Atmospheric deposition and land-surface runoff driven nutrient flushing in Ganga River (India)

Jitendra Pandey\textsuperscript{a}, Usha Pandey\textsuperscript{b}, Anand V. Singh\textsuperscript{a}, Deepa Jaiswal\textsuperscript{a}, Ekabal Siddiqui\textsuperscript{a} and Kavita Verma\textsuperscript{a}

\textsuperscript{a}Ganga River Ecology Research Laboratory, Environmental Science Division, Centre of Advanced Study in Botany, Institute of Science, Banaras Hindu University, Varanasi, India; \textsuperscript{b}Department of Botany, Faculty of Science and Technology, Mahatma Gandhi KashiVidyapith University, Varanasi, India

ABSTRACT

Disproportionate addition of nutrients can alter the nutrient stoichiometric balance of surface water bodies. In the present study, we investigated the atmospheric deposition (AD) and runoff-induced nutrient enrichment and N:P stoichiometric shifts in the Ganga River along a 35 km stretch of Varanasi city. The region receives 8–42 kg ha\textsuperscript{-1} of reactive-N (NO\textsubscript{3}\textsuperscript{-} + NH\textsubscript{4}\textsuperscript{+}) and 0.40–3.10 kg ha\textsuperscript{-1} of PO\textsubscript{4}\textsuperscript{3-} through AD annually. The most polluted Rajghat Site receives \textasciitilde 770.50 tons of reactive-N (N) and \textasciitilde 64.50 tons of PO\textsubscript{4}\textsuperscript{3-} annually as AD input in the sub-watershed; and \textasciitilde 25.10 tons of Nr and 2.09 tons of PO\textsubscript{4}\textsuperscript{3-} directly on the water surface. Concentrations of nutrients in surface runoff increased with AD input irrespective of land use. Among land use categories, the runoff nitrate was highest from agricultural catchment while NH\textsubscript{4}\textsuperscript{+} and PO\textsubscript{4}\textsuperscript{3-} were highest from urban areas. The study showed that the AD-runoff coupled with additional supplies could substantially alter the overall load and stoichiometric ratios of critical nutrients with a consequent effect on ecological functioning of the river in long-run.

Introduction

Agricultural and industrial revolutions in India have led to large increase in atmospheric deposition (AD) of nutrients, yet our understanding of the AD-nutrients impacts on natural and derived ecosystems comes almost entirely from studies in northern Europe and North America. Further, despite the fact that the human alteration of carbon (C) cycle is in part linked with other major biogeochemical cycles, particularly that of nitrogen (N) and phosphorus (P), most of the geosphere-biosphere models do not explicitly consider the changing state of C/N/P coupling and the associated shifts in ecosystem processes including C balance (Elser et al., 2009; Galloway et al., 2008; Gruber & Galloway, 2008; Kalbitz, Solinger, Park, Michalzik, & Matzner, 2000). Such couplings occur at specific elemental stoichiometry and regulate the status of ecosystem processes (Elser et al., 2009; Langley & Megonigal, 2010; Zhang, Li et al., 2019).

Furthermore, although surface waterbodies contribute substantially to the regional carbon dynamics, they are not explicitly considered in global carbon models (Buffam et al., 2011; Gao, Duan, Yan, & Liu, 2020). On a global scale, the atmospheric deposition has become the dominant vector of nutrient supply influencing carbon capture and storage (Baker et al., 2007; Galloway et al., 2008; Liu et al., 2013). Agricultural fertilizer use is among the major sources of atmospheric N. By the year 2020; the agricultural fertilizer use is projected to increase from 14.4 × 10\textsuperscript{6} megatons to 21.9 × 10\textsuperscript{6} megatons in South Asia and from 27.4 × 10\textsuperscript{6} megatons to 45.6 × 10\textsuperscript{6} megatons in Southeast Asia (Beman et al., 2005). These sources coupled with emissions from massive burning of fossil fuels can substantially enhance the AD-N to natural and managed ecosystems (Galloway, Hiram Levy, & Kasibhatla, 1994; Liu et al., 2013).

In many parts of India, current AD-N inputs (Pandey & Pandey, 2009, 2013; Pandey, Pandey, & Singh, 2014a) are high enough to influence the structure and functioning of terrestrial (Clark & Tilman, 2008; Sase et al., 2019) and aquatic ecosystems (Bergström, Jonsson, & Jansson, 2008; Pandey et al., 2014a, 2014b). Tropical aquatic ecosystems, where light and temperature regimes generally remain optimal are more prone to such nutrient inputs (Pandey & Pandey, 2013). The AD-nutrients delivered directly on water surfaces enhance phytoplankton development (Bergström et al., 2008) while those added into the catchment may enhance terrestrial carbon and nutrient supply through land surface runoff (Pandey et al., 2014a) and the coupled effect of these alter the structure and function of receiving ecosystems (Clark & Tilman, 2008; Pandey & Pandey, 2013; Pandey et al., 2014a, 2014b; Suárez & Gebauer, 2019). The thresholds of these critical transitions, however, generally
remain unnoticed until surprising shifts occur. Our recent study showed that the Ganges basin receives ~3.32 Tg Nr and ~173.20 Gg P annually as AD input (Pandey, Pandey, Singh, Tripathi, & Mishra, 2016). This additional supply together with those added as land surface runoff and over 2700 million liters of urban sewage each day could substantially shift the N:P stoichiometry and the pattern of nutrient limitation in the river.

Recent thrust by the Government of India is toward point source generated nutrient inputs (CPCB (Central Pollution Control Board), 2013). Non-point source-driven loading of nutrients, especially AD-linked surplus and coupled land surface runoff, is not yet characterized (Pandey et al., 2014a). The present research aimed to investigate the AD-coupled surface runoff loading of major nutrients (nitrogen and phosphorus) into the Ganga River and the associated nutrient imbalances in the river. Such shifts may result in an ecosystem-level change in the near future. Excessive P supply, for instance, may create a surplus for P and the N becomes scarce and consequently, creating an opportunity to diazotrophic cyanobacteria to dominate (Chen & Hong, 2011). Therefore, scientific understanding of all possible sources, fluxes, and dynamics of nutrients are fundamental in identifying suitable management approaches to restore the river ecosystems.

**Materials and methods**

**Study area**

The three consecutive years of study (2014–2016) was conducted along a 35 km stretch of the Ganga River at four selected sites representing up- and down-stream influences of Varanasi city (25° 18’ N lat. and 83° 1’ E long.). The climatic condition of the study area is tropical with marked seasonality. The summer season represents April to mid-June; the humid rainy season is from late June to September while winter represents November to February. March and October are the transition months. The average rainfall ranges from 870 to 1130 mm. Summer day temperature ranges from 29° C to 46° C. Westerly and southwesterly are the predominant wind direction. The soil is predominantly alluvial fluvisol and has high natural fertility. Soil shows a variable percentage of silt and clay and total organic carbon range from 0.98% to 1.67% (Pandey et al., 2014a; Pandey & Singh, 2017).

Sites were selected based mainly on sources of input and catchment characteristics. Study sites experience variable human disturbances. The Site 1 (Adalpura) is relatively less disturbed. Site 2 (Bypass upstream) represents agricultural influences; Site 3 (Assighat) witness partial urban influence and Site 4 (Rajghat) represent the downstream influence of Varanasi urban core (Figure 1).

**Measurements**

**Atmospheric deposition**

The atmospheric deposition of nutrients was measured from 2007 to 2016 using bulk samplers made up of 5 L high-density polyethylene bottle with a Teflon funnel devised with PVC needles on the top to prevent bird nesting. Samplers were maintained at a height of 2 m and samples were collected biweekly following an identical protocol. Thymol was used as a biocide in the collection bottles to prevent changes in nutrient

![Figure 1. Map of the study area showing the location of monitoring stations.](image-url)
concentration. At the end of the sampling period, the funnels were rinsed with double distilled water to collect the particles deposited on funnel walls. A 50 ml of sub-sample collected in the bottle and a 50 ml sub-sample of the rinsing water was filtered using pre-combusted Whatman glass fiber filter (0.7 µm). Nitrate (NO$_3^-$), ammonium (NH$_4^+$), and phosphate (PO$_4^{3-}$) in the bulk samples were determined spectrophotometrically (Systronics double beam spectrophotometer, 2203, India). The samples were screened for contamination using high soluble reactive – P as an indicator.

**Water chemistry and biology**

The surface runoff sampling stations were selected according to land use; relatively undisturbed landscape, agricultural lands, urban settlement, and woodland. Based on uniform availability, two sites representing the lowest (Site 1, Adalpura) and highest (Site 4, Raighat) AD-inputs were considered for the detailed study. The strategy was to collect runoff water representing the total wash-out feature representing a particular site. There was only one outlet to discharge total runoff from each area marked for the experimental purpose. The runoff samples were collected manually during the rain event, initiated with the first flush, and based on the duration of surface runoff; at intervals of 10 to 30 min.

River water samples were collected at a monthly interval from each site. Samples were collected in triplicate from ~50 m reach directly below the surface (15–25 cm depth) in acid-rinsed plastic bottles. Nitrate-N in water was measured following the brucine sulphanilic acid method (Voghel, 1971; detection limit 0.1–2.0 mg L$^{-1}$). Ammonia-N was measured using the Nessler’s reagent method (Maiti, 2001; detection limit 0.02–1.0 mg L$^{-1}$) while dissolved reactive phosphorus (orthophosphate, DRP) following ammonium molybdate-stannous chloride method (American Public Health Association [APHA], 2017; detection limit 0.01–6.0 mg L$^{-1}$). Dissolved silica (DSi) was determined following Datiallof and Rengel (Diatallof & Rengel, 2001). Chlorophyll a was extracted in acetone and measured spectrophotometrically (Maiti, 2001). The gross primary productivity (GPP) was estimated following the Light and Dark bottle method (American Public Health Association [APHA], 2017). Biogenic silica was determined by acid molybdate method (Strickland & Parsons, 1972) by filtering 500 ml of the sample through 0.6 µm PC membrane filter followed by NaOH digestion. Transparency of water was measured using a Secchi Disc and other variables were measured following standard methods (American Public Health Association [APHA], 2017).

**Statistical analysis**

Water samples were collected in triplicate and data analyzed using analysis of variance (ANOVA). The range of variability was tested using standard errors and the coefficient of variation (cv). Correlation coefficients ($R^2$) were used to test co-variations and regression analysis ($\alpha < 0.05$) was used to test linearity. SPSS package (version 16) was used for statistical analysis.

**Results**

Atmospheric deposition of NO$_3^-$ (AD-NO$_3^-$) in the region ranged from 7.18 to 29.97 kg ha$^{-1}$ yr$^{-1}$; AD-NH$_4^+$ from 1.40 to 13.76 kg ha$^{-1}$ yr$^{-1}$ and AD-PO$_4^{3-}$ from 0.25 to 3.12 kg ha$^{-1}$ yr$^{-1}$ (Figure 2) with values being highest at Raighat and lowest at Adalpura Site. The Raighat receives approximately 770.50 tons dissolved inorganic nitrogen (DIN; NO$_3^-$ + NH$_4^+$) and 64.50 tons dissolved reactive phosphorus (DRP) each year as AD input in the sub-watershed; and approximately 25.10 tons DIN and 2.09 tons DRP directly on the water surface. These values were 3 to six folds higher than those received at Adalpura. AD-input showed a rising trend over time with ~6.7%, 7.2%, and ~8.0% average annual increase in AD-NO$_3^-$, AD-NH$_4^+$, and AD-PO$_4^{3-}$ respectively between 2007 and 2016 (cv<35). At some urban sites, the annual flux of AD-reactive N (AD-Nr; NO$_3^-$ + NH$_4^+$) exceeded 40 kg ha$^{-1}$ with ~8% annual increase. Monthly, AD-input of nutrients peaked in December (Figure 3). The effect of sites and time series on AD-input of N and P were significant ($p < .001$; ANOVA). The AD-N: P declined over time however it did not show specific trend with respect to sites.

Concentrations of nutrients in the surface runoff, although showed coupled effect of AD and land use, increased with AD-input irrespective of land use (Figure 4). The data comparisons were made for four land use categories according to the uniform availability at two sites representing the lowest (Site 1, Adalpura) and the highest (Site 4, Raighat) AD-inputs. Among N species, DIN (NO$_3^-$ + NH$_4^+$) was the dominant N component being exported through the surface runoff. Among land use categories, the runoff flushing of nitrate and dissolved organic nitrogen was highest from agricultural catchment while those of NH$_4^+$ and PO$_4^{3-}$ were highest from the urban settlement (Figure 4). Synchronous to AD-input, consistent increases were observed in surface runoff nutrients. Significant positive correlations ($p < .001$) between nutrients in AD-input and those in runoff water were observed (Figure 5).

The concentrations of nutrients in river water increased downstream (Figure 6). At Raighat Site, mean concentration of NO$_3^-$ ranged from 229.63 to 539.63 µg L$^{-1}$; NH$_4^+$ from 26.63 to 58.89 µg L$^{-1}$ and that of PO$_4^{3-}$ from 71.29 to 197.26 µg L$^{-1}$. River nutrients showed strong positive relationship ($R^2 = 0.81–0.98; p < .001$) with AD- and runoff nutrients (Figure 5). The concentration of dissolved oxygen (DO) and the depth of light penetration declined while the biological oxygen demand (BOD) and other characteristics showed increasing trend.
downstream the study gradient (Table 1). Also, the N:P ratio declined downstream and was generally below 8:1 at Rajghat Site. Si did not appear a limiting nutrient (N:Si<1.30) along the study stretch of the river. Chlorophyll a and gross primary productivity (GPP) showed trends similar to the nutrients and increased downstream (Figure 6). A significant positive correlation ($R^2 = 0.82–0.96; p < .001$) was found between nutrients (AD and river water) and productivity variables (Figure 7).

**Discussion**

**Atmospheric deposition**

The Ganges basin in India is experiencing high input of reactive nitrogen (Nr) and phosphorus (P) through atmospheric deposition (AD) driven by regional emission and atmospheric transports (Pandey et al., 2016; Siddiqui, Pandey, Pandey, Mishra, & Singh, 2020). AD-Nr in many urban-industrial areas of the basin exceeds 40 kg ha$^{-1}$ yr$^{-1}$. Earlier studies have shown atmospheric N deposition between 20 and 60 kg ha$^{-1}$ yr$^{-1}$ in many areas of Europe (Bobbink & Lamers, 2002), 17 to 46 kg ha$^{-1}$ yr$^{-1}$ in many parts of India (Pandey & Pandey, 2009; Pandey et al., 2014a, 2016; Srinivas and Sarin, 2013) and 40 to 80 kg ha$^{-1}$ yr$^{-1}$ in many parts of China (Liu et al., 2013; Zhang, Lin et al., 2019). In this study, NO$_3^-$ appeared as the dominant N component although NH$_4^+$-N to NO$_3^-$ N ratios were high in remote areas indicating an increased contribution from agricultural sources (Liu et al., 2013). The AD-PO$_4^{3-}$ also showed significant spatial variations and the values reported here are

**Figure 2.** Annual trend of atmospheric deposition of NO$_3^-$, NH$_4^+$, and PO$_4^{3-}$ at study sites.
higher than those reported at non-source oriented sites in India (Pandey & Pandey, 2013; Siddiqui et al., 2020) and in a near-coastal rural site at Montseny Natural Park, Spain (Izquierdo et al., 2012). However, the values fall within the range reported at some source-oriented sites in the western part of India in general (Pandey & Pandey, 2009) and in the Ganges basin in particular (Pandey et al., 2016).

Atmospheric deposition of Nr has increased by two to seven folds over pre-industrial period in many countries of the world and is expected to increase similarly over the next 50 years in industrialized nations of Asia and South America with implications for ecosystem structure and functioning (Clark & Tilman, 2008; Galloway et al., 1994; Zhang, Li et al., 2019). The AD- nutrients affect wide areas; reach

![Figure 3. A month-wise trend of atmospheric deposition of nutrient ions at study sites. Data presented for the last year (2016) of the study.](image-url)
Figure 4. Concentrations (mgL⁻¹) of NO₃⁻ (a), dissolved organic nitrogen (DON, b), NH₄⁺ (c), and PO₄³⁻ (d) in surface runoff emerging from different land use categories. Values are mean (n = 12)±1SE. Data comparisons are made for two sites representing the lowest (Site 1, Adalpura) and highest (Site 4, Rajghat) AD-inputs. The runoff samples were collected on an event basis from 1: relatively undisturbed landscape; 2: agricultural lands; 3: urban settlement; and 4: woodland.

waterways via direct deposition onto the water surfaces and via land deposition and subsequent lateral transport. Role of such trans-boundary drivers becomes important for countries experiencing rapid industrial and agricultural intensification. Galloway, Schlesinger, Levy, Michaels, and Schnoor (1995) showed that ~55% of fertilizer N applied to agriculture is re-distributed back to the atmosphere as NH₃ and NOx and 70% to 80% of this emitted N (about 41% of total applied N) is deposited back on land. Integrating over the entire area of the Ganges Basin in India (73.44% of total area is agricultural land that receives 50–120 kg N fertilizer per hectare) and assuming 50% loss through trans-boundary atmospheric transport, the agricultural contribution to atmospheric input amounts >12.5 kg N ha⁻¹ yr⁻¹ which constitutes an average 40% AD-Nr in the watershed (Siddiqui et al., 2020).

An increasing trend in AD-input along the study gradient indicated a strong influence of urban core. Urban-industrial activities intensify as one travels along the gradient from Site 1 to Site 4. Together with agricultural intensification, motor vehicles, fossil-fueled power plants, and industrial activities; atmospheric loading of dust arising from abraded roads and scrubbing effects of urban atmosphere could enhance AD-flux near urban sites. Additionally, particles rich in calcium and magnesium oxides and rock phosphate react with nitric acid and other N oxides to produce calcium and magnesium nitrate and deposit them locally. Substantially, a high input of P at Rajghat could be linked also with the burning of more than approximately 25000 tons of dry wood for the cremation of approximately 36000 dead bodies annually. Biomass burning is an important source of atmospheric N and P (Baker et al., 2007). In this study, AD-P flux appeared significantly higher compared to model results (Mahowald et al., 2008) and AD-N:P stoichiometry declined down the gradient indicating relatively more P loading from biomass burning and other sources. Studies have shown that mineral dust is an important rejuvenator of ecosystem P pool in many parts of the world (Brahney et al., 2014; Sase et al., 2019). Atmospheric P from Asia did account for a major fraction of soil P during four million years of ecosystem development at Hawaii (Chadwick, Derry, Vitousek, Hubeert, & Hedin, 1999). North Atlantic Oscillation (NAO) has been shown to export dust-P from North Africa causing episodic P subsidies to the Mediterranean Sea (Camarero & Catalan, 2012). Studies suggest that although a major fraction of the atmospherically transported P could be of natural origin, local contributions from fertilized agricultural lands and other sources can be a significant source (Camarero & Catalan, 2012). Accordingly, an underestimate of AD-P by the model estimates could be possible due to the inappropriate parameterization of local and regional sources of atmospheric input.

Overland surface runoff

Surface runoff from diffused land-based activities and atmospheric deposition are among the major sources of nutrients loading, causing water quality degradation of surface waters. As rainwater moves over the land, it carries pollutants (nutrients, organic matter, metals,
and other chemicals) flushing these chemicals finally to surface waters including rivers (Gao et al., 2020; Wu, Long, Liu, & Guo, 2012). The magnitude of such addition depends on the intensity of human activities in the catchment. The cultivable area in the Ganges basin consumes about 35% of total fertilizers used in India. Thus, agricultural sources alone could substantially enhance the nutrient load in the Ganga River and its tributaries. In Huai River (China), fertilizers application in the basin has been shown to be the largest non-point source of new N (69% of net anthropogenic N inputs) (Zhang et al., 2015). Studies showed that about 3–20% of P (Caraco, 1995) and 18% of N (Carpenter et al., 1998) applied to croplands are exported to surface waters. The release of nutrients in runoff depends on land use, changes in soil chemistry, topography, geological parent material, biota and microbial consumption and release (Pandey et al., 2014a; Singh & Pandey, 2019; Yang, Wang, Wang, & Zheng, 2016). In this study, the effects of these factors were well indicated by site-wise variations in runoff N and P.

The concentrations of nutrients in the surface runoff, although showed coupled effect of AD and land use, increased with AD-input irrespective of land use. Earlier studies have indicated AD-driven increase in nutrient loss from the catchment (Pandey & Pandey, 2013). The positive influence of atmospheric inputs on surface runoff has been shown on correlation analyses. In this study, runoff chemistry was more strongly

Figure 5. Correlation coefficient ($R^2$) and regression showing linearity in relationships between AD-runoff and river nutrients.
influenced by agricultural sub-catchment. This merits attention to watershed-scale influences because agriculturally dominated areas are the most important non-point source of nutrient pollution (Chen & Hong, 2011; Lee, Cherry, & Edmonds, 2017). Occupying 26.2% geographical area of India, the Ganges basin with 73.44% agricultural land can substantially elevate the runoff fluxes of nutrients into the Ganga River. The sub-watershed scale calculation of surface runoff data reveals that the river receives approximately 225500 kg DIN and 41100 kg DRP annually from the Raighat (17500 ha) sub-watershed. These values were 3 to 5 folds higher than those received from up-stream Adalpura (8400 ha) sub-watershed. Proportionately high P in the runoff emerging from relatively undisturbed land usage and urban landscapes indicates the role of AD-input. Nevertheless, our data indicate, despite wide variability (cv>28), AD–coupled surface runoff could shift N:P stoichiometry in Ganga River.

**Nutrient limitation**

Among the major determinants, light and nutrients are the primary causal factor for the autotrophic growth in aquatic ecosystems. In the present study, the mean concentrations of available-N (NO₃⁻ + NH₄⁺) and PO₄³⁻ were highest at Site 4 (Figure 6). Further, the depth of light penetration declined downstream the study gradient, although light did not appear a limiting factor for the phytoplankton growth in the study stretch. The river receives substantially high

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**Figure 6.** River nutrients and productivity variables measured at study sites, Values are mean (n = 9) ±1SE.

**Table 1.** Summary of environmental variables measured in the river at different study sites. Values are mean (n = 9) ±1SE.

| Variable          | 1        | 2        | 3        | 4        | ANOVA  |
|-------------------|----------|----------|----------|----------|--------|
| pH                | 7.85 ± 0.16 | 7.95 ± 0.19 | 8.43 ± 0.18 | 8.54 ± 0.16 | p < .05 |
| Transparency (cm) | 79.11 ± 4.32 | 70.10 ± 3.72 | 47.93 ± 3.28 | 46.09 ± 2.65 | p < .001 |
| TDS (mg L⁻¹)     | 377.08 ± 22.20 | 468.00 ± 36.19 | 544.07 ± 73.21 | 581.00 ± 63.50 | p < .01 |
| Conductivity (µS cm⁻¹) | 207.80 ± 15.35 | 238.30 ± 15.75 | 272.77 ± 19.63 | 293.25 ± 21.40 | p < .01 |
| DOC (mg L⁻¹)     | 2.62 ± 0.32 | 3.93 ± 0.47 | 5.96 ± 0.57 | 6.98 ± 0.65 | p < .01 |
| Chloride (mg L⁻¹) | 13.40 ± 0.73 | 15.57 ± 1.18 | 25.72 ± 2.20 | 30.27 ± 2.25 | p < .001 |
| Sulfate (mg L⁻¹) | 3.04 ± 0.17 | 3.85 ± 0.29 | 5.36 ± 0.41 | 6.56 ± 0.59 | p < .05 |
| Sodium (mg L⁻¹)  | 4.98 ± 0.69 | 6.98 ± 0.77 | 8.35 ± 0.69 | 9.62 ± 0.78 | p < .05 |
| Potassium (mg L⁻¹)| 2.96 ± 0.21 | 3.82 ± 0.37 | 4.94 ± 0.32 | 4.88 ± 0.31 | p < .01 |
| Magnesium (mg L⁻¹)| 1.55 ± 0.09 | 1.98 ± 0.32 | 2.96 ± 0.22 | 3.59 ± 0.29 | p < .05 |
| Calcium (mg L⁻¹) | 6.99 ± 0.51 | 7.82 ± 0.36 | 8.12 ± 0.44 | 7.81 ± 0.45 | p < .05 |
| Ionic strength (nmol L⁻¹) | 0.87 ± 0.08 | 0.98 ± 0.07 | 1.21 ± 0.07 | 1.69 ± 0.04 | p < .05 |

*Expressed in terms of Secchi depth.
input of nutrients from point sources (urban-industrial effluent) and from non-point sources including atmospheric deposition and land surface runoff. In the Ganges basin, among non-point sources, the contribution from agricultural sources prevails. In tropical aquatic ecosystems, biological productivity is primarily controlled by nutrients. The proportion of nutrients determines which nutrient would limit phytoplankton growth (Hall, Smith, Lytle, & Leibold, 2005). Chlorophyll $a$ and GPP increased downstream following a trend similar to the nutrients. Both these productivity variables mirrored in concordant changes in nutrient concentrations. This shows that phytoplankton growth in the river is stimulated by nutrients. The data showed a positive correlation between AD-N and -P and chlorophyll $a$ ($R^2 = 0.82–0.93; P < .001$).

In the present study, we compared AD-N:P and river N:P stoichiometry with phytoplankton uptake requirement. Earlier studies have indicated that AD-linked changes in N:P supply ratios can shift the pattern of nutrient limitation (Bergström et al., 2008; Elser et al., 2009). Anomalous N:P in lakes (Pandey & Pandey, 2013; Sheibley, Enache, Swarzenski, Moran, & Foreman, 2014), rivers (Pandey et al., 2014b) and seawater (Markaki, Loje-Pilot, Violaki, Benyahya, & Mihalopoulou, 2010) have been linked with variability in AD-N and -P. Stoichiometric mass balance showed that complete utilization of AD-N could fix 463 to 2554 $\mu$mol C m$^{-2}$ d$^{-1}$, while AD-P could fix 61 to 1100 $\mu$mol C m$^{-2}$ d$^{-1}$ through photosynthesis (Pandey et al., 2014a). These values represent 19% to 31% (for N) and 3% to 13% (for P) of average gross primary productivity (GPP) in the river and have relevance from an ecological perspective. Baker et al. (2007) observed that AD-N contributes to 120 to 1290 $\mu$mol C m$^{-2}$ d$^{-1}$ representing 0.7% to 7.6% of average depth-integrated GPP in the Atlantic Ocean. Furthermore, a study of the Western Mediterranean Sea showed that the AD-P which contributes to ~1% of average annual GPP could account for 24–33% of AD-P induced annual production during strong dust events (Izquierdo et al., 2012). Similarly, AD has been shown to contribute 2% to 26% of phytoplankton production and 1% to 35% of GPP within upper 200 m water column of the Eastern Mediterranean Sea (Christodoulaki et al., 2013).

Figure 7. Correlation coefficient ($R^2$) and regression showing linearity in relationships between nutrients (AD and river water) and productivity variables (Chlorophyll $a$ (Chl $a$) and gross primary productivity; GPP).
Atmospheric deposition together with point sources can substantially enhance nutrient concentration during low flow while the surface runoff is the dominant vector of nutrient input to surface waters during the rainy season (Wu et al., 2012). Urban rivers often experience water quality problems due to the discharge of untreated sewage. A study in Great Britain showed that P fluxes were predominantly controlled by urban areas (Worrall & Burt, 2007). Here, the study stretch receives an excessively high amount of urban sewage. The river downstream Varanasi city receives about 194.20 tons of DIN and 48.50 tons of DRP through urban sewage annually (Central Pollution Control Board [CPCB], 2013). These inputs together with those of non-point sources could alter the N:P stoichiometric ratios in the river. In the present study, the pattern of nutrient limitation shows skewed nutrient supply. The study stretch showed N:P < 8:1 indicating that the nutrient limitation for phytoplankton has shifted from P to N. This may affect the diversity and dominance of phytoplankton and ultimately the trophic relations (Elser et al., 2009). Furthermore, as the system moves toward eutrophy, the feedback releases of P from the sediment would further lower the N:P ratio. This has long-term implications and merit attention toward the fact that the management priorities reducing N loading alone may be constrained by high P levels.

Conclusions

The study showed that, in addition to point sources, the Ganga River in Varanasi region receives a high and disproportionate amount of nutrients from atmospheric deposition and land-surface runoff. The concentration of nutrients in surface runoff increased with AD input irrespective of land use. River nutrients showed a strong correlation with nutrients in AD-input and runoff water. Runoff losses for nitrate appeared highest from the agricultural catchment, while those of NH₄⁺ and PO₄³⁻ were highest from urban areas. High and disproportionate addition of nutrients and associated shifts in N:P stoichiometry would potentially alter the ecosystem functioning in long-run. This merit attention both from ecological modeling as well as from a river management perspective.

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