.778	Untreated sewage effluent	Upper Ganga (Rishikesh to Kanpur)	Bowes <i>et al.</i> (2020)	0.01–2.28	Domestic waste and agricultural runoff	Barkot to Prayagraj	Sharma <i>et al.</i> (2017)
	0.92–1.82	Agricultural and urban runoff	Varanasi and Prayagraj	Kesari <i>et al.</i> (2022)	0.52–1.74	Untreated sewage and agricultural runoff	Kalpi	Shukla <i>et al.</i> (2016)
NH <sub>4</sub> -N	0.19–1.50	Sewage discharge	Varanasi	Saxena & Singh (2020)	Trace – 43.34	Industrial sources	Yamunotri to Prayagraj	CPCB (2006)
	1.0–6.5	Discharge from drains	Kanpur	Santy <i>et al.</i> (2020)	0.20–39.90	Sewage sludge	Agra to Prayagraj	CPCB (2021a, 2021b)
SiO <sub>2</sub> -Si	0.19–0.70	Weathering and erosion	Devprayag to Ganga Sagar	Siddiqui & Pandey (2019)	0.01–2.28	Weathering	Barkot to Prayagraj	Sharma <i>et al.</i> (2017)
	3.8–6	Weathering and erosion of rocks	Devprayag to Ganga Sagar	Siddiqui <i>et al.</i> (2019)				

Yamuna River (Table 1). PO<sub>4</sub>-P showed minimum concentration at Mathura and Agra in the dry and wet seasons and maximum concentration at Agra and Prayagraj in the dry and wet seasons, respectively. Similar phosphate values were reported by Sharma *et al.* (2017) in their study of the Yamuna River from Barkot to Prayagraj (0.01–2.28 mg L<sup>-1</sup>) and Shukla *et al.* (2016) in Kalpi (0.52–1.74 mg L<sup>-1</sup>). The major contributors of phosphate in the Yamuna River were untreated sewage and agricultural runoff (Table 2). Although all the sites had PO<sub>4</sub>-P concentration within the WHO (2004) limits, the average PO<sub>4</sub>-P concentration was found to be 13 and 15 times more than that of the unpolluted river in the dry and wet seasons, in the Ganga, and 88 and 27 times more than that of the unpolluted river in the dry and wet season, respectively, in the Yamuna River. Phosphate in the river can be contributed by both natural sources (weathering of rocks) and anthropogenic sources (chemical fertiliser, phosphate mining, and sewage) (Ravi *et al.* 2021). The main factors contributing to high phosphorus content in the Himalayan rivers are high flow rate, high elevation, and rock weathering. When rocks weather, phosphorus is released as colloidal calcium phosphate and soluble alkali phosphates, most of which are delivered to the river waters. Additionally, phosphorus levels in river water rise because of anthropogenic inputs such as superphosphate fertiliser and alkyl phosphate detergents (Ramesh *et al.* 2015). Phosphate undergoes similar hydrolysis as carbonate, thereby increasing the alkalinity of water. The high phosphate concentration in both the rivers in this study can be an additional source of alkalinity in the study area (Chowdhary *et al.* 2020).

The silica concentration mostly ranges from 1 to 30 mg L<sup>-1</sup> in surface water. Generally, the high silica content in natural waters is accompanied by high pH, as the alkaline nature of water enhances the release of silica from the rocks. Water with high silica content is generally high in sodium and low in calcium, and the presence of calcium bicarbonate reduces the solubility of silica in water (Milne *et al.* 2014). SiO<sub>2</sub>-Si concentration in the Ganga River was within the WHO (2004) limit of 100 mg L<sup>-1</sup> with a minimum value at Varanasi in the dry and Prayagraj in the wet season. It was maximum at Varanasi in both seasons. The values of SiO<sub>2</sub>-Si obtained in this study in the Ganga River (0.67–29.9 mg L<sup>-1</sup>) are significantly higher than in earlier studies published by Siddiqui & Pandey (2019) and Siddiqui *et al.* (2019). In the Yamuna River, the SiO<sub>2</sub>-Si concentration was relatively higher (1.12–41.3 mg L<sup>-1</sup>) than in the earlier reported values (0.01–2.28 mg L<sup>-1</sup>) by Sharma *et al.* (2017). The high silica concentration in this study is mainly due to large floodplain areas in the Uttar Pradesh stretch of the river. In the Yamuna River, the minimum SiO<sub>2</sub>-Si concentration was observed at Prayagraj and the maximum



concentration at Mathura in both seasons. The average silica concentration observed in both Ganga and Yamuna rivers during this study was higher than the value reported for the unpolluted river (Table 1). Silica in river water is contributed by the weathering of rocks and is essential for the growth of primary producer Diatoms in the aquatic ecosystem (Ravi *et al.* 2021).

### Seasonal and spatial variations in physicochemical parameters

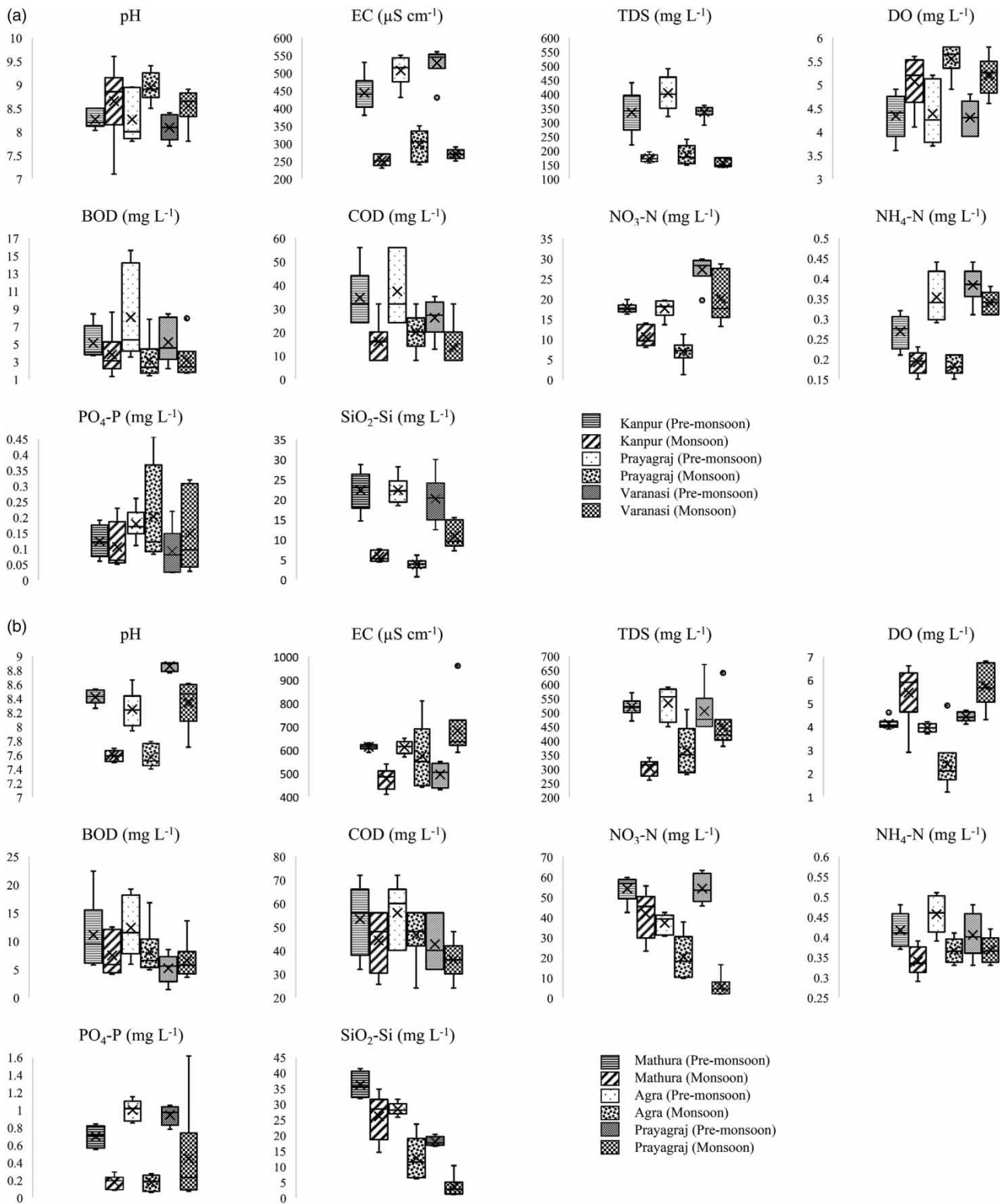
The spatial and seasonal variations for Ganga and Yamuna rivers are given in Figures 2(a) and 2(b), respectively. The result of the one-way ANOVA analysis showing the significant spatial and seasonal variations in dissolved nutrient concentrations for Ganga and Yamuna rivers is given in Table 3. The pH ( $p = 0.42$ ), EC ( $p = 0.48$ ), TDS ( $p = 0.51$ ), DO ( $p = 0.59$ ), BOD ( $p = 0.55$ ), COD ( $p = 0.26$ ), PO<sub>4</sub>-P ( $p = 0.11$ ), and SiO<sub>2</sub>-Si ( $p = 0.79$ ) did not show any significant spatial variation ( $p > 0.05$ ) in the Ganga River, probably because of the similar land use pattern of urban and agricultural land along the selected sites of the Ganga River (Table 3). However, relatively higher concentrations were observed in the downstream regions of the river (Figure 2(a)). The high concentration in the downstream regions indicates the contribution of anthropogenic sources from the catchment areas. A significant spatial variation ( $p < 0.05$ ) was observed in NO<sub>3</sub>-N and NH<sub>4</sub>-N in the Ganga River (Table 3), with maximum values obtained in Varanasi indicating municipal and agricultural discharges into the Ganga River (Figure 2(a)). Varanasi generates around 141 MLD of sewage, of which only 67% is treated, and the rest is dumped into the river adding to the nitrogen pollution in the river Ganga. Apart from sewage, agricultural areas contribute annually about 403 gigagrams (Gg), 186 Gg, and 24 Gg of NO<sub>3</sub>-N, NH<sub>4</sub>-N, and dissolved reactive phosphorus (DRP), respectively, through surface runoff into the river Ganga leading to negative effects on soil buffering capacity, leaching, and eutrophication (Prajapati *et al.* 2020).

The seasonal variation was significant ( $p < 0.05$ ) in pH ( $p = 0.01$ ), EC ( $p = < 0.0001$ ), TDS ( $p = < 0.0001$ ), DO ( $p = < 0.0001$ ), BOD ( $p = 0.01$ ), COD ( $p = < 0.0001$ ), NO<sub>3</sub>-N ( $p = 0.01$ ), NH<sub>4</sub>-N ( $p = 0.01$ ), and SiO<sub>2</sub>-Si ( $p = < 0.0001$ ) with EC, TDS, BOD, COD, NO<sub>3</sub>-N, NH<sub>4</sub>-N, and SiO<sub>2</sub>-Si showing higher mean concentrations in the dry and relatively lower mean concentrations in the wet season. The high concentration in the dry season may be attributed to the reduced volume of water in the rivers, while in the wet season, the pollutants are diluted due to the addition of rainwater (Woldeab *et al.* 2018). DO showed a higher value in the wet season, indicating the addition of fresh water from rainwater (Figure 2(a)). PO<sub>4</sub>-P showed higher values in the wet season, indicating the presence of agricultural areas in the catchment as a contributing source of PO<sub>4</sub>-P, along with soil flushing and transport of suspended particles during the wet season (Figure 2(a)).

The results of ANOVA indicated that spatial variation was not significant ( $p > 0.05$ ) for EC ( $p = 0.50$ ), TDS ( $p = 0.35$ ), BOD ( $p = 0.07$ ), COD ( $p = 0.06$ ), NH<sub>4</sub>-N ( $p = 0.31$ ), and PO<sub>4</sub>-P ( $p = 0.06$ ) in the Yamuna River (Table 3). Still, the downstream areas showed higher values due to the added load from upstream regions (Figure 2(b)). The BOD and COD values showed higher values in the upstream area of Mathura (Figure 2(b)), which may be due to the addition of sewage waste along with the religious activities (offering flowers and other products in the Yamuna River) that occur regularly on the ghats as Mathura is a popular pilgrim spot attracting a large number of people from across the world (Bhargava 2006). The seasonal changes were significant ( $p < 0.05$ ) in pH ( $p = < 0.0001$ ), TDS ( $p = < 0.0001$ ), NO<sub>3</sub>-N ( $p = < 0.0001$ ), NH<sub>4</sub>-N ( $p = < 0.0001$ ), PO<sub>4</sub>-P ( $p = 0.01$ ), and SiO<sub>2</sub>-Si ( $p = 0.01$ ) in the Yamuna River showing lower average values in the wet season indicating the dilution effect due to addition of rainwater in the monsoon period (Figure 2(b)). No significant seasonal change ( $p > 0.05$ ) was seen in EC ( $p = 0.89$ ), DO ( $p = 0.43$ ), BOD ( $p = 0.18$ ), and COD ( $p = 0.06$ ) (Table 3), but the values of EC and DO were relatively higher in the wet season. BOD and COD showed higher concentrations in the dry season in the Yamuna River as the low flow in the dry season further enhanced the concentration of organic pollutants in the river (Figure 2(b)).

### Factors controlling nutrient chemistry

The factors affecting the nutrient chemistry in the Ganga and Yamuna rivers were determined using Pearson's correlation coefficient and R-mode factor analysis. The results obtained by Pearson's correlation for the dry and wet seasons in the Ganga River are presented in Table 4, and for the dry and wet seasons in the Yamuna River are given in Table 5, respectively. COD showed a strong positive correlation with TDS and BOD in the Ganga River in both the dry and wet seasons, indicating organic waste input in the river system from the catchment area. A negative correlation between pH and DO in the Ganga River showed a decrease in the algal population with increasing pH, thereby affecting the rate of photosynthesis (Dubinsky & Rotem 1974). In the wet season, a positive correlation between NH<sub>4</sub>-N and NO<sub>3</sub>-N may be attributed to the breakdown of organic matter from domestic and agricultural discharge into the Ganga River. A positive correlation was observed between



**Figure 2 |** (a) Box plots showing variations in parameters analysed during the study in the Ganga River. (b) Box plots showing variation in parameters analysed during the study in the Yamuna River.

**Table 3** | One-way ANOVA shows spatial and seasonal variations for the Ganga and Yamuna rivers

Parameter	Spatial variation			Seasonal variation		
	F <sub>calculated</sub>	F <sub>critical</sub>	p-value	F <sub>calculated</sub>	F <sub>critical</sub>	p-value
<b>Ganga</b>						
pH	0.88	3.28	0.42	10.87	4.13	0.01
EC	0.75	3.28	0.48	190.56	4.13	< 0.0001
TDS	0.69	3.28	0.51	133.49	4.13	< 0.0001
DO	0.53	3.28	0.59	34.90	4.13	< 0.0001
BOD	0.61	3.28	0.55	7.37	4.13	0.01
COD	1.39	3.28	0.26	20.75	4.13	< 0.0001
NO <sub>3</sub> -N	14.09	3.28	<0.0001	16.25	4.13	0.01
PO <sub>4</sub> -P	2.33	3.28	0.11	0.38	4.13	0.54
NH <sub>4</sub> -N	11.51	3.28	0.0002	15.57	4.13	0.01
SiO <sub>2</sub> -Si	0.24	3.28	0.79	106.85	4.13	< 0.0001
<b>Yamuna</b>						
pH	10.26	3.28	0.0003	29.74	4.13	<0.0001
EC	0.71	3.28	0.50	0.02	4.13	0.89
TDS	1.07	3.28	0.35	30.01	4.13	<0.0001
DO	10.40	3.28	0.0003	0.64	4.13	0.43
BOD	2.95	3.28	0.07	1.88	4.13	0.18
COD	3.04	3.28	0.06	3.85	4.13	0.06
NO <sub>3</sub> -N	4.36	3.28	0.02	29.05	4.13	<0.0001
PO <sub>4</sub> -P	3.07	3.28	0.06	17.62	4.13	0.01
NH <sub>4</sub> -N	1.22	3.28	0.31	22.08	4.13	<0.0001
SiO <sub>2</sub> -Si	17.43	3.28	<0.0001	17.03	4.13	0.01

EC and BOD in the dry season in the Yamuna River system. In the wet season, PO<sub>4</sub>-P was positively correlated with EC and TDS, indicating the contribution from agricultural runoff.

The R-mode factor analysis results are presented in Tables 6 and 7 for the Ganga and Yamuna rivers. The analysis showed five factors in the Ganga River for the dry season. The first factor accounts for a 27.51% variation, with positive loading for BOD and COD and negative loading for DO, indicating the addition of organic matter from industries, livestock, agriculture, and municipal wastewater (Mamun & An 2021). Factor 2 explained a 22.31% variance with positive loading for PO<sub>4</sub>-P, pointing to the contribution from the agricultural runoff. Factor 3 explained a 14.33% variation with positive loading for EC and TDS, showing the contribution of the weathering process. Factors 4 and 5 showed 12.01% and 11.13% variation, respectively, with positive loading for NH<sub>4</sub>-N indicating the sewage contribution from the catchment area. In the wet season, three factors were identified in the Ganga River. Factor 1 explained a 41.60% variation with positive loading for NO<sub>3</sub>-N, NH<sub>4</sub>-N, and SiO<sub>2</sub>-Si, indicating the production and mineralisation of organic matter and sediment transportation from the catchment area. Factor 2 explained a 21.98% variation with positive loading for BOD and COD and negative loading for DO, indicating the addition of organic matter from industries, livestock, agriculture, and municipal wastewater (Mamun & An 2021). Factor 3 explained a 14.52% variation with positive loading for EC, TDS, and PO<sub>4</sub>-P, indicating the contribution of the weathering process in addition to agricultural runoff.

In the Yamuna River, four factors were identified in the dry season. Factor 1 explained a 38.84% variation with positive loading for EC and SiO<sub>2</sub>-Si, and factor 2 explained a 19.59% variation with positive loading for BOD, COD, and negative loading for DO, indicating the contribution of organic matter from sewage waste. Factors 3 and 4 explained 12.04% and 11.38% variation, respectively, with positive loading for TDS and DO for factor 3 and NO<sub>3</sub>-N for factor 4. Three factors were identified for the wet season in the Yamuna River, where factor 1 explained 43.40% variation with positive loading

**Table 4** | Correlation analysis among the parameters of the Ganga River in pre-monsoon and monsoon seasons

	pH	EC	TDS	DO	BOD	COD	NO <sub>3</sub>	PO <sub>4</sub>	NH <sub>4</sub>	SiO <sub>2</sub>
<b>Pre-monsoon</b>										
pH	1.00									
EC	-0.02	1.00								
TDS	0.31	<b>0.58</b>	1.00							
DO	-0.12	-0.21	-0.18	1.00						
BOD	0.32	0.05	0.37	-0.54	1.00					
COD	0.23	0.03	<b>0.53</b>	-0.50	<b>0.76</b>	1.00				
NO <sub>3</sub> -N	-0.12	0.48	-0.17	-0.23	-0.01	-0.25	1.00			
PO <sub>4</sub> -P	-0.14	-0.35	-0.05	0.34	0.01	0.04	-0.56	1.00		
NH <sub>4</sub> -N	-0.36	0.38	0.15	0.19	0.16	-0.15	0.44	0.09	1.00	
SiO <sub>2</sub> -Si	-0.15	-0.01	0.12	-0.14	-0.17	0.14	-0.10	-0.02	-0.06	1.00
<b>Monsoon</b>										
pH	1.00									
EC	0.31	1.00								
TDS	0.35	<b>0.77</b>	1.00							
DO	-0.45	0.01	-0.23	1.00						
BOD	0.49	0.34	0.55	-0.66	1.00					
COD	0.40	0.34	0.55	-0.50	<b>0.73</b>	1.00				
NO <sub>3</sub> -N	-0.36	-0.18	-0.39	-0.04	-0.08	-0.39	1.00			
PO <sub>4</sub> -P	0.18	<b>0.60</b>	0.36	-0.01	0.15	0.28	-0.38	1.00		
NH <sub>4</sub> -N	-0.18	-0.08	-0.45	-0.09	-0.05	-0.32	<b>0.72</b>	0.03	1.00	
SiO <sub>2</sub> -Si	-0.36	-0.18	-0.39	-0.04	-0.08	-0.39	1.00	-0.38	<b>0.72</b>	1.00

Note: bold values indicate significant correlation.

for EC, TDS, and PO<sub>4</sub>-P, indicating the contribution from the weathering process along with agricultural and domestic discharge. Factor 2 explained a 22.54% variation with positive loading for pH, and factor 3 explained a 13.70% variation with positive loading for BOD and NH<sub>4</sub>-N, indicating the contribution from sewage waste in the Yamuna River system.

### DISSOLVED NUTRIENT ELEMENTAL RATIO

The N/Si/P molar ratios in the aquatic system are crucial for aquatic life's survival and are a key indicator of the nutrient limitation of primary productivity. The Redfield ratio was calculated using the concentration of these dissolved nutrients (Nguyen *et al.* 2019). The ratio of DIN to DIP (dissolved inorganic phosphorus), DIN/DIP, for the Ganga and the Yamuna rivers is presented in Figures 3(a) and 3(b), respectively. The DIN/DIP ratio varied from 67.66 to 149.82 in the Ganga River, with the maximum average value of 115 in Prayagraj, 108 in Kanpur, and 83 in Varanasi. During the wet season, it ranged from 15.91 to 146.02, with the maximum mean value of 96 in Prayagraj, 91 in Kanpur, and 64 in Varanasi. The relatively higher DIN/DIP values in Kanpur and Prayagraj may be attributed to the addition of 50% untreated sewage in Kanpur and 57% untreated sewage in Prayagraj that is discharged into the river after treatment (Prajapati *et al.* 2020). All the samples collected during the study (except one from Prayagraj) exceeded the ratio of 16:1 in the Ganga River, indicating the limitation of phosphate for the growth of diatoms (Das *et al.* 2022). In the Yamuna River, DIN/DIP ranged from 43.74 to 163.60 in the dry season and from 16.68 to 586.02 in the wet season, with maximum values obtained at Mathura in the dry and at Agra in the wet season. All the dry and wet samples exceeded the ratio of 16:1 in the Yamuna River, indicating phosphate-limiting conditions for biological productivity. The downstream areas showed a higher DIN/DIP ratio, given the allochthonous and autochthonous load in the river from the upstream regions. The study by Pandey & Yadav (2015) analysed Ganga River water samples in 2013–2014 and found N-limitation due to excess anthropogenic contribution of

**Table 5** | Correlation analysis among the parameters of the Yamuna River in pre-monsoon and monsoon seasons

	pH	EC	TDS	DO	BOD	COD	NO <sub>3</sub>	PO <sub>4</sub>	NH <sub>4</sub>	H <sub>4</sub> SiO <sub>4</sub>
<b>Pre-monsoon</b>										
pH	1.00									
EC	<b>-0.78</b>	1.00								
TDS	-0.35	0.24	1.00							
DO	<b>0.59</b>	-0.44	0.26	1.00						
BOD	-0.48	<b>0.53</b>	0.13	-0.48	1.00					
COD	-0.24	0.27	0.01	-0.32	<b>0.84</b>	1.00				
NO <sub>3</sub>	0.43	-0.18	-0.04	0.42	-0.24	-0.37	1.00			
PO <sub>4</sub>	0.17	-0.19	-0.20	0.08	-0.20	0.00	-0.39	1.00		
NH <sub>4</sub>	-0.16	0.21	-0.25	-0.60	0.29	0.16	-0.37	0.13	1.00	
H <sub>4</sub> SiO <sub>4</sub>	-0.59	<b>0.76</b>	0.13	-0.40	0.40	0.33	-0.06	-0.38	0.03	1.00
	pH	EC	TDS	DO	BOD	COD	NO <sub>3</sub>	PO <sub>4</sub>	NH <sub>4</sub>	SiO <sub>2</sub>
<b>Monsoon</b>										
pH	1.00									
EC	0.29	1.00								
TDS	0.31	1.00	1.00							
DO	0.48	-0.21	-0.17	1.00						
BOD	-0.01	0.31	0.26	-0.42	1.00					
COD	-0.20	-0.40	-0.42	-0.29	0.42	1.00				
NO <sub>3</sub> -N	<b>-0.64</b>	<b>-0.61</b>	<b>-0.61</b>	-0.02	-0.12	0.34	1.00			
PO <sub>4</sub> -P	0.37	<b>0.61</b>	<b>0.65</b>	0.15	-0.17	-0.30	-0.40	1.00		
NH <sub>4</sub> -N	0.36	0.32	0.31	-0.39	0.49	0.27	-0.38	0.12	1.00	
SiO <sub>2</sub> -Si	<b>-0.64</b>	<b>-0.61</b>	<b>-0.61</b>	-0.02	-0.12	0.34	1.00	-0.40	-0.38	1.00

Note: bold values indicate significant loading.

**Table 6** | Factor analysis of the Ganga River in pre-monsoon and monsoon seasons

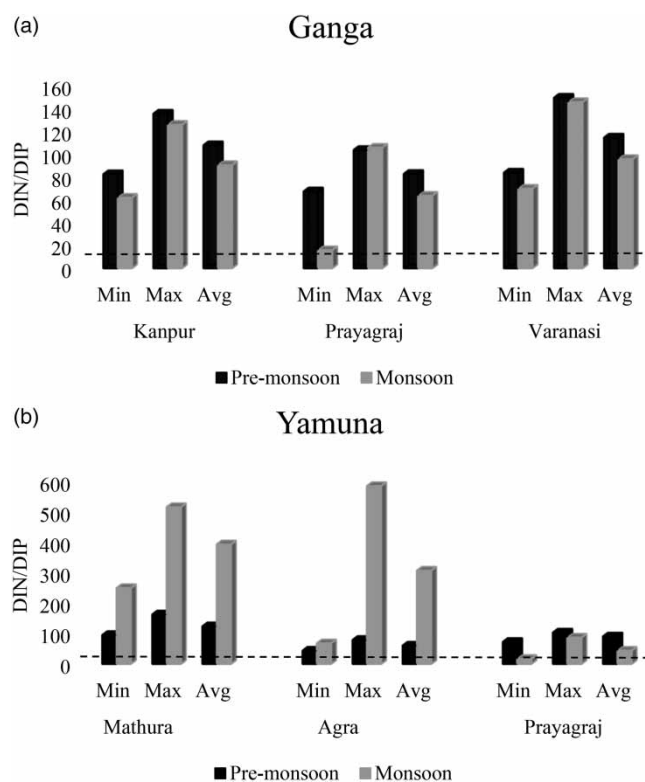
Variables	Pre-monsoon					Monsoon		
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 1	Factor 2	Factor 3
pH				-0.73			0.63	
EC ( $\mu\text{S cm}^{-1}$ )			0.76					0.93
TDS ( $\text{mg L}^{-1}$ )			0.91					0.67
DO ( $\text{mg L}^{-1}$ )	-0.75						-0.87	
BOD ( $\text{mg L}^{-1}$ )	0.92						0.90	
COD ( $\text{mg L}^{-1}$ )	0.86						0.75	
NO <sub>3</sub> -N ( $\text{mg L}^{-1}$ )		-0.84				0.94		
PO <sub>4</sub> -P ( $\text{mg L}^{-1}$ )		0.87						0.81
NH <sub>4</sub> -N ( $\text{mg L}^{-1}$ )				0.87		0.87		
SiO <sub>2</sub> -Si ( $\text{mg L}^{-1}$ )					-0.95	0.94		
Eigenvalue	2.75	2.23	1.43	1.20	1.11	4.16	2.19	1.45
% of variance	27.51	22.31	14.33	12.01	11.13	41.60	21.98	14.52
% of cumulative variance	27.51	49.82	64.16	76.17	87.31	41.60	63.59	78.11



**Table 7** | Factor analysis of the Yamuna River in pre-monsoon and monsoon seasons

Variables	Pre-monsoon				Monsoon		
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 1	Factor 2	Factor 3
pH	-0.91				0.93	0.90	-0.91
EC ( $\mu\text{S cm}^{-1}$ )	0.88				0.91		0.88
TDS ( $\text{mg L}^{-1}$ )			0.78		0.91		
DO ( $\text{mg L}^{-1}$ )		-0.22	0.70			-0.73	
BOD ( $\text{mg L}^{-1}$ )		0.87				0.84	0.70
COD ( $\text{mg L}^{-1}$ )		0.97				0.59	
$\text{NO}_3\text{-N}$ ( $\text{mg L}^{-1}$ )				0.81	-0.73		
$\text{PO}_4\text{-P}$ ( $\text{mg L}^{-1}$ )				-0.79	0.69		
$\text{NH}_4\text{-N}$ ( $\text{mg L}^{-1}$ )			-0.74			0.74	0.74
$\text{SiO}_2\text{-Si}$ ( $\text{mg L}^{-1}$ )	0.76				-0.73		0.76
Eigenvalue	3.88	1.95	1.20	1.13	4.34	2.25	1.37
% of variance	38.84	19.59	12.04	11.38	43.40	22.54	13.70
% of cumulative variance	38.84	58.43	70.47	81.85	43.40	65.94	79.64

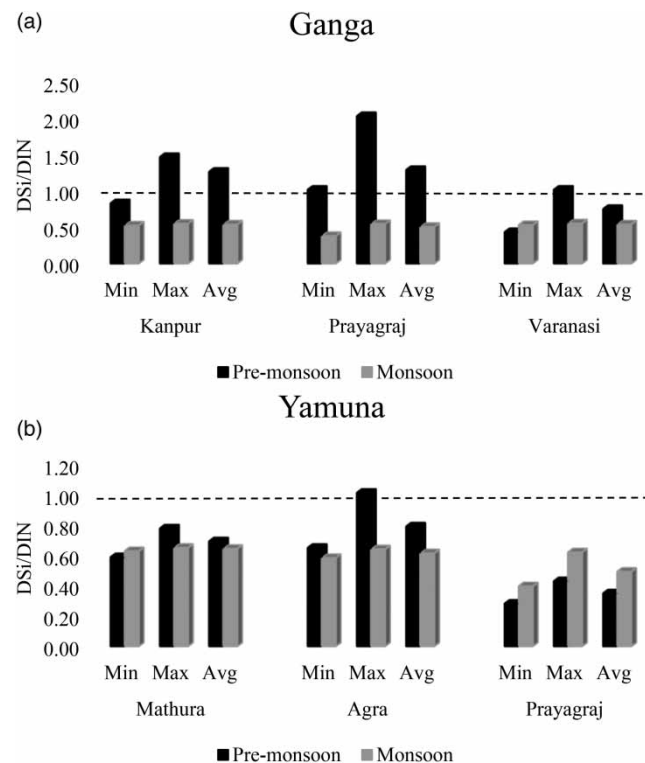
phosphorus in the river, while this study showed P-limitation. Thus, a shift from N-limiting to P-limiting conditions can be observed over a period of ten years due to increased nitrate concentration from point and nonpoint sources in the river and mineralisation of  $\text{NH}_4\text{-N}$  to  $\text{NO}_3\text{-N}$ . Das *et al.* (2022) conducted a study in the Brahmaputra River and found that the DIN/DIP ratio exceeded the 16:1 ratio in 70% of the samples. Sharma *et al.* (2017) also studied the elemental ratio in the Yamuna River and observed the DIN/DIP ratio to be twice the Redfield ratio of 16:1.

**Figure 3** | (a) DIN/DIP ratio along the sampling sites of the Ganga River. (b) DIN/DIP ratio along the sampling sites of the Yamuna River.

The ratio of DSi (dissolved silica) to DIN, DSi/DIN, for the Ganga and Yamuna rivers is given in Figures 4(a) and 4(b). The DSi/DIN ratio was observed to be minimum at Varanasi and maximum at Prayagraj in the Ganga River dry season, indicating increased nitrogen load in the downstream region of the river. The DSi/DIN ratio was relatively low in the wet season compared with the dry season in the Ganga River. It ranged from 0.43 to 2.04 in the dry season, with maximum values in Prayagraj (1.29) followed by Kanpur (1.27) and Varanasi (0.75). In the wet season, it varied from 0.38 to 0.56, with an average of 0.54 in Kanpur and Varanasi, respectively, and 0.51 in Prayagraj. The average value of less than 1 indicates excess nitrogen loading and potential for eutrophic conditions. In the Yamuna River, the ratio ranged from 0.28 to 1.02 in the dry season and from 0.40 to 0.65 in the wet season. The minimum values were obtained at Prayagraj in both seasons, while the maximum was obtained at Agra in the dry and Mathura in the wet season. The DSi/DIN ratio decreased in the wet season compared with the dry season indicating the contribution from agricultural runoff from the catchment area in the wet season. The DSi/DIN ratio was  $<1$  in the Yamuna River in both seasons (except one in the dry season), suggesting Si-limiting conditions in the Yamuna River. Under such conditions of high N, cyanobacteria generally bloom in freshwater. Pandey & Yadav (2015) reported a DSi/DIN ratio of  $<1$  in the summer and  $>1$  in the rainy season in the Ganga River, causing diatom growth. Ravi *et al.* (2021) studied the DSi/DIN ratio in the Ghaghara River to find that the ratio exceeded the 1:1 ratio by almost four times, stimulating the growth of diatoms that form an essential component of the aquatic ecosystem.

### DISSOLVED NUTRIENT LOAD

Rivers are responsible for transporting dissolved nutrients they carry along their course and the disposing of them into the oceans. The annual flux and specific yield of nutrients can be determined using the discharge, drainage area, and concentration of nutrients. The discharge, drainage area, and specific nutrient yield for the Ganga and Yamuna rivers are given in Table 8. The total drainage area of the Ganga River is  $861 \times 10^3 \text{ km}^2$ , and its annual mean discharge is  $380 \text{ km}^3 \text{ y}^{-1}$ , and for the stretch passing through Uttar Pradesh, it is  $294 \times 10^3 \text{ km}^2$  and  $24.03 \text{ km}^3 \text{ y}^{-1}$ , respectively (Rai *et al.* 2021; SMCG 2021; WRIS 2021). The total drainage area of the Yamuna River is  $366 \times 10^3 \text{ km}^2$ , and the annual average discharge is  $131.7 \text{ km}^3 \text{ y}^{-1}$  and for the stretch passing through Uttar Pradesh, it is  $70.437 \times 10^3 \text{ km}^2$  and  $27.76 \text{ km}^3 \text{ y}^{-1}$ , respectively



**Figure 4** | (a) DSi/DIN ratio along the sampling sites of the Ganga River. (b) DSi/DIN ratio along the sampling sites of the Yamuna River.

**Table 8** | Nutrient-specific yield ( $\text{t km}^2 \text{yr}^{-1}$ ) of the Ganga and Yamuna rivers was obtained in this study in Uttar Pradesh and other major Indian rivers

River	Discharge ( $\text{km}^3 \text{y}^{-1}$ )	Drainage ( $10^2 \text{ km}^2$ )	$\text{NH}_4\text{-N}$ ( $\text{t km}^2 \text{y}^{-1}$ )	$\text{NO}_3\text{-N}$ ( $\text{t km}^2 \text{y}^{-1}$ )	$\text{PO}_4\text{-P}$ ( $\text{t km}^2 \text{y}^{-1}$ )	$\text{SiO}_2\text{-Si}$ ( $\text{t km}^2 \text{y}^{-1}$ )	Reference
Ganga (Uttar Pradesh)	24.03	294	0.01	0.30	0.003	0.25	This study
Yamuna (Uttar Pradesh)	27.76	70.437	0.03	3.08	0.05	1.80	This study
Ghaghara	94.4	128	0.08	0.49	0.03	0.96	Ravi <i>et al.</i> (2021)
Godavari	110	313	0.004	0.25	0.04	0.71	Krishna <i>et al.</i> (2016)
Cauvery	21.35	88	0.007	0.011	0.09	0.85	Krishna <i>et al.</i> (2016)
Narmada	45.6	99	0.03	0.46	0.04	0.48	Krishna <i>et al.</i> (2016)

(Upadhyay & Rai 2013; Sharma *et al.* 2017). The Ganga River's annual DIN flux was  $8.96 \times 10^4 \text{ t yr}^{-1}$ , while the Yamuna River's annual flux along the Uttar Pradesh length was  $21.96 \times 10^4 \text{ t yr}^{-1}$ . The Ganga River's annual flux of  $\text{PO}_4\text{-P}$  was  $0.07 \times 10^4 \text{ t yr}^{-1}$ , while the Yamuna River's was  $0.37 \times 10^4 \text{ t yr}^{-1}$  (Table 8). Nitrogen and phosphorus are the major contributors to nutrient pollution in rivers worldwide. A study by Ongley *et al.* (2010) reported that about 81% of nitrogen and 93% of phosphorus is contributed by nonpoint sources in China, while another study by Bowes *et al.* (2009) reported that diffuse sources add around 75% of the phosphorus load in the rivers of UK. It was reported by Carpenter *et al.* (1998) that point sources are responsible for more than 50% of nitrogen and phosphorus discharge, while nonpoint sources contribute more than 90% of the total nitrogen input in the rivers of the USA. In the Ganges River basin, approximately 13.28 Gg (giga-grams) of DIN and 5.29 Gg of DRP were added by point sources annually (Prajapati *et al.* 2020). According to reports of the National Ganga River Basin Authority (NGRBA), the annual fertiliser consumption of the states along the Ganga River is approximately 10 million tonnes, of which 38% is consumed by Uttar Pradesh alone. Such intensive fertiliser use has produced high nitrogen and phosphorus concentrations in the river through agricultural runoff (NGRBA 2011). The annual specific yield of  $\text{NO}_3\text{-N}$  from the Ganga River was  $0.30 \text{ t km}^{-2} \text{y}^{-1}$  significantly lower than that of the Yamuna River ( $3.08 \text{ t km}^{-2} \text{y}^{-1}$ ) in Uttar Pradesh (Table 8). The specific yield of  $\text{NH}_4\text{-N}$  was 0.01 and  $0.03 \text{ t km}^{-2} \text{y}^{-1}$  for the Ganga and Yamuna rivers, respectively. The annual yield of  $\text{PO}_4\text{-P}$  was also higher in the Yamuna River ( $0.05 \text{ t km}^{-2} \text{y}^{-1}$ ) than in the Ganga River ( $0.003 \text{ t km}^{-2} \text{y}^{-1}$ ). Uttar Pradesh is one of the most densely populated states with a population of 257,622,800, generating about 3,851.71 MLD of sewage, ultimately discharged into the river, adding to the nutrient level in the river water (CPCB 2009). Along the Ganga River, the maximum amount of nitrogen was contributed by Varanasi due to the discharge of 33% of the untreated sewage into the river (Prajapati *et al.* 2020), while Mathura contributed the maximum nitrogen load in the Yamuna River from agricultural and domestic sources. Prayagraj contributed the maximum phosphorus load in both rivers due to intensive agricultural activities in the catchment area. The annual flux of  $\text{SiO}_2\text{-Si}$  in the Ganga River was  $7.48 \times 10^4 \text{ t yr}^{-1}$ ; in the Yamuna River, it was  $12.71 \times 10^4 \text{ t yr}^{-1}$ . The  $\text{SiO}_2\text{-Si}$  annual flux was almost the same in all the sites along the Ganga River, but in the Yamuna River, the maximum annual flux was observed at Mathura, followed by Agra and Prayagraj. The specific yield of  $\text{SiO}_2\text{-Si}$  was  $0.25 \text{ t km}^{-2} \text{y}^{-1}$  in the Ganga and  $1.80 \text{ t km}^{-2} \text{y}^{-1}$  in the Yamuna River. The highest silica load was observed in the Varanasi and Mathura sites for the Ganga and Yamuna rivers, respectively. Sen *et al.* (2018) studied the nutrient load of the Pandu River, a tributary of the Ganga River, and found that the ammonium, nitrate, phosphate, and silicate yields were 0.248, 0.162, 0.118, and  $1.08 \text{ t km}^{-2} \text{y}^{-1}$ . The annual yield of nitrate in their study was lower than the other rivers of the world, such as the Amazon ( $0.797 \text{ t km}^{-2} \text{y}^{-1}$ ), Mississippi ( $1.302 \text{ t km}^{-2} \text{y}^{-1}$ ), and Yangtze ( $1.736 \text{ t km}^{-2} \text{y}^{-1}$ ) River, but the phosphate yield was higher in comparison with the Amazon ( $0.009 \text{ t km}^{-2} \text{y}^{-1}$ ), Yangtze ( $0.027 \text{ t km}^{-2} \text{y}^{-1}$ ), and Ganga River, in this study ( $0.003 \text{ t km}^{-2} \text{y}^{-1}$ ). Agriculture runoff and domestic sewage were the main contributors to nutrients. Being a tributary of the Ganga River, the Pandu River also contributes nutrients, increasing the Ganga River's yield of nutrients. Sharma *et al.* (2017) reported a relatively higher annual specific yield of  $\text{PO}_4\text{-P}$  ( $0.17 \text{ t km}^{-2} \text{y}^{-1}$ ) than this study because they studied the whole stretch of the River. However, the specific yield of

$\text{NO}_3\text{-N}$  ( $0.18 \text{ t km}^{-2} \text{ y}^{-1}$ ) was relatively lower than in the values obtained from the Ganga and Yamuna River samples in this study, given the intensive agricultural practices, use of chemical fertilisers and sewage generation in the Uttar Pradesh stretch of rivers.

### INDICATOR FOR COASTAL EUTROPHICATION POTENTIAL (ICEP)

Based on the fluxes of DIN, dissolved inorganic phosphorus (DIP), and dissolved silica (DSi), ICEP is used to calculate the imbalanced nutrient input in the rivers relative to the amount needed for the growth of diatoms (Raimonet *et al.* 2018). It is calculated using the formula given by Billen & Garnier (2007):

$$N\text{-ICEP} = \{NFLx/(14 \times 16) - Si\ Flx/(28 \times 20)\} \times 106 \times 12 \quad (1)$$

$$P\text{-ICEP} = \{PFlx/31 - Si\ Flx/(28 \times 20)\} \times 106 \times 12 \quad (2)$$

$N\ Flx$ ,  $Si\ Flx$ , and  $P\ Flx$  denote the average flux of DIN, DIP, and DSi, respectively. The N-ICEP value for the Ganga River was  $0.09 \text{ kg C km}^{-2} \text{ day}^{-1}$ , and the P-ICEP value was  $-0.04 \text{ kg C km}^{-2} \text{ day}^{-1}$ . The Yamuna River showed comparatively higher values of N-ICEP, i.e.,  $0.26 \text{ kg C km}^{-2} \text{ day}^{-1}$  and the P-ICEP value was the same as that of the Ganga River, i.e.,  $-0.04 \text{ kg C km}^{-2} \text{ day}^{-1}$ . The positive N-ICEP values in both rivers indicate an abundance of nitrogen over silica resulting in the growth of phytoplankton (non-diatom species). This abundance might result from fertilisers coming through agricultural runoff from the catchment area. The algal mass is usually flushed down from the eutrophicated zones causing septic conditions in the downstream regions (Pandey *et al.* 2016). The negative P-ICEP values in both rivers suggest phosphate-limiting conditions for phytoplankton growth. High N will favour minimally silicified diatoms and non-diatom species if P is not a limiting factor.

On the other hand, diatoms that are highly silicified and quickly sinking benefit from high Si:N (Pandey *et al.* 2016). The N-ICEP values of the Ganga and the Yamuna rivers obtained in this study were significantly higher than that of the Ghaghara River, as reported by Ravi *et al.* (2021). The high N-ICEP value might be attributed to the large drainage area and high nutrient input from allochthonous sources in the Ganga and the Yamuna rivers.

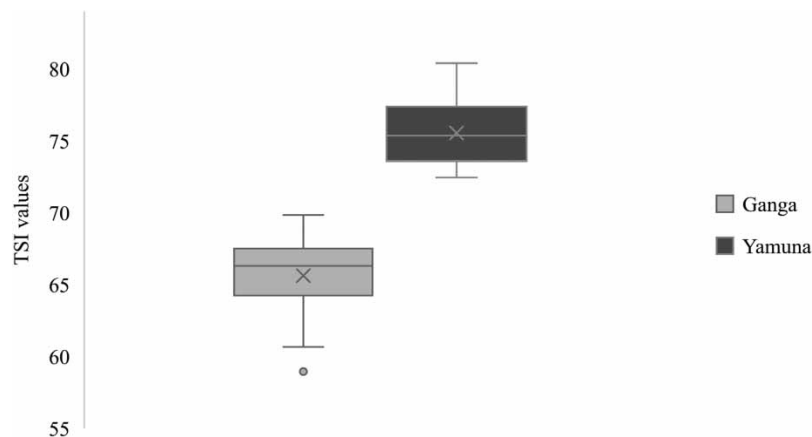
### TROPHIC STATE INDEX

The TSI was determined by using the TSI (Chl a) and TSI (TP) methods for tropical lotic systems given by Lamparelli (2004). The formula used for calculating TSI is as follows:

$$TSI\ (Chl\ a) = 10 \left( 6 - \left( \frac{(-0.7 - 0.6 \times (\ln Chl\ a))}{\ln 2} \right) \right) \quad (3)$$

$$TSI\ (TP) = 10 \left( 6 - \left( \frac{(0.42 - 0.36 \times (\ln TP))}{\ln 2} \right) \right) \quad (4)$$

where TSI (TP) represents the TSI relative to the total phosphorus variable for lotic systems; Chl a refers to the chlorophyll-a concentration ( $\mu\text{g L}^{-1}$ ) in the water, and TP represents the concentration of total phosphorus ( $\mu\text{g L}^{-1}$ ). High TSI values in rivers are a global problem. The trophic status of the Amazon River ranged from super-eutrophic to hypereutrophic, as reported by Affonso *et al.* (2011). The nutrient-enriched water encouraged phytoplankton growth causing further eutrophication associated with an unpleasant smell and release of toxins in the river water. Another study by Li *et al.* (2019) reported that the trophic status of the Yangtze River ranged from light eutrophic to hypereutrophic. The major sources of nutrients in this river were airborne deposition, wastewater plant effluents, surface runoff, and other anthropogenic activities like fishing and littering. Saha *et al.* (2022) examined the trophic status of the Chaliyar River in the Western Ghats. They reported that the water was enriched with nutrients showing mesotrophic to high eutrophic conditions, particularly in the downstream areas. The middle stretch of the Ganga River's trophic status was examined by Prajapati *et al.* (2020), who found that the river samples ranged from oligotrophic to hypereutrophic. The TSI values obtained in the study are presented in Figure 5 for the Ganga and Yamuna rivers, respectively. The final TSI was calculated as the arithmetic mean of TSI (Chl a) and TSI (TP). Based on the values obtained by TSI, the water can be classified as ultra oligotrophic ( $\text{TSI} \leq 47$ ), oligotrophic (47–52), mesotrophic (52–59), eutrophic (59–63), super-eutrophic (63–67), and hypereutrophic ( $\text{TSI} > 67$ ) (Klippel *et al.* 2020).



**Figure 5** | Box plot showing TSI values of the Ganga and Yamuna rivers.

The results indicate that TSI values ranged between 58.95 and 68.94 in the dry season and 59.27–68.11 in the wet season for the Ganga River samples. It was observed that around 6% of the samples in the dry season showed a mesotrophic nature, 11% showed eutrophic, 44% showed super-eutrophic, and 39% showed hypereutrophic conditions in the Ganga River. During the wet season, the majority of samples (50%) in the Ganga River showed super-eutrophic conditions followed by eutrophic (39%) and hypereutrophic conditions (11%). In the Yamuna River, TSI values ranged from 72.44 to 80.39 in the dry season, with all the samples showing hypereutrophic conditions. However, conditions were slightly better in the wet season, where the TSI values varied between 62.17 and 74.71, with 50% of samples showing super-eutrophic characteristics, 39% showing hypereutrophic conditions, and 11% showing eutrophic conditions. The trophic state of the Yamuna River is appalling, with most of the samples showing super-eutrophic to hypereutrophic conditions. The reason for such a trophic state in the river may be attributed to the inflow of nutrients from domestic and agricultural sources present in the catchment area that stimulate algal growth leading to algal blooms and ultimately depleting the quality of water.

## CONCLUSION

The water samples of the Ganga and the Yamuna rivers were analysed for nutrient concentrations to determine the elemental nutrient ratio, nutrient load, eutrophication potential, and trophic state of both rivers. The dissolved nutrients showed a significant spatial and seasonal variation. The nutrient concentration was relatively higher in the Yamuna River than in the Ganga River in Uttar Pradesh due to the presence of more industries and tourist footfall in Agra and Mathura along the Yamuna River. It was also observed that the concentration of most of the parameters was higher in the dry season relative to the wet season in both rivers. Such seasonal differences in the concentration indicated a dilution effect due to rainfall during the wet period. The positive correlation between  $\text{NH}_4\text{-N}$  and  $\text{NO}_3\text{-N}$  indicated the input of domestic and municipal sewage from the catchment area. Factor analysis results indicated that nutrient concentration in both rivers is contributed by both natural and anthropogenic sources present in the catchment area. The average DIN/DIP ratio in both rivers indicated the limitation of phosphate for biological productivity. The DSi/DIN ratio indicates nitrogen loading from the catchment area and potential eutrophic conditions in both rivers. Compared with the Ganga River, the annual specific yields of  $\text{NO}_3\text{-N}$ ,  $\text{NH}_4\text{-N}$ ,  $\text{PO}_4\text{-P}$ , and  $\text{SiO}_2\text{-Si}$  were relatively higher in the Yamuna River, indicating a significant increase in the contribution from anthropogenic sources. Both rivers were at high risk of eutrophication given the abundance of nitrogen, as shown by the positive values of N-ICEP and phosphorus-limiting conditions, as suggested by the negative P-ICEP values.

The estimated TSI value indicated high eutrophication risk, as 44% and 50% of the samples in the Ganga River showed super-eutrophic conditions in the dry and wet seasons, respectively. The condition of the Yamuna River was worse, with all the samples in the dry season and 39% of the samples in the wet season showing hypereutrophic conditions. Both rivers are at high risk, as shown by the ICEP and TSI values, but the health of the Yamuna River requires immediate action. Therefore, proper policy implementation and consistent monitoring are needed to protect this priceless resource. This study generated new information on the trophic status of the Ganga and Yamuna rivers, and this information will be crucial for managing eutrophy and developing nutrient budgets at the regional level. The vision of projects like Namami



Gange and YAP needs proper implementation and monitoring along with strict rules as the deterioration of river water quality by nutrient pollution is still a major concern. Other innovative programmes with equal involvement of public and government are the need of the hour by creating more sewage treatment plants to combat the increasing sewage generation with increasing population, restricting runoff from the agriculture areas by creating buffer zones such as riparian corridors and creating awareness among the masses to raise public understanding of the proper way to use water resources without compromising their quality.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

## CONFLICT OF INTEREST

The authors declare there is no conflict.

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