

Nitrogen transport by rivers of south Asia

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The South Asian rivers show a discharge weighted average $\text{NO}_3\text{-N}$ of 2 mg/l and average sediment-bound N, that is mostly organic, of 0.2%. The reported global average for the uncontaminated river system is of the order of about 0.028 mg/l ($\text{NO}_3\text{-N}$). Hence, our freshwater aquatic systems can no longer be considered natural, at least with respect to nitrogen transport. The average is still below the WHO limit of 100 1 mg/ $\text{NO}_3\text{-N}$ for drinking water, but there are extreme variations in different rivers (Ganges, Krishna, etc.) and at different locations (Cauvery at Tiruchirapalli 29 mg/l, Ganges at Patna, 140 mg/l, etc.). Sediment-bound N is generally less than 1%, but values as high as about 3% have been reported for some rivers indicating rapid transfer of soil organic matter to rivers as particulate organic nitrogen. While the nitrogen story for various groundwater regions is well understood as representing fertilizer run-off, the riverine N is yet to be studied in detail; the link between river processes and global climate change would warrant urgent study of the river system of South Asia, that carries an annual water flux of about 2100 km³ (about 6% of global run-off) and an annual sediment flux of over one billion tons (about 10% of global flux). Rough calculations of available data indicate that the total N flux from rivers to oceans in South Asia is likely to be several factors higher than that indicated by some representative contaminated rivers of the world.

Keywords: Flux, nitrogen transport, rivers, soil particulate organic matter.

NITROGEN in the riverine environment is in the dissolved and particulate forms. The dissolved form has many components – nitrate, nitrite and ammonium, all considered as dissolved inorganic N (DIN), whereas dissolved organic nitrogen (DON) may have several forms and distribution. DIN is primarily derived from soil leaching by surface water during weathering, while DON is derived from soil/sediment–biota interaction¹. Particulate nitrogen is associated with sediments and is derived in a similar manner, as well as from source rock, particularly if the source rock has some nitrogen-bearing mineral assemblage such as NaNO_3 and KNO_3 . The crustal abundance of N is only about 20 mg/g. Mechanical erosion of soil organic matter (SOM) contributes particulate organic nitrogen (PON) to the river system, and it is further enhanced

by local aquatic production within the river system. Nutrient cycling in our environment is of great concern due to the fragile nature of our aquatic system. Global flux² of dissolved nitrogen from all rivers is estimated to be around 4.45×10^{12} g/yr nitrate N (DIN) and 10×10^{12} g/yr DON. Fluxes are generally affected by river run-off, indicating that large rivers may show low fluxes due to dilution of nitrogen, while small streams may show high fluxes due to lack of dilution. C/N ratio in fresh terrestrial plants varies from a low of 69 to a high of 105, whereas in soil organics it is around 18 and in river sediments around 8.8. An additional flux of dissolved nitrogen, primarily derived from fertilizer run-off is estimated to be around 7×10^{12} g/yr. The pre-industrial stream load of N is estimated² to be 110 Tg/yr (110×10^{12} g), which is nearly 50% of the post-industrial N load of about 227 Tg/yr. In some regions of the world, particularly Asia, the increase in N-loading has gone up by a factor of six during this period. In unpolluted streams, average levels of dissolved nitrogen, primarily in the form of nitrate-N, vary from a low of 0.028 mg/l to a high of 1.95 mg/l, whereas for polluted rivers³ dissolved nitrogen varies from a low of 0.54 mg/l nitrate-N to a high of 5.56 mg/l, and nitrogen as ammonium ions³ varies from a low 0.06 mg/l to a high of 29 mg/l. Unlike the earlier simple N-fixation mechanisms in aquatic systems, now the fate of N in rivers is determined by a combination of several factors such as quantity and type of fertilizer input, urban sewage loading, livestock and atmospheric deposition in addition to N-transformation within an ecosystem. River fluxes of about 42 Tg/N/yr are primarily retained in the land mass⁴. N-loading from the Asian land mass has gone up by a factor of three, from a low of about 7.39 Tg/N/yr in pre-industrial times to a high of about 18.71 Tg/N/yr at present. Asia thus shows double the values of N-loading compared to Africa and up to four times that of other continents. Large rivers tend to have small residence times, whereas small rivers have large residence times for N-loading⁵. According to the river database (GEM/UNESCO), only about 40% of rivers has reliable dissolved N values, whereas for organic nitrogen it is even lower, at about 33%. Riverine dissolved N compares well with rainwater that has an average value of about 0.35 mg/l, including DON⁴.

Pollution problems are plenty with respect to practically all major water bodies in India. Nature and distribution of different nutrients such as C, N, P and S in the river system have been studied by several groups in India.

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Table 1. Examples of highest dissolved nitrate/sediment-bound N in rivers of South Asia

| River | Area* (km ²) | Run off* (km ³ yr ⁻¹) | Yield* (mm yr ⁻¹) | NO ₃ (mg/l) | TC% | N% | C/N |
|--|--------------------------|--|-------------------------------|------------------------|------|------|-------|
| Cauvery | 87,900 | 21.4 | 243 | 29.26 | 1.90 | 0.16 | 12.23 |
| Brahmani | 51,822 | 36.2 | 699 | 7.59 | 0.09 | 0.03 | 3.44 |
| Tamaraparani | 4761 | 0.8 | 168 | 0.30 | 0.51 | 0.02 | 25.50 |
| Ganges | 861,404 | 525 | 609 | 40.61 | 0.53 | 0.26 | 2.04 |
| Brahmaputra | 194,413 | 537.2 | 2763 | 1.94 | 0.87 | 0.16 | 5.44 |
| Indus (Pakistan) | 203,671 | | 2350 | 10 | 0.5 | 0.02 | 25.0 |
| Gomti | 30,437 | 7.4 | 243 | 7.03 | 1.03 | 0.53 | 1.94 |
| Mahi | 34,842 | 11.8 | 339 | 0.02 | 0.23 | 0.03 | 8.21 |
| Krishna | 258,948 | 67.8 | 262 | 1.70 | 0.08 | 3.80 | 0.02 |
| Narmada | 98,796 | 41.3 | 418 | 1.43 | 1.36 | 0.51 | 2.69 |
| Tapti | 65,145 | 18.4 | 282 | 2.02 | 2.65 | 0.50 | 5.35 |
| Godavari | 12,812 | 119 | 380 | 8.32 | 1.33 | 0.32 | 4.16 |
| Small west-flowing Kerala rivers (average of 15 rivers) ¹² | 6572 | 92.2 | 11,877.8 | 1.27 | 0.63 | 0.32 | 1.97 |
| West-flowing rivers north of Kerala | 193,562 | 253.6 | 19,602.8 | 74.71 | 0.89 | 0.44 | 2.95 |
| Padma, Meghna and tributaries, Bangladesh | 1,640,000 | 1156.5 | 3380 | 13.26 | 1.08 | 0.11 | 9.80 |
| Brahmaputra and tributaries (India) | 194,413 | 537.2 | 2763 | 1.94 | 0.87 | 0.16 | 5.44 |
| South Asian average | 2,655,054** | 2108.3 | 794 | 2.10 | 0.56 | 0.21 | 2.67 |

*Based on data from Madhavan and Subramanian²⁰. N data compiled from various references and also from author's laboratory.

**Total run-off for South Asia. N and C values are discharge weighted while calculating sub-continental average.

Among these four major nutrients, N is understood little due to several transformations in the aquatic ecosystem. Since the surface environment is generally oxidizing and there are no major mineral sources of nitrogen, the levels of N reported in uncontaminated surface river waters are generally low. For rivers in India the nitrogen database is very low in terms of data availability, dependability and accessibility for riverine systems.

Excess agricultural run-off is generally considered a significant source of dissolved N and decomposition of SOM during transport by rivers leads to variable presence of sediment-bound N in the river system. Data available in the public domain from the websites of the Central Pollution Control Board as well as the Central Water Commission, indicate that most of our rivers carry dissolved N in the form of NO₃-N, primarily derived from fertilizer application in agriculture. Data presented in Table 1 show only some of the high values of dissolved N reported for several rivers of south Asia; in the absence of a specific point source of N for so many rivers, the only common source across the sub-continent is fertilizer run-off to the riverine system.

The WHO drinking water quality standard shows a desirable value of up to 10 mg/l for nitrate-N, whereas most of the rivers in the world in populated regions according to the GEMS database have values about seven times this number. Thus in rivers the levels of dissolved nitrogen are no longer just due to natural processes such as weathering and soil organics, but also due to substantial contribution by human activities. Chemistry of the soil depends on the rock type besides climatic and hydrological factors. Since N is generally present in riverine oxygenic environment as nitrate-N at low concentrations, it was seldom analysed in Indian rivers in the past. There are extensive

databases for nitrates in groundwater where the problem may be serious at specific locations^{6,7}. For surface water, attention is being paid only recently to N-transport in rivers due to increasing public knowledge about environmental contaminants. For example, in a recent report dissolved N levels in the upper reaches of the Ganges due to agriculture input into the riverine system were observed to be significant⁸, whereas in the lower reaches of the Ganges–Brahmaputra–Meghna system the sediment-bound N going into the delta was reported to be average^{9,10}; likewise, the sediment bound organic C and N in the Godavari river system were studied and reported to represent labile organics¹¹. The C/N variation in the sediments in the flow direction of the Ganges was reported to be different from other large world rivers¹².

Data on dissolved nitrates are hence few and for specific locations in some rivers only. Table 1 shows some of the extreme values reported on all forms of N in the major river systems in the Indian sub-continent. As reported earlier^{1,2}, most of the dissolved N is in the form of DON; for rivers in the sub-continent, DON values are generally not reported. This may also be a reason that the average values of dissolved N in our rivers appear to be lower than other river systems in the world, from populated regions¹. Globally, emphasis has generally been to understand the SOM that is the source of DON in rivers. For the Ganges, it can be seen from Figure 1 that the dissolved nitrate-N is much higher than the WHO standard for drinking water. This is not surprising since the long stretch of the river supports more than 300 million people, with a large number of urban areas that contribute sewage in different degrees of treatment to the river, in addition to agricultural run-off. Thus, the Ganges definitely shows the human impact on the riverine nitrate transport. Sev-

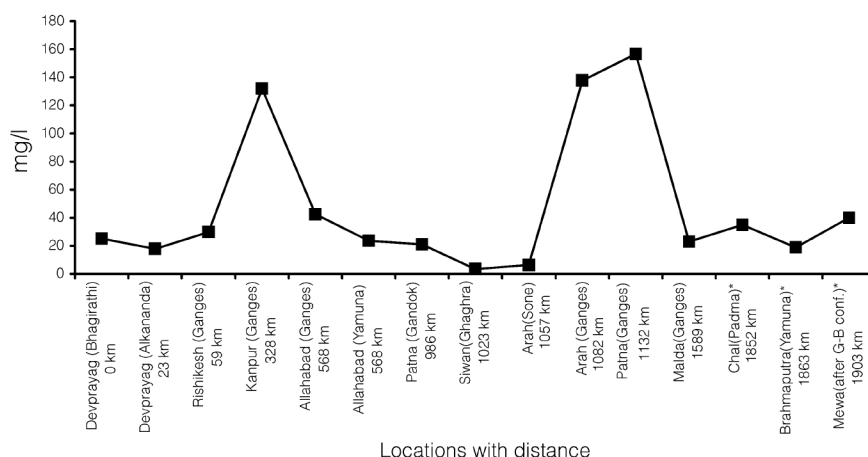


Figure 1. Dissolved nitrate in the Ganges basin.

eral such observations have been made for many rivers such as Cauvery, Tamaraparani, Mahanadi, etc. Brahmaputra has relatively low levels of dissolved N, and after the two rivers meet in Bangladesh, dissolved N for the Ganges drops due to dilution effect. Thus, addition due to human impact and dilution by large river mixing are two important mechanisms in the pathways of riverine dissolved N. The two influx points in the plot represent excess contribution from a point source of pollution, namely urban waste (Kanpur–Allahabad) and agricultural waste (Patna–Malda), resulting in a higher average value for the river. The west-flowing rivers are generally small and also flow through a limited stretch before they empty into the Arabian Sea; these rivers, about 40 in number (20 above the Palghat gap and 20 below the gap that is a natural geological divide), show high average nitrate-N based on several sources of data from different workers and this may also be partly due to compatibility of the database rather exclusively due to pollution problems. Very little spatial variation in the dissolved nitrate as well as NH_4^+ between Devprayag (close to the glaciers) and Rishikesh (the beginning of the habitation stretch of the river) was reported for the Ganges catchment region⁸. However, in the same region, he reported on the temporal variation of the N transport with high values: monsoon showing high values compared to other times at the same locations, the reason being the high leachability of soil-bound N during intense rainfall in the period June–September. This seems to overshadow the dilution factor of the river due to excess flow.

Figure 2a and b shows the variation in dissolved N as well as sediment-bound N in several rivers, flowing into the Bay of Bengal and Arabian Sea respectively, in the South Asian region. Among the east-flowing rivers, the Ganges, as explained earlier, shows the highest levels of both dissolved and sediment-bound N, whereas all other rivers show relatively low levels, below WHO health limits

of nitrate-N. The sediment-bound N in the southern rivers is as high as that of the Ganges due to intensive agriculture in that part resulting in soil run-off during the three month monsoon period. In fact, in the southern rivers¹³, such as the Cauvery, utilization of river water is almost 100%. In some cases groundwater withdrawn from great depths, rich in nitrate, is used as supplement to irrigation water. This in turn gets into the surface water. The role of agricultural run-off on the riverine N for the small Tamaraparani river in the deep south was extensively studied¹⁴.

For the west-flowing rivers, small rivers in the region between Mangalore and Goa show large levels of dissolved N, whereas other small rivers Mahi in Gujarat and Bharathpuzha in Kerala show low average values. The Goa–Mangalore region is in fact fragile and ecologically sensitive with low population density, but mining and associated activities may be responsible for these high values. Many rivers along the Western Ghats from Thiruvananthapuram to Rajkot show high levels of sediment-bound N, indicating soil leaching of organic N in the agricultural and wetland regions. Table 2 suggest that the story of N in groundwater is more complex, since levels are high compared to the surface environment. This is an explosive issue similar to that of arsenic and fluoride in groundwater in South Asia. On the other hand, the fate of N in river sediments is closely linked to that of the organic carbon, as observed by several workers^{7,15}. Rivers in India are no exception either.

Figure 3 shows the relationship between sediment organic N and organic C for the Ganges–Brahmaputra–Meghna (GBM) system¹⁰. This indicates that sediment N is basically organic in origin and derived from the same source, namely either biological degradation of plant debris in weathering region or derived from SOM. Organic matter during high discharge period has low concentration of labile constituents such as amino acid and sugar, and hence is more biodegradable than during the low discharge pe-

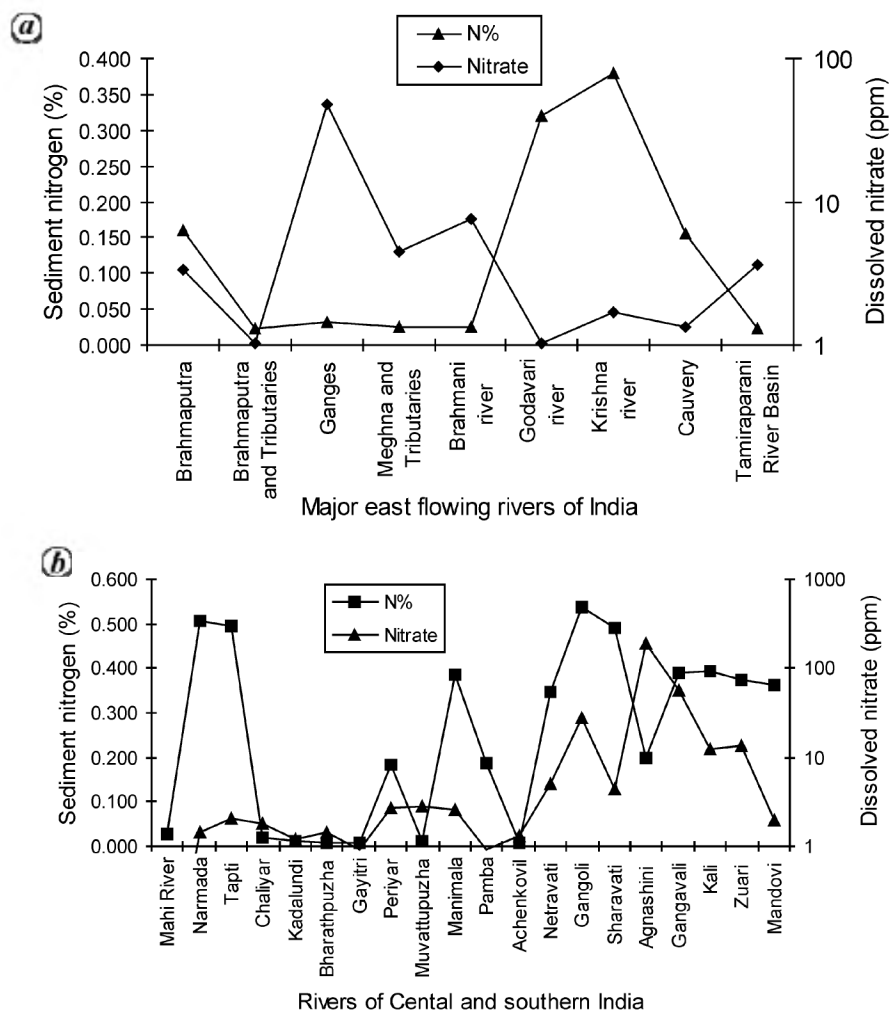


Figure 2. Sediment N% and dissolved nitrate in rivers flowing to (a) the Bay of Bengal and (b) Arabian Sea. (X-axes not to scale.)

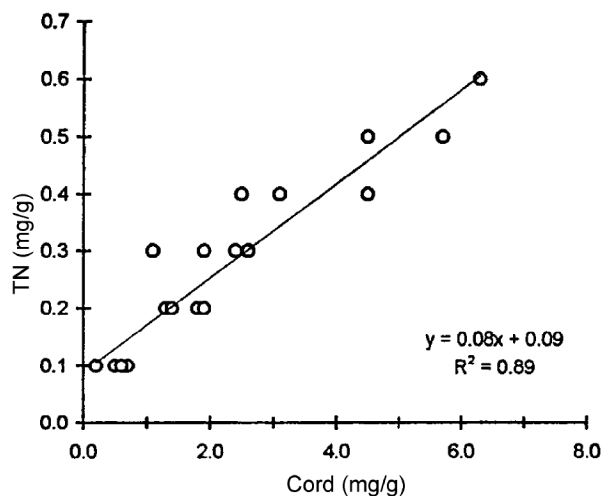


Figure 3. C–N relationship in GBM system, Bengal basin¹⁰.

riod¹¹. C/N ratios for river sediments in the GBM system as well as all east- and west-flowing river systems, with few exceptions, are low in the range 2–11, similar to the average soil values³. Molar ratios of C/N for dissolved species could not be estimated for all rivers, as mentioned in the earlier section, due to lack of reliable data for DON and dissolved organic carbon (DOC) in the sub-continent. A few locations in some rivers such as the Krishna between Kurnool and Vijayawada are under the intense agricultural belt; Tamaraparani is wholly covered with leather industry effluents; Gomti near Lucknow has mixed-mode industrial input. These three systems show high or erratic values of C/N. Otherwise, C/N value is around the average for all rivers in the sub-continent and indicates soil organic control on riverine N transport. Sediment-bound organic matter after burial below the water–sediment interface undergoes rapid degradation and this results in low sediment N in buried sediments. This can be well

Table 2. Nitrate in sub-surface waters in selected regions in India

| Source | Region/state | Groundwater (agricultural belt) (NO ₃ -N mg/l) | Source | Region/district | In groundwater (NO ₃ -N mg/l) |
|--|-----------------------------|---|--|---|--|
| Bijay Singh <i>et al.</i> ⁶ | Aligarh, UP | 61 | Bijay Singh <i>et al.</i> ⁶ | Mahendragarh (H) | 296 |
| | Agra, UP | 54 | | Ambala (H) | 223 |
| | Meerath, UP | 157 | | Bathinda (P) | 95 |
| Subramanian ¹⁷ | Gujarat | 460 | Chadha and Sarin* | Faridkot (P) | 11–500 |
| | Rajasthan | 262 | | Patiala (P) | 5–456 |
| | West Bengal | 48 | | Sangrur (P) | 10–900 |
| | | | | Bhiwani (H) | 5–480 |
| Kanwar Singh <i>et al.</i> ²¹ | Kanpur (UP) – shallow wells | 8–96 | Shirahati <i>et al.</i> ²² | Khurukshetra (H) | 5–360 |
| | | | | Sonepat (H) | 10–1310 |
| | | | | Ludhiana(P) | 12–30 |
| | | | | Kanwar Singh <i>et al.</i> ²¹ (deep wells) | Industrial (UP) |
| Subramanian ¹⁷ | India average | 65 | Jack and Sharma ²³ | Coimbatore (TN) | 9–219 |

*Unpublished data. H, Haryana; P, Punjab; UP, Uttar Pradesh; TN, Tamil Nadu, pers. commun.

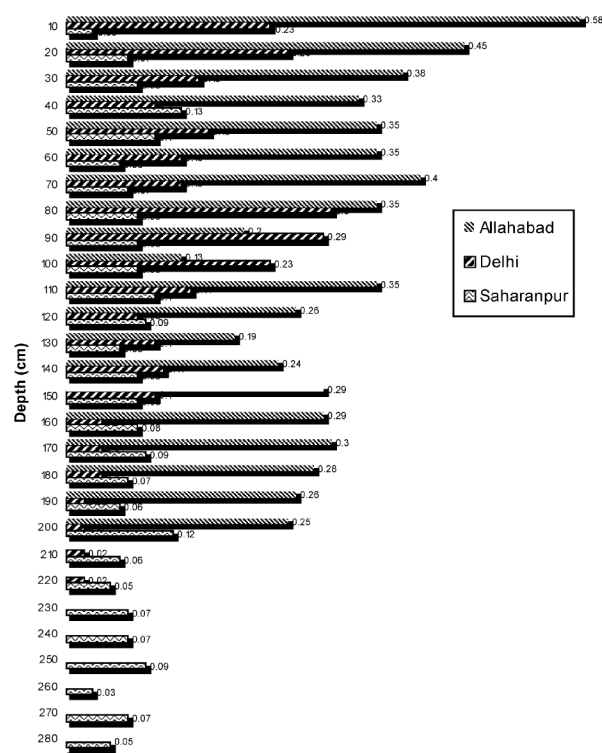


Figure 4. Nitrogen (%) in sediment cores of Yamuna flood plains.

illustrated for the Yamuna river sediments with a thick alluvial and rapid rate of sedimentation¹⁶. Figure 4 shows depth variation in the sediment-bound N at three locations in the river – upper reaches (Saharanpur where the river comes to the plains), Delhi (intense urban set-up)

and Allahabad (river meets the Ganges). Due to dilution effects on account of a large number of rivers joining with enormous sediment load¹⁷, the top sediment layers at Allahabad have higher sediment-bound N values compared to other locations such as Delhi. The depth represents a time interval of about 50 years and at all locations, the trend is negative-low N towards the deep layers and increasing N towards the top surface layer. Similar trends in the N-containing sediment amino acids in the Godavari river system have also been reported¹¹. Under tropical climatic conditions, preservation of N-containing organic matter in sediments is only for a short duration. Hence except in cases of point source-polluted rivers, the story of N in rivers is rather simple and directly linked to the fate of the organic carbon. Rivers in the Indian sub-continent annually carry water flow of about 2100 km³ and sediment load of about a billion tons¹⁸. Given an average value of about 2.10 mg NO₃-N and sediment N of about 0.20% (Table 1), the sub-continental flux comes to about 4 × 10⁹ g DIN/yr (or 0.004 Tg/yr) and 1600 × 10⁹ g PON/yr (or 1.6 Tg/yr, that is, about 10% of global PON input). This is a significant contribution to the global N budget. In recent studies, it has been observed that river-borne N may have some link with the dissolved silica, particle size, discharge as well as latitudinal locations¹⁹. Thus, we need an integrated study of river systems linking all nutrients to fully explore the biogeochemical cycling of nutrients in the environment.

Based on a wide variety of datasets, perhaps generated using different analytical methodologies, and available in the literature, including from the author's group, it appears that the nitrogen riverine story is complicated. South Asian rivers carry N, both as NO₃-N and as sediment-bound N, far in excess of even some representative rivers

studied in global calculations of N budget. While there are several reports on the nitrate levels in several ground-water provinces of the region, surface water has been basically ignored. Rivers are central to any study of climate change due to interaction of factors such as alkalinity, C, N, P and several other parameters in the global water cycle. Any estimate of the global N budget has limitations until fluxes from various large South Asian rivers with high sediment load, extreme flow periods, high population density and intensive fertilizer-based agriculture are studied in detail. The annual 10% increase in fertilizer consumption since 1970 suggests that the excess N in rivers represents this man-made contribution to the N budget, since none of the rivers in the sub-continent has any N-containing minerals in the source rock as well as soils.

Conclusion

Rivers in the Indian sub-continent carry annually water flow of about 2100 km³ and sediment load of about a billion tons¹⁷. Given an average value of about 2.10 mg NO₃-N and sediment N of about 0.20% (Table 1), the sub-continental flux comes to about 4 × 10⁹ g DIN/yr (or 0.004 Tg/yr) and 1600 × 10⁹ g PON/yr (or 1.6 Tg/yr, that is about 10% of global PON input). This is a significant contribution to the global N budget. Due to lack of a reliable database, similar estimates could not be made for the most important dissolved N species, namely DON in the riverine system.

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