Chapter 10
Ecosystem Responses to Pollution in the Ganga River: Key Issues to Address River Management

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10.1 Introduction

During the recent few decades, the anthropogenic activities have dramatically altered the water quality of the Ganga River and its tributaries. Point and nonpoint source-driven inputs contain a variety of organic and inorganic substances including nutrients, dissolved and particulate organic carbon, and metal toxicants. Nutrient enrichment enhances productivity (autochthonous carbon), and this together with atmospheric, terrigenous, and anthropogenic carbon (allochthonous carbon) input causes C eutrophication (Pandey et al. 2014a). The coupled effects of eutrophy and metal pollution are expected to cause long-term consequences, higher in the order of magnitude than could be predicted from short-term, small-scale studies. Despite this, most of the studies conducted on the river Ganges focus generally on eutrophication and some on metal pollution. Accordingly, most of the water treatment technologies consider removal of biological oxygen demand (BOD), i.e., removal of carbon load only. However, recent studies show that eutrophication and metal pollution in the Ganga River most often occur simultaneously (Jaiswal and Pandey 2019a). For instance, sewage-associated inputs contain large amount of carbon and nutrients leading to eutrophication, whereas industrial effluents add quantifiable amount of metals and other pollutants causing toxic effects.

The average population density in the Ganges basin is 712 persons/km^2 as compared to 382 persons/km^2 for India. The river along its 2525 km course flows through 29 megacities, 23 small cities, and 48 townships and receives massive fluxes

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of nutrients and other pollutants. The total wastewater generation in the basin is ~8250 million liters per day (MLD), out of which, 2538 MLD is discharged directly into the river, 4491 MLD into tributaries, and 1220 MLD on land or low-lying areas (CPCB 2013). The Assi drain at Varanasi discharges over 66 MLD of sewage leading to ~156 mg L^{-1} chemical oxygen demand (COD) and 4060 kg day^{-1} biological oxygen demand (BOD) load to the river in this region. Additionally, the drain adds over 535 tons of dissolved inorganic nitrogen (DIN) and 133 tons of dissolved reactive phosphorus (DRP) annually (Yadav and Pandey 2017a). In addition to point sources, the nonpoint sources, such as agricultural runoff from 73.44% agricultural land of the basin containing residues of ~10 million tons of fertilizers and 9000 tons of pesticides, add a sizable amount of nutrients and pesticide to the river. A sub-watershed-scale study by Yadav and Pandey (2017a) shows that the river in Varanasi region alone receives ~289.69 tons of DIN, 47.1 tons of DRP, and 1421.55 tons of dissolved organic carbon (DOC) through surface runoff and ~15.23 tons of DIN and 1.19 tons of DRP through atmospheric deposition (AD) annually. A watershed-scale study by Pandey et al. (2016a) shows that the Ganges basin receives ~3.32 Tg reactive nitrogen (NO_3^- + NH_4^+) and ~173.20 Gg phosphorus (PO_4^{3-}) annually, and the inputs were relatively higher in the middle segment which is considered as the most polluted stretch of the river (CPCB 2013). All these sources add large amount of oxygen-demanding substances and pollutants into the river throughout the year creating tremendous pressure on water quality and ecosystem services such as drinking water supply, recreation, and fisheries (Pandey et al. 2017; Jaiswal and Pandey 2019b; Siddiqui et al. 2019a).

Studies conducted on the Ganga River generally select parameters bifurcating eutrophy and metal pollution and even without considering ecosystem-level consequences. For instance, to address trophic state, biological oxygen demand is generally considered where the sampling is restricted to the upper water column only. The issues such as stratification of dissolved oxygen in the water column, sediment oxygen demand (SOD), dissolved oxygen deficit (DOD), nature of oxygen-demanding substances (ODS), benthic hypoxia, and ecosystem feedbacks have been altogether ignored for this major river system of India. Similarly, for metal pollution, the analysis of pelagic water and freshly deposited sediments are generally considered (Siddiqui and Pandey 2019a). Some of the studies conducted in earth sciences context have taken into account the deep sediment analysis (Verma and Pandey 2019). Studies considering the factors of in situ metal release and its bioavailability are altogether lacking. In particular, no data so far, except few studies conducted in our laboratory, are available on changing state of ecosystem functions coupling feedbacks and ecological assimilation capacity of the Ganga River. The present review is an effort to make a critical analysis on the need for understanding ecosystem responses coupling eutrophy and metal pollution in the Ganga River. This has relevance because our multi-temporal, multi-scale studies suggest the need for identifying the determinants of ecosystem responses to metal pollution and eutrophy for integrated management of the Ganga River (Jaiswal and Pandey 2019a, c).

10.2 Causes of Pollution and Eutrophy in Ganga River

10.2.1 Metal Pollution

The heavy metal pollution is gaining global attention because of their abundance, toxicity, nonbiodegradable nature, and persistence in the environment (Fu et al. 2014). The unprecedented increase in urbanization, industrialization, and economic development enhances the addition of heavy metals to water bodies worldwide. Both the natural and anthropogenic sources, including rock weathering, soil erosion, domestic and industrial effluents, agricultural leachate, coal burning, etc., contribute to water pollution (Singh and Pandey 2014; Alvarez-Vazquez et al. 2017). Both point and nonpoint sources contribute to metal pollution in the Ganga River (Yadav and Pandey 2017a).

In the Ganges basin, ~2500 MLD industrial waste is generated (Trivedi 2010), and the middle segment (from Kannauj to Varanasi) adds the largest amount of industrial effluents to the river. The industrial sectors, including tannery, battery, and electroplating and heavy duty in Kannauj and Kanpur city; engineering in Allahabad; and locomotives and carpet industries in Varanasi city, are considered to be main sources of metal pollution. Tanneries alone constitute ~58% of grossly polluting industries in the middle stretch of the Ganga River. Besides this, a large amount of metals are added through tributaries in the main river. For example, over 359 industries add their effluents to the Yamuna tributary which is finally released to the Ganga River (CPCB 2016). Recent studies conducted in our laboratory show long-distance atmospheric transport as well as deposition of metals in the Ganga River (Pandey and Pandey 2009; Pandey et al. 2010). A recent study (Pandey et al. 2010) shows that the Ganga River receives 0.78–18.65 g ha^{-1} year^{-1}Cd, 0.48–-6.28 g ha^{-1} year^{-1} Cr, and 152.7–447.50 g ha^{-1} year^{-1} Zn in Varanasi region only through atmospheric deposition. A basin-scale study by Siddiqui and Pandey (2019a) shows that only ~44.44% samples of Cr and 33.33% of Cd are below their respective permissible limits of 50 and 3.0 μg L^{-1} (Bureau of Indian Standards, BIS 2012). Similarly, ~54.63% samples of Cu, ~ 66.66% of Pb, ~44.44% of Mn, ~66.66% of Fe, and ~33.33% of Ni samples along the basin have exceeded their permissible limits.

The overall concentrations of metals in the river are influenced by multiple factors such as the magnitude of external loading, source partitioning, chemical composition, adsorption, and episodic events driven by fluctuating river flow, sediment delivery, and urban-industrial discharge (Yadav and Pandey 2017a; Jaiswal and Pandey 2018). The sediment composition, redox potential, pH, and cation exchange capacity of the system are the major determinants that regulate dissolution, precipitation, absorption, and complexation of metals in the sediment and, consequently, their bioavailability, associated toxicity to aquatic organisms, and impact on the food web (Jaiswal and Pandey 2018, 2019d; Siddiqui and Pandey 2019a; Verma and Pandey 2019).

10.2.2 Nutrient Loading

Nitrogen (N) and phosphorus (P) are considered as most critical nutrients because their demand to supply ratios generally lie at unity or below. Because of this reason, they become limiting nutrients for phytoplankton growth. Excessive input of these nutrients, although increases food production and stimulates plant growth, causes detrimental effects on surface waters including rivers. Rivers receive nutrients from the airshed, in the form of atmospheric deposition (AD), and watershed in the form of leaching and runoff (Pandey et al. 2014a; Bellmore et al. 2018). A global-scale study has shown that during the period of 1860–2005, the reactive N (Nr) deposition has increased from ∼15 Tg to 187 Tg which could be doubled by 2050 (Galloway et al. 2008). Further, AD adds over 3.7 Tg of P annually at global scale (Tipping et al. 2014). Studies show AD-N input range between 1.54 and 40 kg ha^{-1} $year^{-1}$ in inland water bodies of the world (Edokpa et al. 2015; Bellmore et al. 2018) and between 12 and 38 kg ha^{-1} $year^{-1}$ in many parts of India (Pandey 2011; Pandey and Pandey 2013; Siddiqui et al. 2019b). It varies between 9.72 and 42.85 kg ha^{-1} $year^{-1}$ in the Ganga River, an amount high enough to change the Ganga River ecology (Singh and Pandey 2019). Basin-scale extrapolation of a recent study shows that through AD, ∼2.77 Tg DIN and ∼0.13 Tg DRP are deposited in the basin and ~ 5.31 Gg DIN and 0.37 Gg DRP are added directly on the Ganga River surface annually (Singh and Pandey 2019). Additionally, the river receives a large amount of nutrients from tributaries and sub-tributaries (Mishra et al. 2016; Yadav and Pandey 2017a).

In Ganges basin, over 2723 MLD municipal sewage is generated, out of which only ~1200 MLD is flushed to the river after treatment. These urban effluents add ~13.28 Gg DIN and 5.29 Gg of DRP annually into the river. Surface runoff also adds huge amount of nutrient to surface waters. A sub-watershed-scale estimation in Varanasi region shows that agricultural land adds ~403, 186, and 24 Gg $year^{-1}$; woodland adds ~67, 30, and 19 Gg year¯1; and built-up area adds ~11, 55, and 34 Gg $year^{-1}$of NO_3^-, NH_4^+, and DRP, respectively, through surface runoff. The basin-scale extrapolation of these data shows that the river receives ~193 to 1181 Gg DIN and ~59 to 218 Gg DRP annually through surface runoff. The river transports ~31.58 Gg of DIN and 3.97 Gg of DRP annually to the Bay of Bengal (Singh and Pandey 2019). These overall quantitative estimations show that, along with the point sources, the nonpoint sources also add a large amount of nutrients to the Ganga River across its length which needs proper attention and management.

10.2.3 Carbon Enrichment

Along with point sources, the atmospheric deposition and surface runoff are important regulators of autochthonous and allochthonous C pool in the Ganga River (Pandey et al. 2014a, 2015a; Siddiqui et al. 2019b; Siddiqui and Pandey 2019b).

In Varanasi region, the autochthonous carbon varies between 256.6 and 567.8 kg C ha^{-1}. Across the river length, the autochthonous input contributes ~102.58 Gg of organic C annually (Singh and Pandey 2019). Comparative studies of Goldstein and Galbally (2007) and Hallquist et al. (2009) show that, at global scale, the total organic carbon (TOC) deposition increased from 305–645 to 950 Tg over a period of only 2 years. The Ganga River in Varanasi region receives ~110.8–558.6 tons organic carbon through atmospheric deposition, ~1421.55 tons DOC through surface runoff, and 364.0–1456.3 tons organic carbon through Assi drain (Yadav and Pandey 2017a). Basin-scale extrapolation showed that the basin receives ~1.81 Tg TOC each year through atmospheric deposition of which ~4.26 Gg is added directly on to the river surface (Singh and Pandey 2019). Surface runoff exports 16.16 to 26.90 Tg TOC and 9.19 to 16.46 Tg DOC, whereas the point sources add over 110 Gg of TOC to the river annually (Singh and Pandey 2019).

Studies show that a large amount of carbon in rivers and streams comes from terrigenous sources (Pandey et al. 2014a; Siddiqui et al. 2019b). Because nonpoint source C of terrestrial origin is flushed mainly through monsoon season runoff, this C is largely transported to the sea. The Ganga River leads to a burial of $\sim 1.1 \times 10^{12}$ mol sediment-driven organic carbon each year in the Bengal Fan which is ~10% of the global organic carbon burial flux in the continental margins (France-Lanord and Derry 1997). At global scale, rivers export ~611 Tg carbon per year (Cole et al. 2007) from which the contribution from South Asian rivers alone is ~7% (42.9 Tg $year^{-1}$) (Patra et al. 2013). The Ganga-Brahmaputra with ~7 Tg C $year^{-1}$ contributes the largest share in global DOC export to the oceans (361 Tg $year^{-1}$) (Patra et al. 2013).

10.3 Ecosystem Responses to Pollution and Eutrophy

10.3.1 Shifts in Microbial Enzyme Activity

The riverbed sediments, an important component of riverine ecosystem, are a biologically active and comparatively stable zone and support benthic communities which play an important role in ecosystem functions including biogeochemical cycling, secondary production, carbon metabolism, and sedimentation of carbon, nutrients, and heavy metals (Covitch et al. 2004). Recent studies have established that sediment microbial extracellular enzymes (EEs) can be used as an indicator of carbon and nutrient limitation/acquisition and to uncover the influence of regional-scale anthropogenic stressors (Sinsabaugh et al. 2009; Yadav and Pandey 2017b; Jaiswal and Pandey 2018, 2019e). The substrate-specific nature of EEs makes them important tools to investigate the functional profile of microbial communities as influenced by human-induced alterations (Sinsabaugh and Linkins 1990). The EE activities show quantifiable and instantaneous response (for instance, toward substrates and toxicants) even to small alterations in the ecosystems (Paerl et al. 2003). As the microbes play vital role in mediating the biogeochemical cycles and regulating the ecosystem structure and functioning, these have been proved to be the most suitable parameters for quantification of shift in ecosystem responses toward alteration in organic matter (substrate) and heavy metals (inhibitors) (Sinsabaugh et al. 2008; Jaiswal and Pandey 2018). Long-term sustainability and stability of an ecosystem depends, in a major way, on functionally active microbial communities, and such measurements provide the actual picture of health condition of an ecosystem. Further, because they constitute the key node connecting detritus trophic chain, any change in their metabolism affects the whole ecosystem processes including organic matter decomposition, nutrient cycling, and food web. Measurement of enzyme activities requires a small quantity of sample, generally proved to be simple, accurate, cost-effective, and rapid. Studies have shown that EE activities can be used as an index of microbiological functional diversity and integration of these with other physical and chemical measurements can provide important information on which ecosystem management strategies can be keyed (Jaiswal and Pandey 2019a).

As the microbial functional diversity involves various metabolic processes, a representative set of enzymes that control the key metabolic pathways/processes can be used to assess the microbial response to changing carbon, nutrients, and heavy metal concentrations. The extracellular enzyme β-D-glucosidase can be used as a measure of C acquisition (Sinsabaugh et al. 2009) and alkaline phosphatase (AP) as a proxy of P starvation (Duhamel et al. 2010), while protease can be used as an indicator of N mineralization (Rejsek et al. 2008). Further, because the fluorescein diacetate hydrolytic bioassay (FDAase) involves three major groups of enzymes (lipases, esterases, and proteases), which contribute to organic matter decomposition, it can be used as an indicator of total microbial activity (Schnürer and Rosswall 1982). The FDAase can directly be correlated with biomass and ATP content (Fontvieille et al. 1992). The microbial metabolic quotient (ratio of basal respiration to substrate-induced respiration) is used as an index to measure adversities in environmental conditions for soil microbes (Wardle 1993).

The microbial structure and functioning in aquatic ecosystems are generally influenced by episodic events driven by stormwater and intermittent flushing of urban-industrial effluents. Anthropogenic input of nutrients increases the autochthonous C which, along with the allochthonous C, induces EE activities. Studies have shown that EE activities can be used as a better substitute of sediment and water quality variables because of their direct linkages with carbon and nutrients as well as with the concentration of toxicants in water and sediments (Hill et al. 2006; Jaiswal and Pandey 2018). In addition to carbon and nutrients, rivers receive huge amount of metals from natural and anthropogenic sources, a large fraction of which is deposited in the bed sediments. Heavy metals are potentially toxic to microbial community and influence the overall ecological structure and functioning (Jaiswal and Pandey 2018, 2019e). Organic carbon in sediment forms complex with metals and often buffers their bioavailability and, consequently, the toxicity (Jaiswal and Pandey 2019e). Thus, the investigations on relationships between EE activities, substrate (carbon), and total and bioavailable metal concentration (toxicants) can provide important cues through which the state of river health and ecotoxicological implications can be appropriately assessed. In a recent study, we found positive correlations of EE activities (FDAase, β-D-glucosidase, protease) with C, N, and P and negative correlations with heavy metals (Jaiswal and Pandey 2018, 2019e). Earlier studies show significant positive correlations of heavy metals with microbial metabolic quotient (qCO_2) indicating further that heavy metals are major stressors affecting microbial activity (Wardle 1993).

These results suggest that EE activities in the riverbed sediment can be a sensitive indicator of C, N, and P status in the river. Further, the metals accumulated in the sediment inhibit EE activities, although C-rich sediment can reduce the toxic effects probably by reducing the bioavailability (Jaiswal and Pandey 2018). A recent study conducted in the Ganga River has shown that when total heavy metal concentration (ΣTHM; a sum of six most common heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn) of human-impacted riverine systems) exceeds 347.44 μg g^{-1}, it becomes detrimental to EE activities. However, if a site has very high concentration of TOC, this limit may reach 472.53 μg g^{-1} indicating a modulatory effect of TOC in metal toxicity (Jaiswal and Pandey 2019a). The study further shows that the stimulatory effect of substrate on EE activities declines when ΣTHM exceeds 284.73 μg g^{-1} (Jaiswal and Pandey 2019e). Thus, the EE activities can be a good indicator of river response toward metal pollution and C eutrophy in large rivers, and the accuracy has displayed to be higher than other biological variables (Pandey and Yadav 2017; Jaiswal and Pandey 2018, 2019e).

10.3.2 Shift in Aquatic Diversity

One of the major impacts of human-induced environmental change is the loss of biodiversity and altered ecosystem processes. A recent global-scale study by Hooper et al. (2012) reveals that biodiversity loss can be considered as one of the major drivers of ecosystem change. Accordingly systematic database on interaction among biodiversity loss, environmental change, and associated impacts on ecosystem functioning is necessary. The Ganga River, which is under strong influence of anthropogenic perturbations, has been identified as a system with a massive shift in aquatic diversity and abundance. The Ganges dolphin has been an indicator species of this river, but due to increasing pollution load, this species is now at the boundary of extinction (Bashir et al. 2010). Dolphins are now found in some restricted locations of the upper stretch, and even there they are under threat due to increasing pollution and decreasing deepwater pools (Bashir et al. 2010). A sharp decline in abundance of major carp and spawn has been reported due to massive exploitation, habitat fragmentation, water abstraction, and increasing pollution load (Jhingran and Ghosh 1978). Besides this, large-scale reduction in clupeid fisheries has been reported due to increasing pollution in the river. This has increased the pressure on other commercially important fishes, such as *Aorichthys seenghala* (Sykes) and *Aorichthys aor* (Ham.), causing a threat to these species as well (Seth and Katiha 2003). A study conducted by Singh and Sharma (1998) reported 14 abundant, 7 vulnerable, 15 low-risk, 1 data-deficient, and 2 endangered fish species in

Alaknanda of upper Ganges. The exotic species are comparatively stronger, cause habitat modification, and generate competition for food, light, and other resources. Singh et al. (2010) have reported that abundance of exotic fishes such as *Cyprinus carpio* and *Oreochromis niloticus* in the Ganga River has negatively influenced the economically important indigenous fishes such as *Catla*, *Labeo rohita*, and *Cirrhinus mrigala*. Khanna et al. (2007) have reported that prolonged exposure of fishes to deteriorated environmental conditions causes severe irreversible damage to scale circuli and lepidonts resulting in loosening of scales.

The excessive inputs of nutrients promote phytoplankton growth. Although they are the basis of food chain, they can be harmful to human and other vertebrates as they release toxic substances (Ariyadej et al. 2004). At Kanpur (Jajmau), *Phormidium*, *Aphanocapsa*, and *Oscillatoria* have been reported in abundance (Singh et al. 2014). These species generally occur at places with high concentration of nutrients. A study conducted in Varanasi region has reported negative relationship between benthic algal biomass and DOC and a positive correlation with Secchi depth suggesting the role of water transparency (Pandey 2013). Furthermore, large biomass of *Phormidium uncinatum* was reported in high DOC region. The study suggests that the increasing DOC concentration is changing the light climate and fate of benthic producers in the Ganga River (Pandey 2013). A point source-linked study at Bijnor (UP) has reported the prevalence of pollution-tolerant species *Synedra*, *Cocconeis*, *Spirulina*, *Botryococcus*, and *Chlamydomonas*. Sensitive species such as *Cladophora* and *Euglena* disappeared from these sites (Negi and Rajput 2013). In another study of Kanpur region, abundance of Chlorococcales members such as *Microcystis aeruginosa*, *M. flos-aquae*, *Chroococcus minutus*, *C. varius*, *C. minor*, *Aphanocapsa grevillei*, *A. montana*, *Aphanothece microscopica*, and *Coelosphaerium kuetzingianum* has been reported (Singh et al. 2014). The prevalence of these species indicates conditions less conducive for sensitive species.

A shift in microbial diversity, in response to human perturbations, has also been reported in the Ganga River (Singh et al. 2013; Reddy et al. 2019). For example, multiple drug resistance has been observed in coliform, fecal coliform, fecal streptococci, and *E. coli* between Fatehgarh and Kannauj (Malik et al. 1995). A large number of multiple antimicrobial-resistant, Shiga toxin and enterotoxin-producing *E. coli* and virulence traits of *Enterococci* have been reported in the Ganga River near Kanpur city between Bithoor to Shuklaganj region (Lata et al. 2009). Due to increasing human intervention, a large number of harmful bacterial species including *Bacillus*, *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and *Salmonella typhi* have been reported in the most polluted stretch of the river between Kanpur and Varanasi (Singh et al. 2013).

10.3.3 Shifts in Diatom Diversity

Being fast growing, phytoplankton responds quickly to nutrient, temperature, and light regimes. Because light and temperature do not generally observe as limiting in tropics, nutrients are considered as the principal determinants. For this reason, phytoplankton is considered as an indicator of nutrient pollution and eutrophy. Nutrients influence phytoplankton growth in terms of absolute concentration and in specific elemental ratios. The specific stoichiometric ratio (Redfield ratio) of N, P, and Si (16:1:16) is important for the balanced growth of phytoplankton specifically for diatoms (Turner et al. 2003). Recent studies have reported a shift in this ratio due to disproportionate input of nutrients in lakes and rivers (Pandey et al. 2014b, 2016b). This shift in stoichiometry would alter the ecosystem structure and functioning in due course of time with long-term irrecoverable consequences (Pandey et al. 2014b). The shifts in nutrient stoichiometry affect a diverse group of primary producers, specifically diatoms which are R-strategic (high reproductive potential) phytoplankton and show rapid change in their growth with changes in aquatic ecosystems. Besides nutrient stoichiometry, the changes in ionic strength, pH, light penetration, and temperature also affect the diversity and abundance of diatoms (Potapova and Charles 2003).

Benthic diatoms are an important group of protists that show niche specialization against nutrient pollution and light regime shifts. Because this group grows by attaching to certain substrate, they can be used as a selected group to assess responses especially in lotic systems. In response to atmospheric deposition of N in oligotrophic alpine lakes and P enrichment in temperate lakes, species such as *Asterionella* and *Fragilaria* have been reported to constitute the dominant group (Saros et al. 2005). The Ganga River receives, along with point and nonpoint sources, huge amount of N and P through atmospheric deposition (Pandey et al. 2013, 2014a, 2016a) suggesting that these inputs will also have strong effect on the distribution of diatoms. In an earlier study conducted along 268 km stretch from Allahabad to Varanasi downstream, we found a significant shift in diatom abundance and diversity in concordance with the changing state of carbon and nutrient pollution (Pandey et al. 2017). A significant decline in species diversity was observed with decreasing N/P stoichiometry, and, except for a few species which are adapted to high nutrient concentrations, the sites with nutrient-rich condition showed less overall diversity of diatoms. Species adapted to nutrient pollution, especially to P pollution, are accommodated in heterogeneous habitats through dominance transference (Fig. 10.1 and Table 10.1), which helps in the restoration of ecosystem functioning under adverse conditions (Pandey et al. 2017). Using an appropriate statistical tool, P-loving species can easily be grouped in one cluster (Fig. 10.2).

The N- and Si-limiting condition could shift the diatom assemblages from P-sensitive to P-tolerant species. The freshwater diatom species have high content of Si compared to the marine species (Conley et al. 1989). Thus, the relative availability of dissolved silica (DSi) regulates the proportion of siliceous diatoms in freshwater bodies (Conley 1997). Centric diatom bloom farmer, *Cyclotella,* a highly silicified diatom, is of growing concern in eutrophied rivers (Tavernini et al. 2011) and is reported to enhance the export of biogenic silica and C to the river sediment (Pandey et al. 2015a, b). The shift in environmental variables such as light and nutrients changes diatom species composition (Bere and Tundisi 2011). A study conducted in Varanasi region has shown increasing abundance of *Cocconeis*,

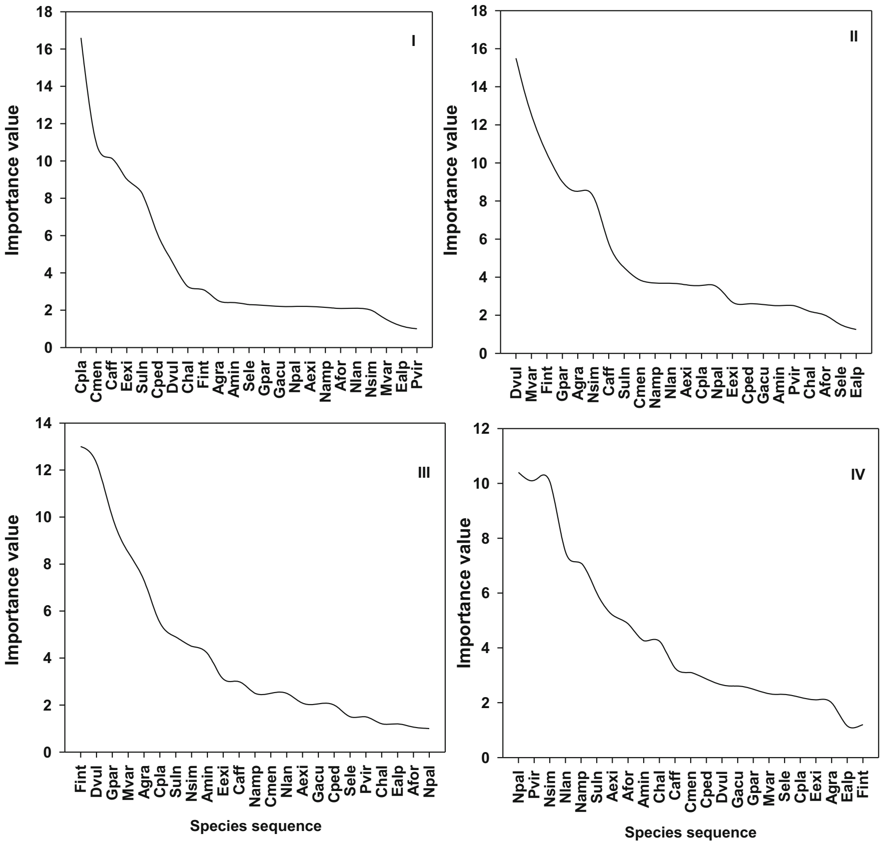

Fig. 10.1 Dominance-diversity curve of benthic diatoms at four study sites (I, Yamuna; II, Assi; III, Varuna; and IV, Gomti confluences with the Ganga River). (*Reprinted from Pandey et al. 2017, with permission from Current Science)

Cyclotella, *Hyalodiscus*, and *Aulacoseira* and declining abundance of *Diatoma* (Pandey et al. 2015b). Species such as *Achnanthidium*, *Amphipleura*, *Asterionella*, *Craticula*, and *Cyclotella* were found to be more abundant at highly polluted downstream sites; and nutrients and DOC were found to be the major regulator of abundance variabilities. At high N/P and Si/P stoichiometric ratios, species such as *Hyalodiscus*, *Navicula*, *Nitzschia*, etc. have been found in abundance (Pandey et al. 2015b).

Further, the abundance of *Aulacoseira* has been shown to correlate with high P loading (Walsh and Wepener 2009), while that of *Synedra* and *Cocconeis* has been linked with P-limiting condition (Walsh and Wepener 2009). The species such as *Pinnularia* and *Diatoma* are able to tolerate mesotrophic to eutrophic conditions (Muscio 2002; Walsh and Wepener 2009), and *Gomphonema* can tolerate eutrophic to hypereutrophic condition (Walsh and Wepener 2009). Ponader and Potapova

Table 10.1 Explanation of abbreviations used in Figs. 10.1 and 10.2

Abbreviation	Full form
Aexi	*Achnanthes exigua*
Amin	*Achnanthidium minutissimum*
Afor	*Asterionella formosa*
Agra	*Aulacoseira granulata*
Cped	*Cocconeis pediculus*
Cpla	*Cocconeis placentula* var. *lineata*
Chal	*Craticula halophila*
Cmen	*Cyclotella meneghiniana*
Caff	*Cymbella affinis*
Dvul	*Diatoma vulgare*
Eexi	*Eunotia exigua*
Ealp	*Eunotia alpine*
Fint	*Fragilaria intermedia*
Gpar	*Gomphonema parvulum*
Gacu	*Gyrosigma acuminatum*
Mvar	*Melosira varians* Agardh
Nlan	*Navicula lanceolata*
Nsim	*Navicula simplex*
Namp	*Nitzschia amphibia*
Npal	*Nitzschia palea*
Pvir	*Pinnularia viridis*
Sele	*Surirella elegans*
Suln	*Synedra ulna*

(2007) have reported high growth of *Achnanthidium* in polluted water including those affected by acid mine drainage. Similarly, studies have reported high growth of *Surirella*, *Amphipleura*, and *Craticula* at sites affected with urban discharge and are known to be tolerant to high concentration of nutrients (Muscio 2002). Studies on heavy metal-diatom responses are limited. Species such as *Nitzschia* has been shown to grow under metal contamination if coupled with nutrient-rich condition (Trobajo et al. 2013).

10.4 Dissolved Oxygen Deficit and Ecosystem Feedbacks

One of the most general ways of aquatic ecosystems to respond to increasing anthropogenic perturbations is the reduction in dissolved oxygen (DO) level. Development of hypoxic/anoxic zones in aquatic ecosystems is among the most widespread and deleterious effects of anthropogenic influences on global scale (Diaz and Rosenberg 2008). High input of oxygen-demanding substances (ODS) increases the rate of decomposition to an extent greater than the rate of oxygen supply (Rabalais et al. 2010) leading to dissolved oxygen deficit (DOD) in the system. Besides this,

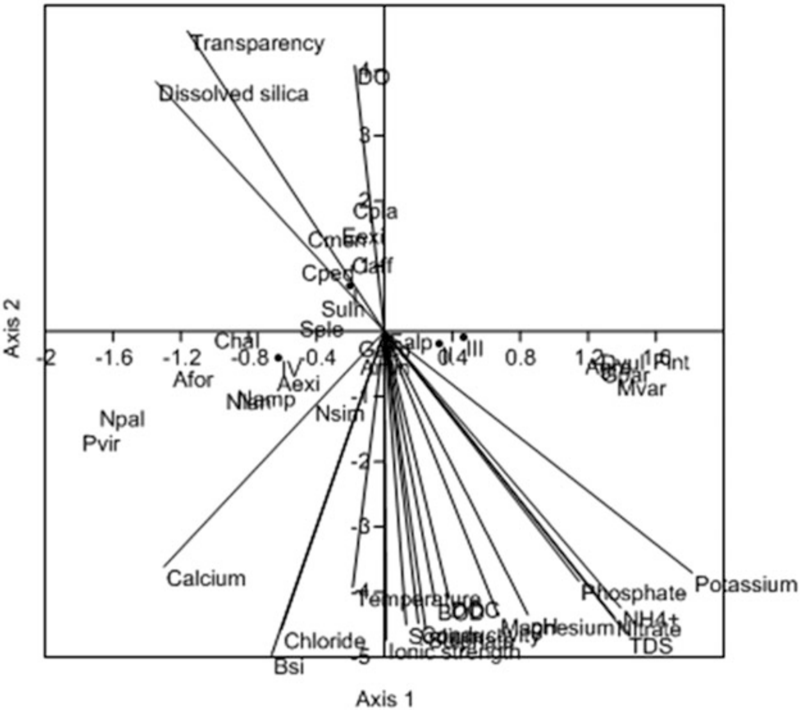

Fig. 10.2 The CCA bi-plot showing diatom species and environmental variables in the ordination space of four different quadrants. (*Reprinted from Pandey et al. 2017, with permission from Current Science)

increasing autochthonous carbon and temperature coupled with reduced flow also contribute to oxygen depletion in riverine ecosystems (Jaiswal and Pandey 2019b; Pandey et al. 2019). Accordingly, the variations in DO and associated shift in DOD can be used to get insight into the human-induced alterations in biological and chemical processes operating in river ecosystems. Studies have shown that the riverbed sediment consumes a large amount of DO from the overlying water leading to increased dissolved oxygen deficit at sediment-water interface (DOD_{sw}) (Jaiswal and Pandey 2019b). Benthic hypoxia/anoxia has been reported in the Gulf of Mexico (Rabalais et al. 2001), in the St. Lawrence River (Gilbert et al. 2005), and in the Arabian Sea and the Bay of Bengal (McCreary et al. 2013). The DOD_{sw} affects microhabitats (Mackenzie et al. 2000) and biogeochemical processes controlling nutrient cycling (Diaz and Rosenberg 2008) and causes habitat fragmentation leading to a shift in the benthic community and trophic cascade (Rabalais et al. 2001). At low DO (<2.0 mg L^{-1}), benthic organisms start showing abnormal behavior, and mass mortality and a shift in community structure can be observed if the level below 0.5 mg L^{-1} persists for a longer time (Diaz and Rosenberg 2008).

Most of the studies conducted so far on the Ganga River consider only biological oxygen demand (BOD) and chemical oxygen demand (COD) to describe oxygen linkages and measure the organic pollution load and health status of the river (Tare et al. 2003; Dwivedi et al. 2018). The sediment oxygen demand (SOD) has been reported to share >50% of total oxygen demand (MacPherson et al. 2007) but is a more neglected cause of increasing DOD in the Ganga River. The SOD has two components: biological sediment oxygen demand (BSOD), which is associated with benthic respiration and microbial decomposition of organic matter, and chemical sediment oxygen demand (CSOD), the oxygen consumed in the oxidation of Fe, Mn, and NH_4^+ (Higashino et al. 2004). A study conducted along a 518-km-long segment of the middle stretch of the Ganga River and downstream of two point sources showed high SOD and DOD_{sw} and development of hypoxia/anoxia at many locations of the river (Jaiswal and Pandey 2019b). This merits attention because wastewater treatment technologies generally address removal of BOD only. The increasing load of other chemicals in the river is also causing a greater risk to DO and needs proper management.

Episodic development of hypoxic/anoxic zones is considered as a signal of critical health of an aquatic ecosystem as the DO less than 2 mg L^{-1} can cause lethal to sublethal effects on benthic organisms and fish (Diaz and Rosenberg 2008). Hypoxia/anoxia-induced ecosystem consequences include loss of biodiversity, changes in organic matter processing and nutrient cycling, decreased resistance to invasion and ecosystem functioning, and ultimately reduced resistance to natural and human perturbations (Solan et al. 2004; Carstensen et al. 2014). Further, the hypoxic/anoxic conditions affect secondary production which ultimately influences the food web (Carstensen et al. 2014). These conditions lead to ~75% reduction in burrow productions which reduces the sediment oxygenation exacerbating the problem further (Middelburg and Levin 2009).

The benthic hypoxia/anoxia generates positive feedbacks such as sediment-P release, sediment-metal release, and denitrification (Conley et al. 2002; Eyre and Ferguson 2009) which result in massive alteration in nutrient and metal cycling (Hu et al. 2001; Villnäs et al. 2012). In a study conducted in the Ganga River, we found a high rate of sediment-P release at sites with high dissolved oxygen deficit (Jaiswal and Pandey 2019b; Pandey et al. 2019). The phosphate bounded to iron oxides in oxygenated sediments is released to the overlying waters when the oxides are reduced under hypoxic/anoxic condition (Middelburg and Levin 2009). The increased flux of P from bed sediment alleviates P limitation (Conley et al. 2002) and propels phytoplankton production (Cardinale 2011) leading to DOD which delays the recovery further (Jaiswal and Pandey 2019b). The oxygen deficit in the benthic region accelerates denitrification (Eyre and Ferguson 2009). Studies have reported severe hypoxia/anoxia at the Bay of Bengal, and it has been urged that even a small change in oxygen level will lead to a drastic change in nitrogen balance (Bristow et al. 2017). We have reported a high rate of denitrification downstream of point sources and tributary confluences at sites where DO_{sw} was below 2.0 mg L^{-1} (Jaiswal and Pandey 2019f; Pandey et al. 2019). The study sites with high denitrification also have high concentrations of total organic carbon (TOC), nitrate, and total nitrogen (TN) which are known to enhance the rate of denitrification (Piña-Ochoa and Alvarez-Cobelas 2006). The organic carbon concentration affects denitrification as it generates electron source for denitrifying enzymes (Dodla et al. 2008). The increase in NH_4^+ efflux ultimately stimulates phytoplankton growth and in turn increases hypoxia/anoxia at sediment-water interface making the recovery of ecosystem even more difficult (Middelburg and Levin 2009).

About 85% of metal inputs to the river deposit in the bed sediments (Zhang et al. 2016). However, the benthic hypoxic/anoxic condition leads to enhanced efflux of metals from sediment to overlying waters (Jaiswal and Pandey 2019d). The hypoxia/anoxia affects the redox condition of sediments and in turn provides positive feedback to sediment-metal release (Jaiswal and Pandey 2019d). The metals in the sediment are adsorbed onto organic carbon, iron, and manganese oxides and clay particles (Eggleton and Thomas 2004) in different ways such as occlusion in amorphous materials, absorption at the surface of oxy-hydroxides of Fe and Mn, complexation with organic matter, and incorporation with sulfides (Zhang et al. 2014). A high DOD_{sw} causes reduction of nitrate and oxy-hydroxides of iron and manganese leading to increased release of metals from riverbed sediment (Eggleton and Thomas 2004). We found a high rate of sediment-metal release in the Ganga River at sites associated with hypoxia/anoxia such as the locations close to drain mouth, tributary confluences, and sites downstream of cities (Jaiswal and Pandey 2019d). Significant increase in Fe and Mn releases at DO < 2.0 mg L^{-1} has been reported by Banks et al. (2012) in an incubation experiment, by Fu et al. (2014) for Jialu River, and by Liu et al. (2019) in microcosm experiments. Banks et al. (2012) found increased dissolved fraction of Zn, Pb, Cd, and Cu from contaminated sediments even at very short-time hypoxic conditions. Liu et al. (2019) have reported significant increase in bioavailability of Zn, Pb, Cd, Cu, and Cr under severe hypoxic condition (DO, 0–2.0 mg/l). For the Ganga River, an increase in benthic metal bioavailability has been reported at locations with $DO_{sw} < 2.0$ mg L^{-1} (Jaiswal and Pandey 2019d).

Enhanced release of metals at sediment-water interface has toxicological implications. Different forms of the metals show different degree of mobility, chemical interactions, biological availability, and toxicity (Xu et al. 2017). The mobile and bioavailable fractions of metals cause greater toxicity to aquatic organisms (Eggleton and Thomas 2004). Thus, assessing the bioavailable fractions and the factors affecting their concentration and release can be helpful in understanding transformations, transport, and impact of metals in the aquatic environment (Morelli and Gasparon 2014). Various studies have shown the impact of metal toxicity on benthic ecosystems in terms of increased mortality and biodiversity loss (Stark et al. 2004), effect on colonization and dispersal (Stark et al. 2004), and reduced reproduction rate and population growth (Vicente-Martorell et al. 2009). Increased fraction of bioavailable metals have been shown to cause more negative impacts on epibenthic and pelagic invertebrates and fishes (Vicente-Martorell et al. 2009). Given that the Ganga River is the home of a diversity of economically important fisheries (Rao 2001) and other aquatic organisms, a decrease in DO, development of hypoxic zones, and consequent release of bioavailable metals will lead to death of these organisms, influencing trophic cascade and the nutritional and livelihood security to human consumers.

10.5 Shifts in Carbon Sequestration

Although freshwater ecosystems cover relatively less geographical area (less than 4% of the Earth's surface), they play a critical role in the global carbon cycle because of the high rate of respiration and carbon sequestration (Cole et al. 2007). The inland water bodies transport huge amounts of carbon from land to the ocean and perform a major role in carbon transit. Recent studies have shown that the inland water bodies emit the carbon in the amount close to those absorbed by organisms on Earth's land surface and in oceans (Raymond et al. 2013). Further, in freshwater bodies, more carbon is buried each year than those in vast oceanic floor (Aufdenkampe et al. 2011). Global studies have shown that every year about 2.7 billion metric tons of carbon reaches to the inland water bodies through different sources (Raymond et al. 2013). Half of this carbon is respired and returned back to the atmosphere as CO_2 (Bastviken et al. 2011; Raymond et al. 2013), ~0.4 billion tons of carbon is buried in bed sediments, and ~0.9 billion tons is exported to oceans (Aufdenkampe et al. 2011). Human interference such as land use change is dramatically affecting the carbon cycle in freshwater bodies. Nutrient input to freshwater bodies increases the algal blooms which absorb carbon from the atmosphere and increase the carbon sequestration (Pacheco et al. 2013). However, on decomposition and respiration, this carbon is released to the atmosphere and the cycle goes on (Bastviken et al. 2011; Borges et al. 2015).

A worldwide study by Cole et al. (2007) reveals that ~87% of the lakes are CO_2-supersaturated and the average pCO_2 is about three times higher than the overlying atmosphere. Thus, due to increasing human pressure, the surface waters may become a source rather than a sink of atmospheric CO_2. Recent studies have established that this CO_2 flux from rivers and stream is enough to affect the regional C budget at landscape scale (Raymond et al. 2013; Jaiswal et al. 2018). Amazonian rivers, for instance, have been reported to emit CO_2 more than ten times of the amount of C exported to the ocean (Richey et al. 2002). One of the main reason of high CO_2 efflux from rivers is in situ breakdown of young organic matter (Richey et al. 2002). Recent studies have indicated that the human-impacted Ganga River is receiving an increasingly high amount of carbon from terrestrial sources (Pandey et al. 2014a). In an earlier study, conducted at land-water interface (LWI) of the Ganga River, we found that the LWI is outgassing a huge amount of CO_2 into the atmosphere indicating that due to increasing human perturbations many parts of the Ganga River are now converted into a source of CO_2 (Jaiswal et al. 2018; Jaiswal and Pandey 2019e).

The organic matter degradation and carbon cycling are controlled by microbial extracellular enzyme (EE) activities (Sinsabaugh et al. 2009). The anthropogenic input of carbon (allochthonous C) causes a shift in microbial community structure and functioning, including organic matter degradation and carbon cycle. The EE activity is influenced by human inputs such as carbon, nutrients, and heavy metals (Pandey and Yadav 2017; Jaiswal and Pandey 2018). Carbon and nutrients act as substrate and enhance the EE activities, while heavy metals act as toxicant and thus reduce the EE activities. As most of the human-impacted rivers receive a high amount of toxicants along with carbon and nutrients (Jaiswal and Pandey 2019a), a deviation has also been reported regarding the carbon sequestration in these rivers. Studies have reported a reduced rate of decomposition and C mineralization even at low concentration of metals (Nwachukwu and Pulford 2011). In a study, we found a contrasting result regarding the carbon decomposition and sequestration along the middle stretch of the Ganga River (Verma et al. 2019). In the sites rich in carbon and nutrients and where metal concentrations did not exceed the toxic threshold (ΣTHM $<$ 360 μg g^{-1}), an increase in CO_2 emission was observed. These sites were also reported with high EE activities as organic C enhances microbial activity. However, at sites with high metal concentration (ΣTHM $>$ 360 μg g^{-1}), a significant reduction in CO_2 emission was recorded (Jaiswal and Pandey 2019e). This could be linked with the fact that increased metal concentration negatively influences the microbial activity and carbon degrading enzymes (β-D-glucosidase and FDAase) leading to reduction in microbial ability to metabolize carbon sources (Jaiswal and Pandey 2018). A high C/N ratio was also reported at these sites, further indicating higher accumulation of C relative to release (Verma et al. 2019). Overall, our studies with the Ganga River clearly indicate that metal pollution in eutrophic lotic systems enhances C storage relative to flux (Jaiswal and Pandey 2019e; Verma et al. 2019).

These results indicate that the metals cause physiological constraints in carbon breakdown and consequently enhance C accumulation. If the heavy metal concentration continues to increase, as expected in future, the CO_2 emission and C degradation may not be proportionate to the amount of carbon the human-impacted rivers are receiving. This will lead to enhanced C accumulation relative to flux in anthropogenically impacted large rivers.

10.6 Alternative Alert Systems

10.6.1 Extracellular Enzymes

Biomonitors play an important role in identifying shifts in ecosystem structure and functioning, recognizing the causal factors, and understanding the consequences. Unlike terrestrial ecosystems, where most of the shifts are quantitatively detectable (Oliver et al. 2015), scientists often face a number of limitations in identifying specific and universal biomonitors for changes in water quality and trophic status of riverine ecosystems (Lafont 2001). The major challenges for lotic ecosystems are the recurrence of variable and multiple anthropogenic perturbations, climate change, hydrological forcing, and connectivity with other domains such as watershed and airshed, which influence the universality and specificity of a biomonitoring tool (Pearson et al. 2016).

Studies generally use variables such as biological oxygen demand (BOD), chlorophyll **a** biomass (Gholizadeh et al. 2016), phycocyanin (Ahn et al. 2007), microinvertebrates (Turley et al. 2016), and diatom indices (Potapova et al. 2004;

Rimet and Bouchez 2012) as biomonitoring tools for assessment of water quality in different parts of world. The benthic diatoms have been established as a more stable predictor of trophic state and human perturbations as they respond directly to nutrient and carbon inputs (Pan et al. 1996). This merits attention because benthic diatoms grow attached to a certain substrate and thereby are less influenced by lotic forces of river ecosystems (Pandey et al. 2017). Wide distribution of diatoms supports the suitability and universality of diatom indices to be an indicator of eutrophy. However, such indices have been reported to be less suitable in geographical regions other than those where these were actually developed reducing the universal applicability of diatom-based tools across the globe. Other biomonitoring tools that have been generally used in the assessment of human impact on river waters are biological measures of eutrophication such as algal growth and pigments (Potapova et al. 2004). However, the relationships of algal community, chlorophyll **a**, biomass, and nutrient concentrations are often influenced by environmental factors such as climate, upstream basin size, river width, and flow (Pan et al. 1996) which question the applicability of these determinants in lotic ecosystems. The suitability of animal organisms as biomonitor also is hampered by factors such as mobility, feeding behavior, and position in trophic state (Rimet and Bouchez 2012).

The riverbed sediments, an important component of riverine ecosystems, are a biologically active and comparatively stable zone, which plays an important role in ecosystem functions including biogeochemical cycling, carbon metabolism and sedimentation, secondary production, and nutrient and heavy metal removal from the water column (Covitch et al. 2004). Because microbial community constitutes the key component of detritus system and any change in their metabolism affects the whole ecosystem processes including organic matter decomposition and nutrient cycling, their functional and structural attributes provide an actual picture of the health condition of an ecosystem. Studies have shown that enzyme activities can be used as an index of microbiological functional diversity and combining enzyme activities with other physical and chemical measurements can provide important information regarding ecosystem stability (Nannipieri et al. 2002). The sediment-based determinants such as the extracellular enzymes have been proved to be the most suitable parameter for quantification of shift in ecosystem responses toward alteration in organic matter (substrate) and heavy metals (inhibitors) (Sinsabaugh et al. 2008; Jaiswal and Pandey 2018, 2019a).

The extracellular enzymes β-D-glucosidase, alkaline phosphatase, and protease are used as indicator of C acquisition, P starvation, and N mineralization, respectively (Rejsek et al. 2008; Sinsabaugh et al. 2009; Duhamel et al. 2010). Similarly the fluorescein diacetate hydrolytic essay (FDAase) is used as an indicator of overall microbial activities (Schnürer and Rosswall 1982). The latter involves all the three major group of enzymes (lipases, esterases, and proteases) that mediate organic matter decomposition (Fontvieille et al. 1992). The substrate such as carbon and nutrients cause stimulatory effect, while toxicants such as heavy metal inhibit the activities (Sinsabaugh et al. 2008). Our multi-year and multi-scale studies confirm these relationships validating them for the riverbed sediment of the Ganga River

(Yadav and Pandey 2017b; Jaiswal and Pandey 2018, 2019a) indicating that extracellular enzymes can be used as an alternative alert system against increasing human pressure.

10.6.2 Elemental Stoichiometry

Elemental stoichiometry, the mass balance of key elements (C, N, P, and Si) in an ecosystem (Elser et al. 2009), has a central role in the theory of resource ratio competition between alga (Makulla and Sommer 1993), consumer-driven nutrient recycling (Elser et al. 2009), and food chain efficiency (Sterner et al. 1998). The N/P/Si Redfield ratio (16:1:16) is essential for balanced growth of phytoplankton specifically for diatoms (Turner et al. 2003). The changes in relative proportion of these nutrients define which nutrient to limit phytoplankton growth (Elser et al. 2009). A major factor to influence this ratio in the Ganga River is the increasing use of N and P fertilizers to meet the demand of food of overpopulated Ganges basin. About 10 million tons of chemical fertilizers are applied in the Ganges basin, which represent 45% of India's total annual fertilizer consumption. These N and P fertilizers reach to the river through atmospheric deposition, leaching, and runoff in the form of highly mobile NO_3^- and PO_4^{3-} ions. Unlike human-induced increases in the concentration of N and P at global scale, the Si concentration in most cases is either stable or declining. Hydrologic shifts in the watershed may reduce Si concentration by as much as 50% (Correll et al. 2000). A shift in this ratio causes cellular nutrient imbalances and induces a change in phytoplankton composition, biogeochemical cycles, carbon sequestration, biological diversity, and trophic cascades (Elser et al. 2009; Pandey and Yadav 2015). Therefore, the N/P/Si ratio is considered as a sensitive indicator of aquatic health and food web structure. The absolute concentration of nutrients and their stoichiometric ratios can be used together as a comprehensive predictor of eutrophy across broad landscapes as represented by large rivers.

Studies show that the disproportionate nutrient loading and management efforts have changed the canonical N/P stoichiometric ratios in many aquatic ecosystems of the world including India (Pandey and Yadav 2015; Pandey et al. 2016a). The anthropogenic causations that enhance N and P input do not generally lead to a proportionate increase in the concentration of Si in rivers. Indeed, some of the anthropogenic activities such as river damming decrease the amount of Si reaching to the coast. Further, low flow season induced increase in riverine primary productivity and nutrient uptake, and subsequently the sedimentation of diatoms leads to loss of adsorbed silicate from the water column (Conley 1997). Since Si is essential for the growth of diatoms, a deviation in the supply of Si may change the magnitude of diatom-driven C sequestration. Studies have shown that a decrease in N/P ratio causes a shift in the dominance in phytoplankton assemblage toward diazotrophic cyanobacteria (Elser et al. 2000; Pandey et al. 2017). A shift in N/P ratio toward $<$16:1 changes the phytoplankton community and promotes P-favored taxa.

Similarly, the Si/N ratio below 1 leads to reducing the proportion of diatoms/ siliceous algae in the phytoplankton assemblage and consequently causes a shift in the higher trophic levels (Gilpin et al. 2004). Further, the Si-limiting condition leads to enhance non-diatom algal growth (Pandey et al. 2017). The excessively higher concentration of N and P compared to Si is causing a dramatic shift in the phytoplankton composition, changing the pattern of community dominance toward green or blue-green algae (Teubner and Dokulil 2002) including those in the Ganga River as indicated also by high concentration of phycocyanin at nutrient-rich sites (Pandey et al. 2016b). Further, as the system moves toward eutrophy, feedbacks at sediment-water interface may increase P supply and consequently promote the growth of P-favored harmful algal species (Pandey et al. 2017). Thus, the changing pattern of nutrient limitation and the resulting competition for resources in phytoplankton would decrease the proportion of less adapted algal species, increasing the share of non-siliceous diatoms in the community and consequently decreasing the C sequestration and compromising the ecological assimilation capacity of the river.

The atmospheric deposition (AD) of N and P has increased tremendously in various parts of the world (Galloway et al. 2008) and is continuing to rise in the Ganges basin (Siddiqui et al. 2019b). Since N and P are the major component of AD, a potential shift in AD-N/P ratio will alter N/P ratios of surface waters which would shift phytoplankton composition. Many of the temperate European and North American lakes have been reported to be suffering with this problem (Bergstrom and Jansson 2006). As the Ganga River receives large but disproportionate input of nutrients through point and nonpoint sources including atmospheric deposition, at many locations, the river experiences shifts in N/P/Si stoichiometry and the proportion of specific nutrient availability (Pandey et al. 2016b). A watershed-scale study from Devprayag to Ganga Sagar (Pandey et al. 2016a) has reported that at polluted sites, the ratio of N/P remained below 16:1 indicating that P is no more a limiting nutrient in the river and concordantly the abundance of dominant diatom genera has also changed. Diatom species such as *Diatoma vulgaris*, *Fragilaria intermedia*, and *Gomphonema parvulum* were found abundantly at sites characterized by high P, whereas species such as *Cocconeis placentula*, *Cyclotella meneghiniana*, and *Cymbella affinis* were found at sites with low phosphorus concentration (Pandey et al. 2017). The results further revealed a relatively lower proportion of Si ($Si/P < 16:1$) in the Ganga River than the required ratio to meet cellular Si for diatoms. A higher N/Si ratio shows that if this condition is continued, it will lead to Si limitation in the long-term future (Pandey et al. 2016a).

A study of Mississippi River has shown that excessive N and P input as compared to Si is causing severe eutrophication in the river (Turner et al. 2003). Shifts in stoichiometric ratios affect the quantity as well as quality of primary production. With increasing N input, an increase in the cellular N/P ratio of terrestrial and aquatic plants has been reported (Elser et al. 2009). This change in cellular N/P ratio affects various metabolic processes ultimately leading to a cascade of effects ranging from shift in growth of individual organism to alteration in species composition and community functioning (Pandey et al. 2017). A classic example of this type of ecosystem response is the shift in population of *Daphnia* (a freshwater zooplankton).

Daphnia enjoys a P-rich lifestyle and encounters potential P deficiency when cellular P declines (Elser et al. 2000). Thus, the population of *Daphnia*, which can be used as an indicator of P eutrophy, will decline sharply under N-rich condition. These studies have led to conclude that the shifts in nutrient stoichiometry can be used as an alternative response indicator of shifting ecosystem structure and functioning driven by increasing natural and anthropogenic perturbations.

10.6.3 Diatom-TEP Linkages

Diatoms, a highly diverse group of photosynthetic protists and widely used indicators of environmental shifts, are producers of transparent exopolymeric particles (TEP). The diversity and abundance of these primary producers are affected by absolute nutrient concentrations, stoichiometry, ionic strength, pH, light penetration, and temperature (Potapova and Charles 2003). The abundance of diatoms is often negatively influenced by high concentrations of nutrients because only some species can grow in nutrient-rich condition. The species adapted to high nutrient concentrations remain generally accommodative to heterogeneous habitats by dominance transference (Pandey et al. 2017). As already mentioned, the N/P/Si ratio is the most important factor that drives the diatoms diversity and abundance. The decrease in N/P ratio decreases the species diversity although P-loving diatoms proliferate rapidly (Pandey et al. 2017). Increased N/Si ratio leads to Si limitation with potential effects on the quantity (cell number and biomass) as well as quality (composition of biomass) of diatom assemblages (Davidson and Gurney 1999). Alterations in the abundance of specific diatom species, assemblage, and cellular metabolic states affect the microbial trophic transfer and population of meso-zooplankton (Miralto et al. 1999) with overall effects on carbon export and biogeochemical cycling.

Diatoms produce acidic polysaccharides in the form of transparent exopolymeric particles (TEP). The size of TEP ranges from >0.4 μm to <200 μm and is stained with the Alcian blue. Diatoms with C_4 photosynthetic pathway are prolific in carbon capture and storage under excess N supply and may accumulate excessive carbon (Riebesell et al. 2007). To maintain a normal physiological state (C/N ratio, for instance), the excessive carbon is excreted in the form of acidic polysaccharides which are ultimately converted into TEP. Because of their ability to form coagulates and aggregates, the TEP play an important role in the regulation of DOC-POC pump and carbon sequestration. Additionally, high-density particles such as heavy metals get aggregated enhancing the density of TEP and consequent sedimentation of nutrients, metals, and pathogens (Passow et al. 2001). The results of a recent study (Pandey et al. 2017) reveal that to cope up with changing nutrient concentrations and their stoichiometric ratio, the diatoms increase the production of TEP which enhances the sedimentation and removal of turbidity and other harmful components. This is an important mechanism responsible for high self-purification capacity of the Ganga River (Pandey et al. 2017). The study further shows that to compensate the reduction in TEP under excessive human pressure, the diatom tends to accommodate through dominance transference. The low-profile guilds representing species such as *Cocconeis placentula*, *Cymbella affinis*, *Cyclotella meneghiniana*, and *Synedra ulna* were found abundantly at P-poor sites, and high-profile guilds representing species such as *Diatoma vulgaris*, *Gomphonema parvulum*, and *Fragilaria intermedia* were present at P-rich sites (Pandey et al. 2017).

The excessive nutrient loading alters the diatom dominance pattern (Fig. 10.1 and Table 10.1), and a marked skewness in diatom dominance-diversity linkages has been observed in the Ganga River (Pandey et al. 2017). The synchrony between skewness and altered water quality shows the ability of diatoms to cope with nutrient stressors and disturbances. Among the TEP producers, species such as *Cocconeis placentula*, *Cyclotella meneghiniana*, and *Cymbella affinis* have been reported to flourish at nutrient-poor sites, while *Aulacoseira granulata*, *Diatoma vulgaris*, *Melosira varians*, and *Fragilaria intermedia* show extensive growth in nutrient-rich condition (Pandey et al. 2017; Fig. 10.2). These results indicate that the diatom ecological guilds can be used as holistic and alternative indicators of short-term changes or disturbances in the aquatic environment. Additionally, the dependence of TEP on Chl **a** biomass and N/P stoichiometry makes it an indicator of trophic status and nutrient pollution. Because the TEP production is maintained partly by changes in diatom dominance-diversity linkages despite variable ecological conditions and human perturbations, the TEP coupled diatom dominance transference can be used as a key node to cue nutrient pollution and ecological assimilation capacity of anthropogenically impacted large rivers.

10.6.4 Ecological Response Index

Quantitative estimation of ecosystem responses against increasing human perturbations has become a growing research area in aquatic pollution control. Despite urgent need, only few studies so far are available, providing a universal index to quantify holistic changes in the water quality (Satyamurthy 2017). For a universal applicability, an index should have intricate links with ecosystem structure and functioning (Peterson and Stevenson 1992). Sediment-based biomonitoring tools are now being suggested to be more accurate in designing empirical relationships to uncover the ecosystem responses and magnitude of degradation (Turley et al. 2016; Pandey and Yadav 2017).

For lotic ecosystems, where hydrologic forcing drives unpredictability, selecting a suitable response variable is difficult. There is no study so far available, except Jaiswal and Pandey (2019a), linking simultaneously the carbon-heavy metal-ecosystem responses to quantitatively predict the human-driven alterations in large rivers (Table 10.2). The indices developed so far for the assessment of pollution load, toxicity, and trophic status, such as enrichment factor (Buat-Menard and Chesselet 1979), trophic state index (Carlson 1977), potential ecological risk index (Håkanson 1980), pollution load index (Tomilson et al. 1980), pollution index (Nemerow 1991), and geoaccumulation index (Müller 1969), consider the

Table 10.2 Indicators/indices of eutrophy and metal pollution used in water quality assessment

Index/indicator	Water body	References
FDAase	Ganga River	Jaiswal and Pandey (2019a)
Dissolved oxygen deficit	Ganga River	Jaiswal and Pandey (2019b)
CO_2 emission coupled extracellular enzyme activities	Ganga River	Jaiswal and Pandey (2019e)
N/P/Si ratio	Oceans	Redfield (1958)
Diatom indices	Rivers	Potapova et al. (2004) and Rimet and Bouchez (2012)
Transparent exopolymeric particles (TEP)	Ganga River	Pandey et al. (2017)
Daphnia	Freshwater systems	Elser et al. (2000)
Phormidium uncinatum	Ganga River	Pandey (2013)
Microinvertebrates	Rivers and streams	Turley et al. (2016)
Chlorophyll **a** biomass	Ganga River, lake	Tare et al. (2003) and Pandey and Pandey (2013)
Phycocyanin	Rivers	Ahn et al. (2007)
Light penetration	Ganga River	Pandey (2013)
Alkaline phosphatase	Ganga River	Pandey and Yadav (2017)
Water quality index	Inland water bodies	Brown et al. (1972)
Diatom dominance transference	Ganga River	Pandey et al. (2017)
Biological oxygen demand	Ganga River	Dwivedi et al. (2018)
Diatom pollution tolerance index	Freshwater systems	Muscio (2002)
Trophic state index	Lake	Carlson (1977)
Enrichment factor	Tropical North Atlantic Ocean	Buat-Menard and Chesselet (1979)
Potential ecological risk index	Lakes and other limnetic systems	Håkanson (1980)
Pollution load index	Estuaries	Tomilson et al. (1980)
Pollution index	Inland water bodies	Nemerow (1991)
Geoaccumulation index	Rhine River	Müller (1969)
Modified pollution index	Estuarine and marine environment	Brady et al. (2015)
Contamination factor	Lakes and other limnetic systems	Håkanson (1980)
Modified ecological risk index	Brisbane River	Duodu et al. (2016)
Ecological response index[a]	Ganga River	Jaiswal and Pandey (2019a)

[a]First index that simultaneously predicts C eutrophy and metal pollution in large rivers

concentration of individual variable/metal pollutant at a time. These indices generally address the "status" and not the functionality of how the ecosystem is exactly responding to human perturbations (Table 10.2). Further, the versatility of these indices is influenced by hydrological factors, sediment load, and sensitivity of the chosen determinants. The natural ecosystem receives a number of toxicants so the effect should be governed by their cumulative concentration (Håkanson 1980). Also, the organic carbon in a water body may reduce the toxic effect of metals making it difficult to establish a linear dose-response relationship under in situ condition (Håkanson 1980). In human-impacted rivers, eutrophication and metal pollution generally occur simultaneously. Thus, for an accurate measurement of river health, it is important to understand how the ecosystem responds toward human perturbations.

As a solution of this problem, Jaiswal and Pandey (2019a) developed an "ecological response index (ERI)" which is able to quantitatively predict ecosystem response to C eutrophication and metal pollution in large rivers. The index was developed using carbon and its response determinant (fluorescein diacetate hydrolytic assay, FDAase) and a sum of six heavy metal concentrations in an empirical relationship as below (Jaiswal and Pandey 2019a):

$$\text{Ecological Response Index} = \frac{\text{FDAase} \times qM}{\sum_{i=1}^{n} (M_i)}$$

where FDAase = fluorescein diacetate hydrolytic activity; qM = microbial quotient; and (M_i) = concentration of i^{th} metal.

The ERI, as a quantitative predictor of eutrophy and metal pollution, was validated using Carlson's trophic state index (TSI) (Carlson 1977), Håkanson's risk index (RI) (Håkanson 1980), and Duodu's modified ecological risk index (MRI) (Duodu et al. 2016). Strong relationships among these indices indicated that the ERI is highly appropriate for quantitative prediction of metal pollution and trophic state of lotic ecosystems. Based on ERI, Jaiswal and Pandey (2019a) concluded that the ERI between 0 and 24 represents extreme metal pollution (toxic condition), between 25 and 38 indicates combination of eutrophy and metal pollution, 39 to 77 represents hypereutrophic condition and low metal pollution, 78 to 155 indicates eutrophic condition, and 156 to 320 represents the oligotrophic state of the river ecosystem. The ERI can be used as an alternative ecological tool for appropriately addressing concordant changes in ecological functioning with stronger mechanistic linkages between the causal factor and associated responses. Besides this, it is stable, widely applicable, and cost-effective in addressing the impact of multiple human stressors on functional shifts in riverine ecosystems.

10.6.5 Ecosystem Feedbacks

A positive feedback in an ecosystem begins when a driving force is likely to cause a transitional shift (Jaiswal and Pandey 2019f). Positive feedbacks are self-enhancing and are among the most prominent signature of transitional shift where the changes in ecosystem processes are expected to lead to development of alternative stable states (Scheffer et al. 2001). It occurs in a feedback loop leading to enhance the magnitude of even small perturbations. Positive feedbacks are widespread in nature ranging from cellular- to system-level processes and may lead to ecosystem-level consequences if it persists for longer duration (Dai et al. 2013). These nonlinear responses of ecosystems to environmental changes cause destabilization of nutrient cycling and other ecosystem processes leading to delay in the recovery from disturbances. Although various studies have emphasized the importance and relevance of understanding these processes in ecosystem restoration (Scheffer et al. 2001), identification and quantification of positive feedbacks for riverine ecosystems are very difficult.

High input of oxygen-demanding substances leads to development of hypoxic/anoxic zones which trigger positive feedbacks in aquatic environments. The dissolved oxygen (DO) plays the most important regulatory role in aquatic ecosystem structure and functioning. The oxygen deficiency causes dramatic changes in benthic communities and thus leads to noticeable changes on ecosystem functioning, species richness, and abundance, ultimately leading to development of alternative stable states. Some of the important feedbacks associated with benthic hypoxia/anoxia include the denitrification, sediment-P release, and sediment-metal releases. These functional shifts coupled with increased dissolved oxygen deficit (DOD) lead the system toward alternate stable states and development of fragmented patches with varying species composition, nutrient and metal concentrations, and shift in trophic state and food webs (Scheffer et al. 2001; Pandey et al. 2019).

Studies conducted by Jaiswal and Pandey (2019d, 2019f) reveal a high rate of denitrification, sediment-P release, and sediment-metal release at sites downstream of point sources, tributary confluences, and downstream cities along the Ganga River. These locations did show DO_{sw} below 1.5 mg L^{-1} indicating that the benthic hypoxia has generated positive feedbacks leading to the release of sediment-bound nutrients and metals to the overlying water. The release of nutrients and metals from the sediment accelerates eutrophication enhancing the DOD further. Also, the ecological communities and ecosystems respond to human perturbations in different ways. For instance, some processes are enhanced but respond smoothly and gradually to changes in environmental conditions, whereas some variables show instantaneous response and others may remain inert until a threshold condition is reached at which the ecosystem responds abruptly (Scheffer et al. 2009). Studies show that the extracellular enzymes can be used as a suitable predictor of ecosystem responses toward carbon, nutrient, and metal enrichment (Sinsabaugh et al. 2009; Jaiswal and Pandey 2019a). Because, the carbon and nutrients stimulate microbial activities, a concordant increase in the enzyme activity can be used as an indicator of eutrophy. Opposite to this, the heavy metal pollution causes toxic effects leading to a sudden decrease in the enzyme activity even in the presence of high concentration of carbon and nutrients (Jaiswal and Pandey 2018, 2019a). Because the carbon chelates metals leading to a reduction in toxicity, in ecosystems with prevalence of toxicants and stimulants, the toxic impact is reduced to a certain extent. The shifts in these responses can be used as alternative alert systems for understanding the health and level of deterioration of human-impacted riverine ecosystems.

10.7 Conclusions and Suggestions

Quantitative estimation of ecosystem-level responses against increasing human perturbations has become a growing research area in aquatic pollution control. However, despite urgent need, only few studies so far are available providing a universal index able to quantify holistic changes in the water quality. Studies conducted on the Ganga River generally consider parameters bifurcating eutrophy and metal pollution and, in most cases, without considering ecosystem-level consequences. A critical analysis of available studies/data and emerging trends leads to the following conclusions/suggestions to cue management strategies on the Ganga River:

1. Future research needs to focus on the changing state of ecosystem functions coupling human perturbations with ecosystem feedbacks such as denitrification, sediment-P and sediment-metal release, and ecological assimilation capacity of the Ganga River.
2. Because in human-impacted rivers eutrophication and metal pollution generally occur simultaneously, multi-temporal and multi-scale data base is needed for understanding ecosystem responses coupling eutrophy and metal pollution in the river.
3. The wastewater treatment technologies, available so far, generally address removal of biological oxygen demand (BOD) only. Because the increasing load of other oxygen-demanding substances (ODS) is contributing substantially to dissolved oxygen deficit (DOD) causing a greater pressure on overall dissolved oxygen (DO) levels, these need proper control and management. Also, advance metal removal technologies are needed because metal pollution in the river is continuing to rise.
4. Because sediment-based biomonitors are relatively stable and because microbial extracellular enzymes (EE) respond concordantly to carbon and metal enrichment, the EE activities such as β-D-glucosidase and FDAase can be a good indicator of river responses toward metal pollution and C eutrophy.
5. Shifts in nutrient stoichiometry can be used as an alternative response indicator of shifting ecosystem structure and functioning, driven by increasing anthropogenic perturbations. Diatom ecological guilds, rather than individual species, can be used as a holistic indicator of short-term disturbances in the aquatic environment. Initiatives can be taken to enhance micro-niches to increase the diversity of diatoms, the most important water purifiers in the Ganga River. Furthermore, because the production of transparent exopolymeric particles (TEP) is maintained partly by changes in diatom dominance-diversity linkages, the TEP coupled diatom dominance transference can be used as a key node to cue nutrient pollution and ecological assimilation capacity of the river.

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