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Authors: Pandey, Jitendra, Tripathi, Shraddha, and Pandey, Usha

Source: Air, Soil and Water Research, 9(1)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/ASWR.S32780

Anthropogenically Induced Shifts in N:P:Si Stoichiometry and Implications in Ganga River

Jitendra Pandey[1], Shraddha Tripathi[1] and Usha Pandey[2]

[1]Ganga River Ecology Research Laboratory, Environmental Science Division, Centre of Advanced Study in Botany, Institute of Science, Banaras Hindu University, Varanasi, India. [2]Department of Botany, Faculty of Science and Technology, Mahatma Gandhi Kashi Vidyapith University, Varanasi, India.

ABSTRACT: Human-induced N:P:Si imbalances and associated shifts in nutrient limitation in Ganga River remain relatively uncertain despite recent studies highlighting its importance. The goal of this watershed-scale study was to investigate the nutrient-limiting status of Ganga River, as influenced by atmospheric deposition (AD) and catchment runoff together with urban–industrial development. AD was highest in middle watershed, where AD of NO_3^- ranged from 10.56 to 28.93, AD of NH_4^+ from 4.26 to 15.42, and AD of PO_4^{3-} from 1.82 to 2.94 kg ha^{-1} $year^{-1}$. The results showed that AD-coupled catchment runoff is an important factor, in addition to direct urban–industrial release, causing N:P:Si imbalances that lead to N over P limitation (N:P $<$ 16:1) and Si over N limitation (Si:N $<$ 1) in the river. The skewed N:P:Si ratios observed here may have important effects on phytoplankton/diatom growth and trophic cascades and consequently on river ecology. This study that forms the first report on changing atmosphere–land–water N:P:Si linkages suggests that the current policy on Ganga rejuvenation needs to focus more strongly on cross-domain drivers of stoichiometric imbalances and approaches to minimize them.

KEYWORDS: atmospheric deposition, diatom, elemental stoichiometry, Ganges basin, nutrient limitation

CITATION: Pandey et al. Anthropogenically Induced Shifts in N:P:Si Stoichiometry and Implications in Ganga River. *Air, Soil and Water Research* 2016:9 35–43 doi:10.4137/ASWR.S32780.

TYPE: Original Research

RECEIVED: December 24, 2015. **RESUBMITTED:** February 10, 2016. **ACCEPTED FOR PUBLICATION:** February 14, 2016.

ACADEMIC EDITOR: Carlos Alberto Martinez-Huitle, Editor in Chief

PEER REVIEW: Five peer reviewers contributed to the peer review report. Reviewers' reports totaled 1653 words, excluding any confidential comments to the academic editor.

FUNDING: Part of this research has been funded by the University Grants Commission, New Delhi. The authors confirm that the funder had no influence over the study design, content of the article, or selection of this journal.

COMPETING INTERESTS: Authors disclose no potential conflicts of interest.

CORRESPONDENCE: jiten_pandey@rediffmail.com

Provenance: the authors were invited to submit this paper.

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Introduction

Anthropogenic-driven shift in biogeochemical cycle of nitrogen has become a serious global issue.[1] As human alteration of nitrogen cycle is in part linked with other major biogeochemical cycles particularly that of carbon[2] and phosphorus,[3] such alterations become critical for ecosystem-level changes. Biogeochemical shifts influence nutrient balance in terrestrial[4] and aquatic ecosystems,[2,5] with more pronounced effects in developing countries, where the release of nutrients of human origin is continuing to rise.[6] In seasonally dry tropical regions of North India, extensive landscape transformation accompanied by massive use of fertilizers with urban–industrial factors drastically influences the aquatic ecosystem functioning.[7,8]

Water bodies with naturally low N or P are highly sensitive to the external input of these nutrients.[9] The N:P ratio (referred to as *Redfield ratio*) is an important indicator of which nutrient is limiting the phytoplankton growth.[10] For instance, if N:P ratio is >16:1, P is most likely to be the limiting nutrient and if N:P ratio is <16:1, N limits the phytoplankton growth.[10] Similarly, stoichiometric ratio of N, P, and Si (16:1:16) is an indicator of nutrient limitation for diatoms[11] that, despite widespread silicon limitation, contribute to more than 20% of the world primary production annually.[12] Disproportionate input of nutrients may change their stoichiometric ratios and, consequently, the pattern of ecological nutrient limitation.[5,13,14] The N:P stoichiometry in many aquatic systems of the world has skewed as a result of disproportionate nutrient loads and management efforts.[15] Contrary to N and P loadings that have increased over recent decades due to anthropogenic drivers, silicon loading, which is predominantly controlled by natural factors,[16] has remained relatively constant or declined.[11]

The global demand for P exceeds supply,[17] which is likely to induce P limitation.[18] Tropical ecosystems are considered more P-limited than nontropical ecosystems.[19] However, unlike Africa and Russia witnessing P deficit in cereal crops,[18] most part of India receives sufficient P as agricultural fertilizer.[20] Furthermore, of the 26 teragram (Tg; 10^{12} g) P applied to croplands worldwide annually, ~9 Tg is contributed by livestock slurry and manure.[21] In India, due to large livestock sources, increases in N supplies are paralleled by a similar increase in P. These subsidies coupled with atmospheric deposition (AD) and domestic sewage shift N:P ratios, unlike other parts of the Northern Hemisphere, toward P,[7,22] challenging the classical paradigm of surface water phytoplankton productivity being naturally limited by P.[14] As specific elemental stoichiometries regulate ecosystem functioning, anthropogenic-driven shifts in elemental ratios change not only the ecological nutrient limitation[5] but also the biogeochemical cycles and climate change drivers.[23] The Ganga River receiving high input of urban–industrial effluents, AD, and agricultural runoff may experience significant change in N:P:Si stoichiometry along its 2525 km course, with long-term effects on water quality and ecological nutrient limitations. However, no report, so far, is available considering explicitly the factors of shifting N:P:Si stoichiometry and associated changes in the trophic status of Ganga River. In this watershed-scale study, we evaluate the drivers of changing N:P:Si stoichiometry and possible implications on ecological nutrient limitation in the Ganga River. We expect that the Ministry of Water Resources, River Development and Ganga Rejuvenation, Government of India, may warrant watershed-scale research initiatives to understand the shifting state of atmosphere–land–water linkages and associated changes in the water quality and ecosystem resilience of Ganga River.

Materials and Methods

Study area. The heterogeneously patched Ganges basin in India (Fig. 1), extending between 21° 40′ 39″ and 31° 27′ 39″ N latitude and 73° 13′ 00″ and 89° 09′ 53″ E longitude, covers an area of 8,04,671 km^2, which accounts for 26.2% of geographical area of India supporting a major part of the country's population. The Ganga River having its origin at Gangotri in the Himalayas traverses a distance of 2525 km emptying its water into the Bay of Bengal (Gangasagar). In the plains, there is only a small slope of less than 1°.[24] The main sources of water in the river are snowmelt from the Himalayas, rainfall, and subsurface flow. The Ganges basin is among the most fertile and heavily populated river basins in the world. The river flows through 29 megacities, 23 small cities, and 48 townships.

The climatic conditions range from subtropical in upstream to tropical humid toward east. A year shows distinct seasonality: a hot and dry summer (March–June), a humid rainy season (July–October), and a cold winter season (November–February). Average annual rainfall varies between 550 and 2500 mm, with the western side receiving less rainfall.[25] More than 90% of the annual rainfall occurs during monsoon season (from July to September), causing low flow conditions during dry periods. During summer, daily temperature varies between 29°C to 46°C, and during winter night, the lowest temperature at rare occasions drops below 4°C. Soil of the region consists of eutric cambisols and shallow luvisols with variable fertility range.[25] Land use (LU) in the basin consists of extensive agricultural lands (73.44% of total basin area), forests and woodlands, urban–rural settlements, scrubland, and bare soils.

We collected samples from three subwatersheds (SWs) along 2241 km transect from Devprayag (30° 09′ N, 78° 30′ E) to Howrah to Diamond Harbour (22° 11′ N, 88° 14′ E). The study stretch constitutes about 88.8% of river length. SWs chosen for detailed study are representative of LU/land cover (LC) as well as of anthropogenic pressures. SWI (Devprayag to Haridwar; 94 km) represents an upper Gangetic agroclimatic zone covering 17% of drainage basin with rice–wheat

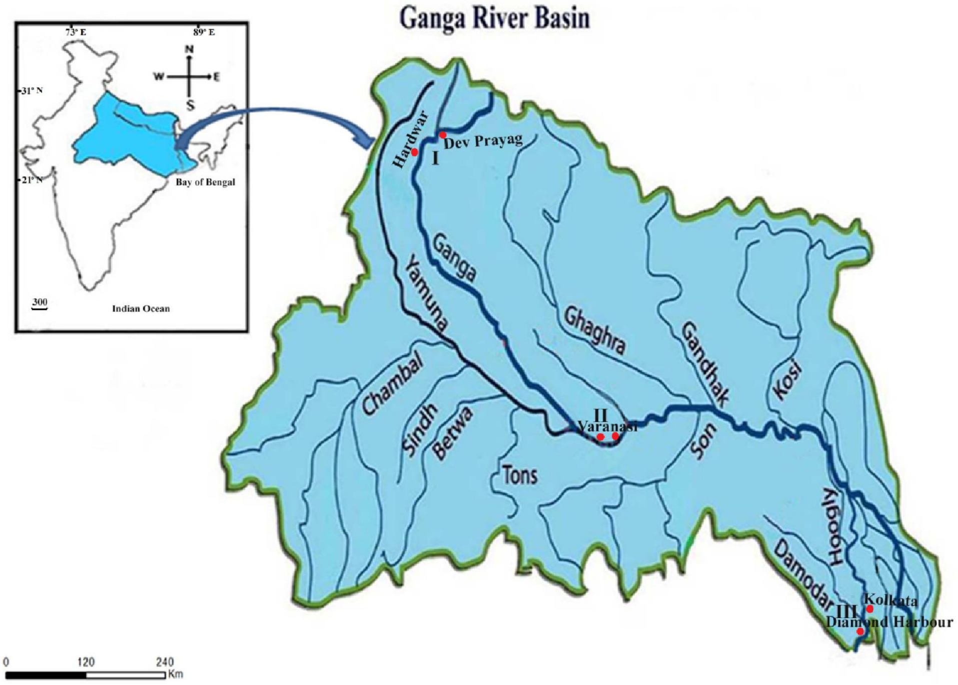

Figure 1. The study zones of Ganges basin. I: SWI represents Devprayag to Haridwar (94 km); II: SWII represents upstream to downstream Varanasi city (37 km); and III: SWIII represents Howrah to Diamond Harbour (70 km).

cropping system. Besides sewage input from Rishikesh and Haridwar, a number of industrial units discharge effluents into the river. Haridwar city (>0.3 million population) witnesses nearly 60,000 floating population every day. SWII (Varanasi region; 37 km) is chosen to represent middle Gangetic agroclimatic zone covering 16 million hectares high rainfall areas with rice–wheat cropping. Cities such as Kanpur (population, ~5 million; 150 industrial units and 80 tanneries), Allahabad (population, >1.2 million), and Varanasi (population, >1.5 million) add massive amount of pollutants to the river. SWIII (Howrah to Diamond Harbour; 70 km) is representative of a lower Gangetic agroclimatic zone with rice-based cropping system and 8% area of drainage basin. Kolkata (population, >14 million), one of the highly industrialized cities of the world, adds massive amount of sewage and industrial wastes in the river. Samples were collected between March 2012 and June 2015 (SWI), January 2012 and June 2015 (SWIII), and January 2006 and June 2015 (SWII).

Sampling and analysis. The AD was collected using bulk samplers.[5] To prevent changes in nutrient concentrations, thymol was used as a biocide in the collection buckets.[26] AD samples were screened for contamination using high soluble reactive P as an indicator[27] and analyzed for NO_3^-, NH_4^+, and PO_4^{3-} spectrophotometrically.

The runoff sampling stations were chosen based on different land usages, such as relatively undisturbed natural landscape, agricultural lands, urban areas, and woodlands. Runoff samples collected manually during rain event[5] were analyzed for dissolved organic carbon (DOC), dissolved organic nitrogen (DON), nitrate (NO_3^-) nitrogen, ammoniacal (NH_4^+) nitrogen, and dissolved reactive phosphorus (DRP). Water samples were also collected monthly from the midstream of the river from each site, directly below the surface (15–25 cm depth). DOC in water samples was estimated using $KMnO_4$ digestion procedure.[28,29] Nitrate N was estimated using brucine sulfanilic acid method,[30] ammoniacal-N using Nessler's reagent method,[31] and total dissolved nitrogen (TDN) following high-temperature persulfurate digestion.[29] DON was computed as TDN minus dissolved inorganic nitrogen (DIN), where DIN represents the sum of NO_3^--N and NH_4^+-N.[32] DRP (orthophosphate) in the runoff and river water was determined following ammonium molybdate–stannous chloride method.[29] Dissolved reactive silica (DSi) was measured following the method of Sauer et al,[33] and biogenic silica (BSi) following the method of Michalopoulous and Aller.[34] Chlorophyll *a* (Chl *a*) biomass was measured using acetone extraction procedure[31] and gross primary productivity (GPP) following light and dark bottle method.[29] Transparent exopolymeric particles (TEPs) were determined spectrophotometrically.[35]

Statistical analysis. Significant effects of site and time series were tested using analysis of variance (ANOVA). Samples were collected in replicates, and all the measurements were considered in ANOVA model. Coefficient of variation (CV) with least significant difference ($\alpha = 0.05$) across time was computed for expressing data variability and correlation coefficient (R^2), and regression analyses were used for testing linearity in relationships. Confidence limits above 95 ($\alpha < 0.05$) were considered as significant. SPSS package (version 16) was used for statistical analysis.

Results

Atmospheric deposition. The AD of nutrients varied with site. SW variations were largest at SWII (CV > 26), except for AD of PO_4^{3-}. Inputs were highest in SWII with AD of NO_3^- ranging from 10.56 to 28.93 kg ha^{-1} year^{-1} and AD of NH_4^+ ranging from 4.26 to 15.42 kg ha^{-1} year^{-1}. AD of PO_4^{3-} was also highest in SWII and lowest in SWI (Table 1). AD of DSi followed a similar trend, and among the nutrients, AD input was highest for DSi.

Surface runoff. DOC, dissolved inorganic nitrogen (DIN), and DON all were highest in the runoff emerging from agricultural subcatchment, while DRP was highest in the runoff emerging from woodland subcatchment (Fig. 2).

Table 1. AD (kg ha^{-1} year^{-1}) of nutrients in three SWs of Ganges basin.

SUB-WATERSHED	n*		NO_3^-	NH_4^+	PO_4^{3-}	DSi
I	17	Mean	14.30	5.46	1.18	22.60
		Range	9.20–19.10	2.56–8.20	0.75–1.33	15.20–28.71
		CV	22	17	24	24
II	114	Mean	23.53	12.96	2.57	36.00
		Range	10.56–28.93	4.26–15.42	1.82–2.94	24.47–42.25
		CV	26	28	27	30
III	31	Mean	21.80	9.40	1.97	31.50
		Range	10.20–28.72	3.50–12.90	1.46–2.33	21.20–37.58
		CV	22	24	31	27

Notes: Samples were collected between March 2012 and June 2015 (SWI), January 2012 and June 2015 (SWIII), and January 2006 and June 2015 (SWII). Data for January–February 2006 (SWII) and 2012 (SWI) are included in the normalized average of subsequent year-winter season. n*: number of samples collected during sampling period.
Abbreviation: CV, coefficient of variation.

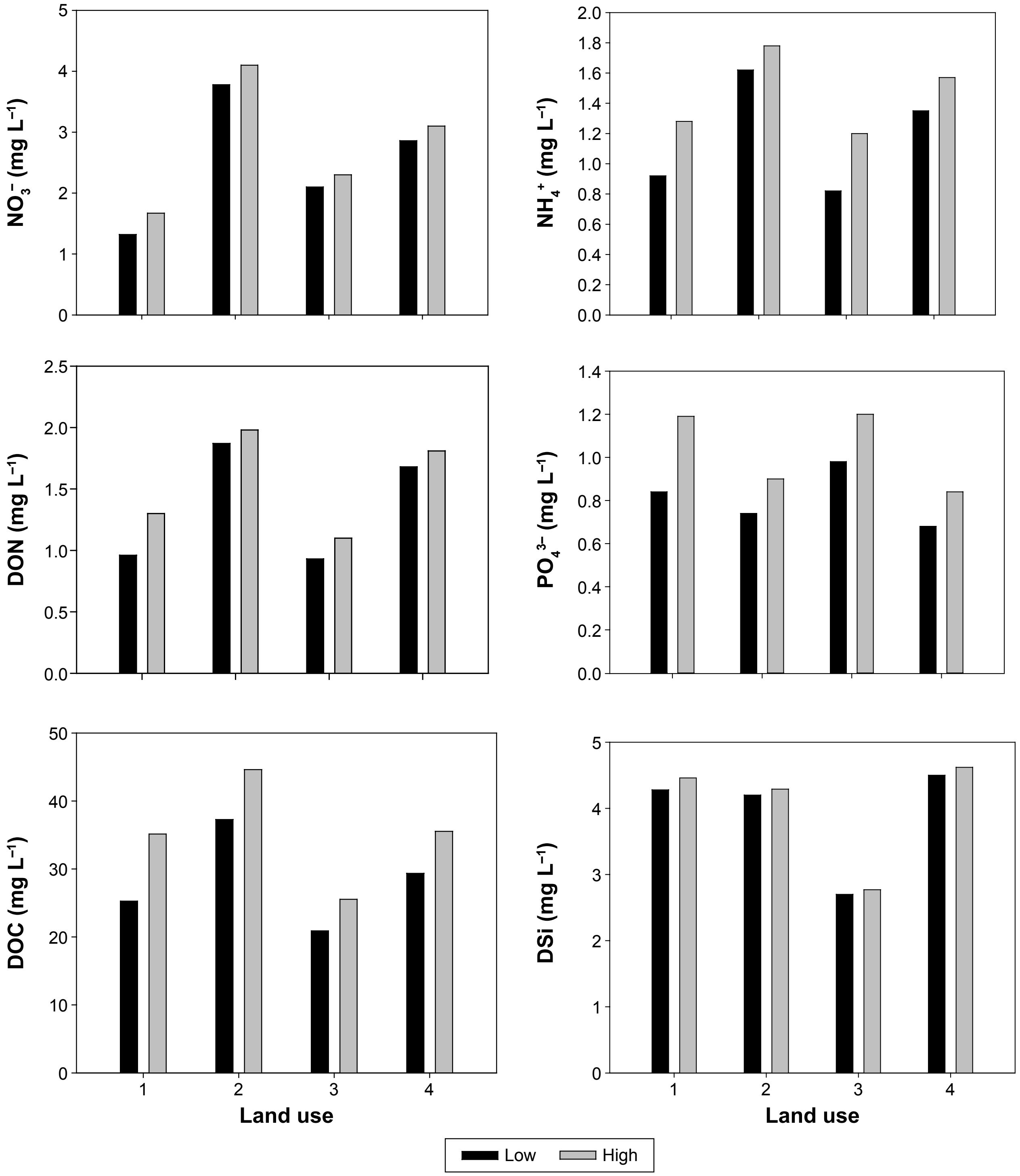

Figure 2. Overland surface runoff (lateral flow) concentrations (mg L^{-1}) of NO_3^-, NH_4^+, PO_4^{3-}, and DSi, emerging from different LU categories. Data comparisons are made in SWII for two subsites representing low and high AD inputs. First flush concentrations are included in the mean. Samples were collected for each LU category on event basis. 1: relatively undisturbed natural site; 2: agricultural land; 3: urban area; and 4: woodland.

Both nutrients and DOC in the runoff were high at sites receiving high AD, irrespective of catchment LU. Except for urban LU, DSi in the runoff exceeded 4 mg L^{-1}. NO_3^- was lowest in the runoff emerging from relatively undisturbed natural site, PO_4^{3-} was lowest in woodland runoff, and NH_4^+ was lowest in urban runoff (Fig. 2).

River water chemistry and biology. Concentrations of DIN and DRP in river water increased over time and were highest in SWII followed by SWIII and SWI (Table 2). Dissolved silica (DSi) increased downstream. Concentration of DOC showed significant ($P < 0.001$) between-site variation and was highest at SWII (Fig. 3). Chl *a* biomass

Table 2. Concentrations of nutrients in Ganga river.

SUB-WATERSHED	n*		NO_3^-	NH_4^+	DON	PO_4^{3-}	DSi
I	16	Mean	140.30	38.00	37.49	29.40	264.30
		Range	89.44–167.60	26.15–49.30	24.81–47.22	12.00–44.80	207.50–327.85
		CV	25	30	27	32	23
II	60	Mean	280.11	69.95	70.24	74.77	326.00
		Range	226.54–450.67	51.05–96.74	48.79–94.67	62.50–102.10	309.70–346.58
		CV	24	33	28	36	27
III	16	Mean	201.00	56.70	54.87	52.85	333.50
		Range	151.50–325.83	42.22–93.58	41.00–86.70	44.80–81.50	301.00–348.40
		CV	31	32	28	33	33

Notes: All values are in µg L^{-1}. Data are presented for summer low flow of 2012–2015 (SWI and SWIII) and 2006–2015 (SWII). n*: number of samples.
Abbreviation: CV, coefficient of variation.

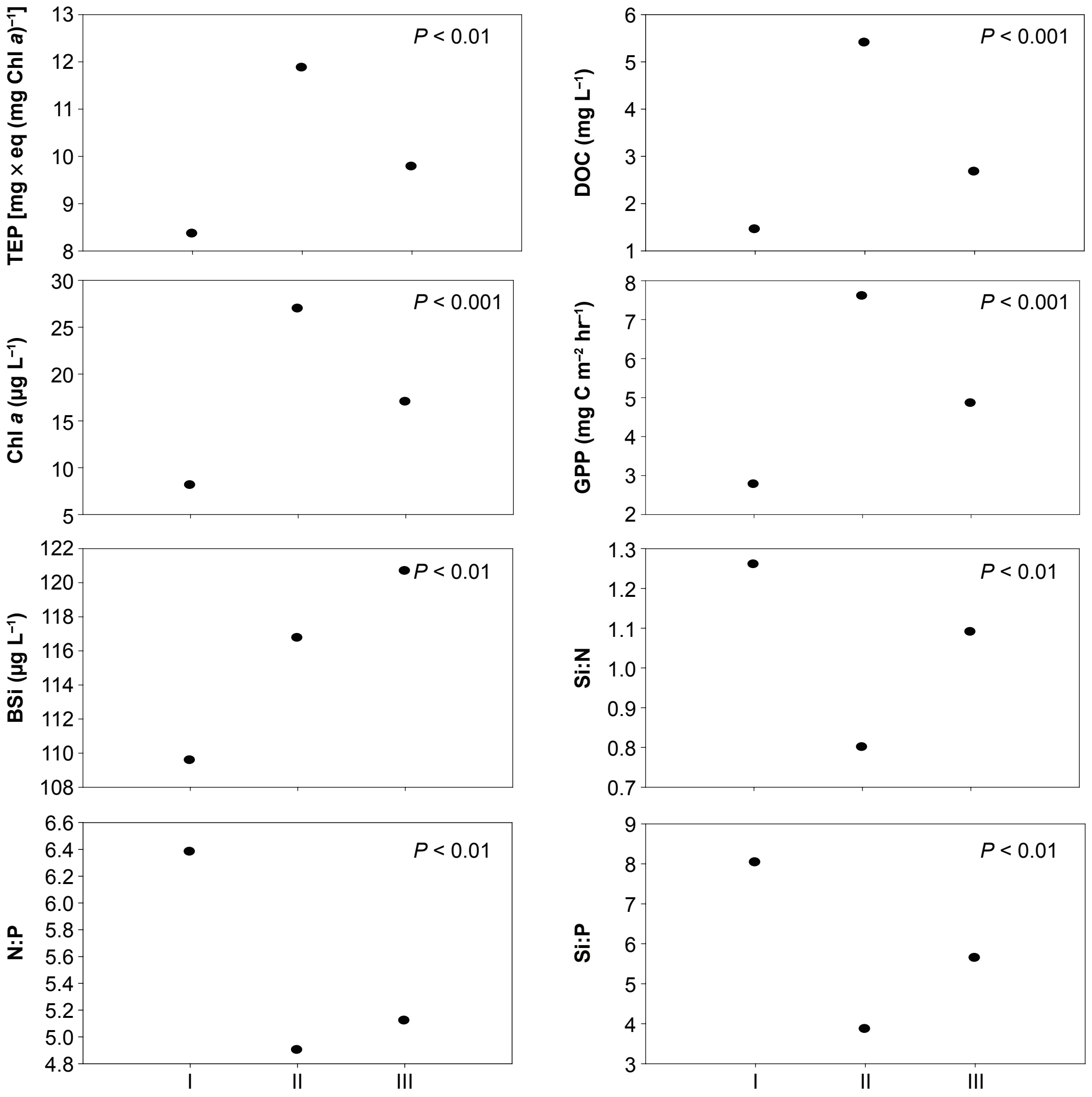

Figure 3. Schematic representation of BSi, TEPs, Chl *a*, GPP, and DOC in relation to nutrient stoichiometry in Ganga river. The *P* values shown on the graph indicate significant differences between SWs marked as I, II, and III.

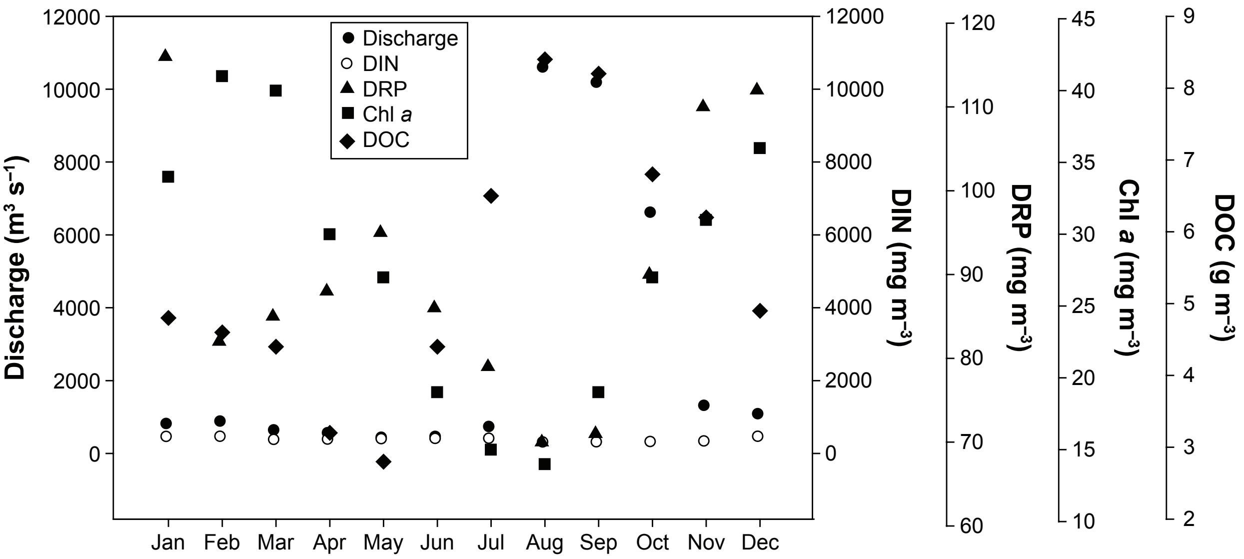

Figure 4. Mean monthly river discharge and associated variation in DIN, DRP, Chl *a*, and DOC in SWII.

and GPP showed synchrony with nutrients. TEPs showed a trend similar to Chl *a* biomass and GPP (Fig. 3). BSi, which increased downstream (Fig. 3), ranged from 86.44 to 131.35 μg L^{-1} at SWI and 92.5 to 137.20 μg L^{-1} at SWII. The N:P stoichiometry remained highest at SWI and lowest at SWII (Fig. 3), with an overall N:P ratio of <6.5. The Si:N and Si:P stoichiometries did show a similar trend. During low flow, the Si:N remained <1.25 and in many parts of the river it was <1. Seasonally, however, it varied between <1 (in summer months) and >1.4 (in monsoon months). Similarly, Si:P ratio was low in summer and high in monsoon. Intra-annually, DOC was positively correlated ($P < 0.001$) with river discharge, while nutrients and Chl *a* biomass showed asynchrony (Figs. 4 and 5).

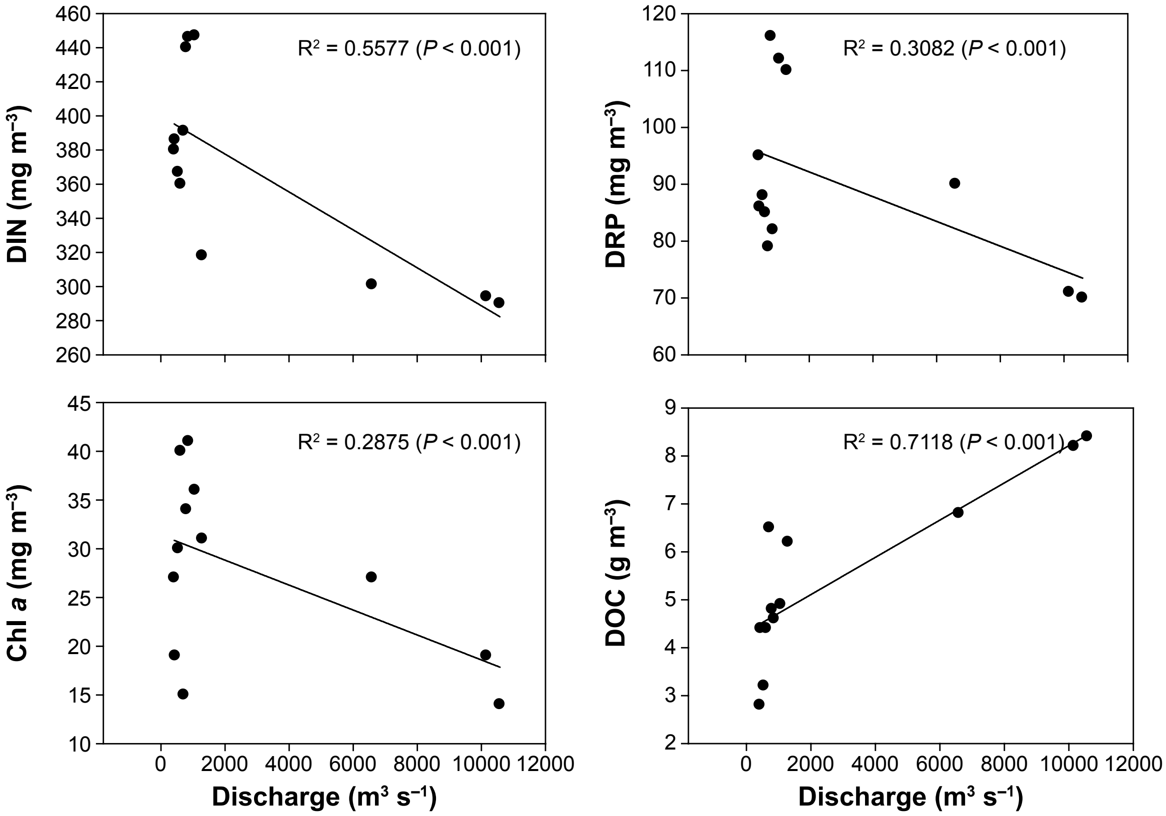

Figure 5. Relationship of nutrients, Chl *a*, and DOC with river discharge.

Discussion

Atmospheric deposition. During recent years, AD has emerged as an important source of nutrient supply in the Indian subcontinent.[6,36] Our earlier studies have shown that the middle Gangetic plain is consistently witnessing rising input of AD nutrients with more than 1.4- to 1.6-fold increases in AD of NO_3^- and more than 1.5- to 2.3-fold increases in AD of NH_4^+ in the last 10 years.[5–7] The AD inputs of N observed in this study, although remained lower than those reported in industrial and agriculturally intensified areas of China,[37] are almost parallel to those previously recorded in United States and Western Europe in the 1980s.[38] Human activities such as agriculture, transport, and energy consumption are considered accountable for increases in AD inputs.[37] Along with urban–industrial activities, extensive agriculture with massive fertilizer input accounts for rising AD inputs of N and P in the Ganges basin.[6] Additionally, the region witnesses massive biomass burning, an important source of P.[39] Besides other biomass burning usage, the region receives emission from burning of more than 36,000 dead bodies using more than 25,000 tons of dry wood in the process of cremation annually.[5]

Surface runoff. The observed trends in nutrients and DOC in the runoff indicate coupled effect of AD and LU/LC characteristics. Nutrients in surface runoff responded positively to AD inputs. Earlier studies have shown that AD enhances nutrient losses from catchment.[22] Furthermore, hydrological release of carbon and nutrients from land depends on geological parent material, biota, and LU. Site-wise differences in runoff chemistry indicated that agricultural LU contributed maximally in the lateral transport of DIN and DOC. On the watershed scale, this would be an important factor for Ganga River. Occupying 26.2% of total land area of India, this drainage basin with more than 73.44% agricultural land and massive fertilizer input can substantially elevate runoff fluxes of carbon and nutrients into the river. Although DIN and DRP in surface runoff increased at polluted sites, N:P stoichiometric ratio did show an opposite trend. As we found highest concentration of P in urban runoff at SWII receiving highest AD of P, we interpret AD to be an important determinant of skewed N:P. Nevertheless, our data indicate that, in addition to point sources, nonpoint sources such as AD and land surface runoff could induce N:P stoichiometric shift in Ganga River.

Stoichiometric shifts and implications. The major objective of the present study was to understand human-induced N:P:Si imbalances and possible ecological implications in Ganga River. Changes in nutrient concentrations in the river were large, and we attempted to explore the possible drivers. The overall results show that the synergy among AD, hydrological nonpoint discharge, and sewage input regulate variations in river water quality. The river receives large quantity of nutrients through AD and surface runoff along with point sources of input from 29 megacities, 23 small cities, and 48 townships. The data presented here show AD to be an important source of N and P input to Ganga River. Earlier studies have shown a consistently rising trend in AD input and lateral transport of nutrients to lakes and rivers in many parts of India.[5,8,22] Intensive studies conducted in the middle segment of Ganga River[5,6] showed that AD input contributes, almost on similar spatiotemporal scale, large fluxes of DIN and DRP as direct deposition and through land surface runoff to the river.

When nitrate-N exceeds 100 μg L^{-1}, the DIN:DIP is generally above the Redfield ratio (16:1), which implies P limitation of phytoplankton growth.[11] We found N:P to be $<$16:1, indicating that anthropogenic flushing has led phytoplankton productivity in Ganga River to be limited by N. Data from several synoptic studies in the central-west and northeast India spanning from 1998 to 2015 show N:P stoichiometry to have skewed toward N limitation.[5–7,22] Human-induced increases in nutrient fluxes are not evenly distributed.[40] Activities, such as agriculture, for instance, which generally increase N and P in surface waters, cause a decline in Si fluxes.[41] Furthermore, as silicate loading is predominantly controlled by natural factors, human-induced increases in N and P could shift the Redfield N:P:Si. As small but sustained P subsidies determine whether primary productivity is limited by N or P,[14] a consistently rising flux of P is expected to determine the ecology of Ganga River. The results of this study indicate that the Ganga River is moving toward low N:P and Si:N ratios. Many parts of the Ganga River are likely to have both N and Si limitations; therefore, it becomes increasingly important to monitor nutrient stoichiometric ratios in the river.

A change in elemental stoichiometry affects nutrient limitation. Consequently, the growth and dominance–diversity of phytoplankton, their consumers, and the overall community structure are altered.[11] As Si forms diatom frustules and regulates proton buffering,[42] Si limitation prevents growth of diatoms and, if P is not limiting, high N (Si:N $<$ 1) would favor slightly silicified diatoms and nondiatom species. Contrarily, high Si:N ($\geq$1) enhances heavily silicified and rapidly sinking diatoms. In this study, Si:N ratios varied between $<$1 (in summer) and $>$1.4 (in monsoon). Although the biological uptake of Si is an irregular process and can fluctuate in time,[43] it may lead to DSi consumption of $>$90% during diatom growth.[44] Thus, in an annual cycle, the proportion of slightly silicified and heavily silicified diatoms, and consequently the sedimentation removal of carbon and nutrients, may vary. Some recent studies have shown that BSi in rivers can be of same order of magnitude as DSi,[45,46] suggesting that phytolith might represent the main contributor of BSi in rivers. Here, DSi was two- to threefold higher than BSi during low flow, indicating that diatoms share a major contribution to BSi in rivers. Phytolith input remains low during low flow when the uptake of DSi by diatoms, and consequently BSi of diatom origin, is enhanced.[47] Although heavily silicified diatoms favor reducing water column turbidity by accelerating vertical carbon flux and sedimentation rates, both the cases can promote harmful algal blooms and sporadic hypoxia.[48] This study was further extended to relate TEPs with river water chemistry. The polysaccharides exuded by diatoms result in the formation of TEPs that helps in carbon sequestration and removal of nutrients and heavy metals.[49] Stickiness of TEPs favors aggregate formation,[50] and adsorption of heavy metals and calcium carbonate increases the density and consequently fastens the sinking.[49] In this study, BSi explained >71% variability in TEPs, indicating diatoms to be the major predictor of TEPs. The production of TEPs varies with chlorophyll, physiological status of cells, N:P stoichiometry, and diatom species.[35] As reported in earlier studies,[51] TEPs showed a trend similar to Chl *a* and GPP but was asynchronous to elemental stoichiometry. TEPs increased with declining N:P, indicating enhanced carbon excretion for balancing cellular C:N.[52] Furthermore, when P is not limiting, at low Si:N (<1), as observed here, less silicified diatoms and nondiatom species with low direct sinking rates predominate. Under such condition, enhanced production of TEPs indicates that the diatom–TEP synergy is one of the natural mechanisms that underlines the self-purification capacity of Ganga River.

Conclusions

The present study, which forms the first report on watershed-scale N:P:Si imbalances in Ganga River, concludes that AD-coupled land surface runoff is an important factor causing N:P:Si imbalances leading to N over P limitation and Si over N limitation. A switchover from P to N limitation causes species shift with poor quality food for consumers, whereas Si-limited phytoplankton are poorly represented by diatoms. Such changes may influence C sedimentation and trophic cascades in the long-term future. As the river is an important source of drinking water and fishing, we urge that skewed N:P:Si triggered shifts in diatom-associated trophic cascades would lead to economic loss. The current policy on Ganga rejuvenation needs to focus more strongly on cross-domain drivers of stoichiometric imbalances and approaches to minimize them. Furthermore, the riverine fluxes of DSi are important for marine productivity, and therefore, this study merits attention as the Ganga River and its tributaries are the largest transporters of silica to the North Indian Ocean.

Acknowledgments

We thank the Head, Centre of Advanced Study in Botany, Institute of Science, Banaras Hindu University, for facilities and the Council of Scientific and Industrial Research for fellowship to ST.

Author Contributions

Conceived and designed the experiments: JP. Analyzed the data: JP, ST, and UP. Wrote the first draft of the manuscript: UP. Contributed to the writing of the manuscript: ST. Jointly developed the structure and arguments for the paper: JP, ST, and UP. Made critical revisions and approved the final version: JP. All the authors have reviewed and approved the final manuscript.

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