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Modeling the transformation dynamics of organic and inorganic nitrogen in rivers

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Abstract

This study investigated the transformation of organic and inorganic nitrogen in river water mediated by microorganisms through controlled laboratory experiments. These decomposition coefficients for nitrogen fractions provide valuable parameters for river water quality modeling and nutrient cycling assessments. Water samples were stored in the dark for 20 days, after which concentrations of particulate organic nitrogen (PON), dissolved organic nitrogen (DON), ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) were determined. Both the labile and recalcitrant parts of PON and DON showed a lot of variation between different rivers and even between different places within the same river. The decomposition rate coefficients for total organic nitrogen (TON), particulate organic nitrogen (PON), labile PON (LPON), dissolved organic nitrogen (DON), labile DON (LDON), NH_4^+, and NO_2^- were computed via 3 distinct modeling approaches. Data from five rivers in Bangladesh fit well with models based on exponential decay equations, resulting in an average kTON of 0.025 per day. In Model 2, where the pathway is PON → DON → NH4+ → NO2- → NO3-, the average decomposition rates were 0.028 per day for PON, 0.187 per day for DON, 0.492 per day for NH4+, and 0.830 per day for NO2-. In Model 3, which follows the pathway LPON → LDON → NH4+ → NO2- → NO3-, the rates were 0.091 per day for LPON, 0.451 per day for LDON, 0.648 per day for NH4+, and 0.950 per day for NO2-

1. Introduction

The transformation of organic matter (OM) from particulate to dissolved to inorganic forms by microorganisms is a key part of the decomposition process. Particulate organic matter (POM) and dissolved organic matter (DOM), mainly coming from land sources, are the main sources of organic nitrogen (ON) in rivers. There is a wide variety of POM and DOM, with molecules ranging from simple, easily usable ones like sugars and amino acids to complex components like lipids, cellulose, and humic substances that are not typically broken down. The decomposition of OM is a multi-step process starting with the physical breakdown of the material and ending with the biochemical transformation of complex organic molecules into simpler organic and inorganic forms. Aquatic environments differ from terrestrial systems in the main factors that drive OM decomposition, largely due to environmental factors like continuous water availability and frequent oxygen shortages. Decomposition rates expressed in degree-days help normalize temperature effects, allowing

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more accurate comparisons between ecosystems. Organic nitrogen includes two main types: dissolved organic nitrogen (DON) and particulate organic nitrogen (PON).

PON refers to nitrogen in dead organic matter and living organisms, whereas DON includes a wide range of organic compounds, from small molecules like urea and amino acids to peptides, proteins and microbial agents. issolved inorganic nitrogen (DIN), comprising ammonium, nitrate, and nitrite, represents another significant source of nitrogen in aquatic ecosystems. Activity microbes is closely linked to the breakdown of POM and DOM, as extracellular enzymes made by microorganisms break down larger molecules. However, enzyme production depends on the amount of OM available and helps bacteria survive when energy and nutrients are scarce. The activity of these enzymes is affected by environmental conditions such as temperature, pH, and the availability of substrates. Moreover, bacterial growth is hindered when inorganic nitrogen or phosphorus is low, even if organic carbon is present.

Proteins make up most of the biochemical composition of POM, In contrast, dissolved organic matter (DOM) is primarily composed of readily degradable molecules, including amino acids, carbohydrates, and vitamins.

Typically, phytoplankton contain protein (25-50%), polysaccharides (5-50%), lipids (5-20%), pigments (3-20%), and nucleic acids (20%). Although the effects of increasing autochthonous and anthropogenic organic matter inputs on river function are still being discussed, their negative impacts are well known. Human activities in watersheds have increased labile organic matter in freshwater systems compared to semi-labile organic matter. DOM can increase biochemical oxygen demand, create harmful by-products during disinfection, and increase the adsorption of metal pollutants, among other things. POM and DOM are further divided into labile and recalcitrant fractions. Phytoplankton, macrophytes, and epiphytic algae produce components of labile DOM through photosynthesis or extracellular organic carbon release. Bacteria primarily degrade proteins, cellulose, starch, chitin, and other humic macromolecules, which generally contain lower concentrations of nitrogen and phosphorus. However, decomposition processes depend greatly on the ecological conditions of the water body. Decomposition rates in aquatic ecosystems play a key role in water quality and affect the availability of nitrogen for algal growth.

Traditionally, Water quality models for streams and rivers typically include only the decomposition rates of labile particulate organic matter (POM) and dissolved organic matter (DOM). For instance, the CE-QUAL-W2 User Manual (Version 3.5) specifies default decomposition rates of 0.08 d^{-1} for labile POM and 0.10 d^{-1} for labile DOM. However, using more accurate decomposition rate coefficients in river water quality models would improve predictions of water quality and help develop better strategies for managing eutrophication. Mathematical modeling is a powerful tool for studying decomposition, as it can simulate the decline of various nitrogen fractions during decomposition and provide accurate rate coefficients. Quantifying these rates is essential for understanding nitrogen cycling and the extent of organic matter metabolism.

The aim of this study was to investigate temporal changes in organic and inorganic nitrogen in river water and evaluate their accessibility for algal growth.

2. Material and Methods

2.1. Study sites

Bangladesh, which is in a subtropical area, experiences changes in rainfall, temperature, and humidity throughout the year. Rainfall varies a lot from one season to another, but temperature changes are not as big. About 80% of the yearly rain falls during the monsoon season, which starts in June and ends in September. The rest of the rain happens during the dry season, which goes from October to May. In January, the average temperature across the country is around 10 degrees Celsius. All the rivers that were studied are major rivers in the Dinajpur district of Bangladesh. Most of the land near the river basins is used for homes, businesses, animals, and farming. The river stretches are short, and the areas they drain are not very large. The water surface has a gentle slope due to the natural shape of the land. Because the soil in Bangladesh is sandy, there is a lot of erosion along the riverbanks.

2.2. Collection of water samples and their analyses

Samples of water were obtained from five rivers in Dinajpur, Bangladesh: the Dhapa River (sites 1-4), the Punorbhava River (sites 5-8), the Atrai River (sites 9-12), the Jamuna River (sites 13-16), and the Kharkharia River (sites 17-20).

All the sampling spots are shown in Figure 1. Each site had four sample copies. The sampling sites and times were chosen so that they covered the different water flow patterns and the natural changes in the physical and chemical properties of the water. The bottles and glass equipment were washed with a detergent that does not contain phosphorus and then rinsed with ultra-pure water. They were also rinsed again with ultra-pure water after being soaked in 10% (v/v) hydrochloric acid for 24 hours. The filtrates were then kept at 20 degrees Celsius in a dark incubator for studying decomposition.

Typically, a 0.45 micrometer membrane is used to separate dissolved and particulate forms. However, this membrane can't distinguish between colloidal particles. Nitrate was measured using the cadmium reduction method (APHA, 2005). Nitrite content was measured using an autoanalyzer without cadmium reduction. DTN was determined using the cadmium reduction method after filtering with a GF/F filter (0.45 micrometre) and digesting with persulfate. Ammonia was measured using the spectrophotometric method (APHA, 2005). Total nitrogen (TN) was measured using the cadmium reduction method after a certain amount of time. The samples were collected in pre-cleaned polyethylene bottles that had been thoroughly rinsed with surface water. Once collected, the samples were kept at 4 degrees Celsius in the dark. A 200 micrometre filtration net was used to remove particles before persulfate digestion. Dissolved organic nitrogen (DON) was calculated as DTN minus the sum of nitrite, nitrate, and ammonium.

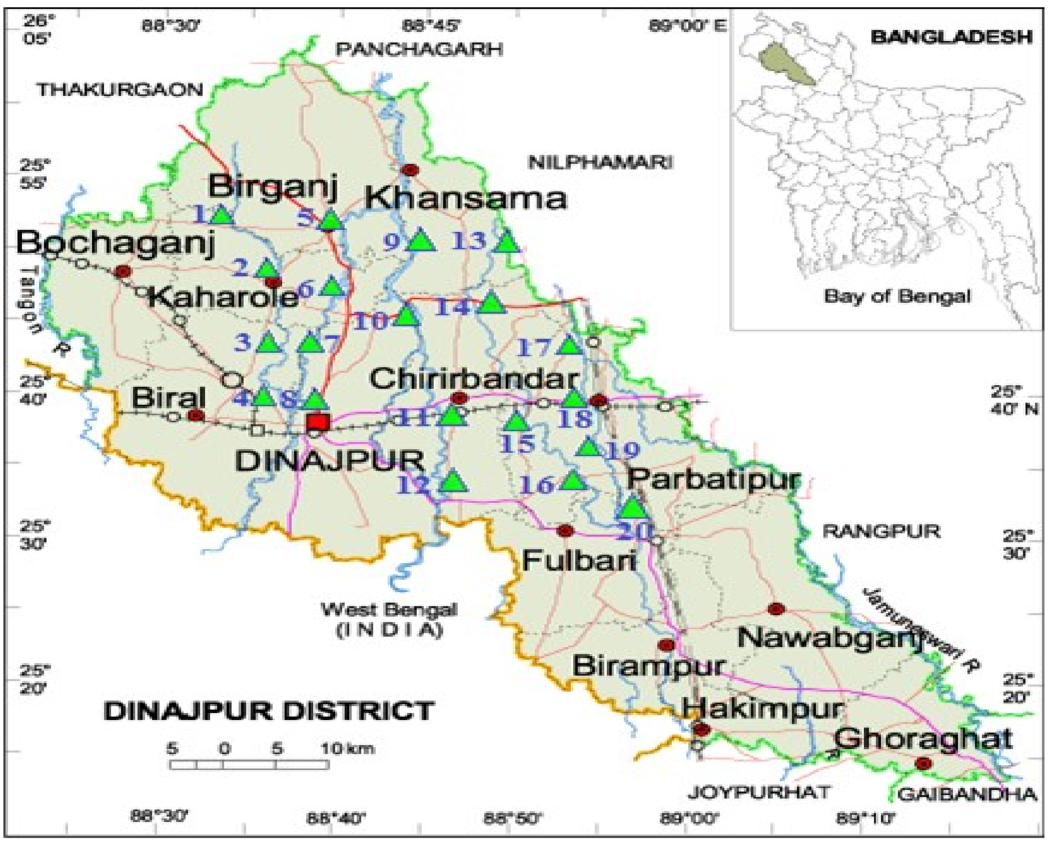

Figure 1. Map of the sampling sites of five rivers

The Dhapa River (1-4 site), the Punorbhava River (5-8 site), the Atrai River (9-12 site), the Jamuna River (13-16 site), and the Kharkharia River (17-20 site) of Dinajpur, along with the map of Bangladesh

Particulate organic nitrogen (PON) was calculated as the difference between TN and DTN. Therefore, total organic nitrogen (TON) is the sum of PON and DON. The measurements of PON and persulfate digestion were also taken. Don was calculated as DTN minus the sum of nitrite, nitrate, and ammonium. PON was calculated as the difference between TN and DTN. Therefore, TON is the sum of PON and DON. The measurements of PON were also considered.

Dissolved oxygen (DO) levels were determined via DO meter, while temperature, pH, and electrical conductivity (EC) were quantified with portable meters (Thermo, Orion). After treating the water with potassium permanganate and sodium hydroxide and digesting it, chemical oxygen demand (CODMn) was measured by titration. Following GF/F filtration (0.45 µm), dissolved inorganic phosphate (DIP) was measured by adopting the molybdenum blue method (APHA, 2005).

2.3. Models applied for calculating nitrogen decomposition rates.

The decomposition rates of organic and inorganic nitrogen were estimated using a set of interrelated differential model equations, each capable of describing changes in various nitrogen fractions. Exponential decay models are commonly applied to analyze the breakdown of organic matter (Moorhead et al., 1996). Using the differential method, it is possible to estimates of decomposition sequences, and data from the incubation experiment were used to calculate the corresponding decomposition rate constants through optimization. A total of eleven differential models were employed to determine nitrogen rate constants for decomposition estimated by employing a first-order integration technique and an iterative Runge-Kutta algorithm within an Excel-based framework.In this method, each computational step is executed sequentially in a systematic manner to accurately approximate the solution.

Model 1: Total organic N →Dissolved inorganic N (NH_4^+, NH_3, NO_2^-, NO_3^-)

$$d(\mathrm{TON})/_{dt} = -k_{\mathrm{TON}}(\mathrm{TON})$$

where, TON= total organic N concentration
kTON= TON decomposition rate coefficient [per day]
t = decomposition time [day]

This approach posits that all organic nitrogen decomposes uniformly into dissolved inorganic nitrogen (NH4+, NH3, NO2−, NO3−) without separating it into particulate organic nitrogen (PON) and dissolved organic nitrogen (DON).

Model 2: PON→DON→NH_4^+→NO_2^-→NO_3^-

This model divides the nitrogen pools into separate compartments to depict the sequential decomposition process.

- PON is decomposed into DON.
- DON is mineralized to ammonium (NH_4^+).
- NH_4^+ is oxidized to nitrite (NO_2^-).
- NO_2^- is further oxidized to nitrate (NO_3^-).

The system can be expressed as:

$$d(PON)/_{dt} = -k_{\mathrm{PON}}(\mathrm{PON})$$

$$d(\mathrm{DON})/_{dt} = k_{\mathrm{PON}}(\mathrm{PON}) - k_{\mathrm{DON}}(\mathrm{DON})$$

$$d(NH_4^{+})/_{dt} = k_{\mathrm{DON}}(\mathrm{DON}) - k_{\mathrm{NH_4^+(1)}}(\mathrm{NH_4^+})$$

$$d(\mathrm{NO_2^-})/_{dt} = k_{\mathrm{NH_4^+(1)}}(\mathrm{NH_4^+}) - k_{\mathrm{NO_2^-(1)}}(\mathrm{NO_2^-})$$

$$d(\mathrm{NO_3^-})/_{dt} = k_{\mathrm{NO_2^-(1)}}(\mathrm{NO_2^-})$$

The derivative of "d(DON)" with respect to "dt" equals "k" times "PON" minus "k" times "DON".

The rate of change of the concentration of hydrogen ions with respect to time is equal to the rate constant k_DON multiplied by the concentration of dihydrogen monoxide, minus the rate constant k_NH4+ times the concentration of dihydrogen monoxide multiplied by the concentration of hydrogen ions.

The rate of change of nitrogen dioxide with respect to time is equal to the difference between the production rate of nitric oxide and the consumption rate of nitrogen dioxide.

The rate of change of "N" (O2-) with respect to time is equal to the product of the rate constant "k" and the concentration of "N" (O2-) raised to the power of minus one.

Table 1. Water quality characteristics of the studied rivers in Bangladesh

Parameters	Units		Dhapa	Punorbhava	Atrai	Jamuna	Kharkharia	Mean
Temperature	C	Mean	22.3	24	22.8	24.6	24.8	23.7
		SD	1.6	1.3	1.8	1.2	0.9	1.4
pH		Mean	6.7	7.1	6.8	7.0	6.8	6.9
		SD	0.4	0.2	0.5	0.2	0.4	0.3
EC	$\mu S.cm^{-1}$	Mean	124	160	152	153	225	163
		SD	12	38	27	30	36	29
DO	$mgO_2.L^{-1}$	Mean	7.8	9.2	8.0	8.7	8.4	8.4
		SD	0.6	1.5	0.7	0.6	0.8	0.8
CODMn	$mgO_2.L^{-1}$	Mean	4.5	4.5	5.2	3.5	3.2	4.2
		SD	0.8	0.9	0.9	0.8	1.5	1.0
DIP	$\mu g.L^{-1}$	Mean	27	45	23	20	30	29
		SD	15	19	10	9	16	14
NH_4^+	$mg.L^{-1}$	Mean	0.179	0.195	0.136	0.068	0.172	0.150
		SD	0.077	0.074	0.063	0.070	0.059	0.069
NO_3^-	$mg.L^{-1}$	Mean	2.960	1.880	1.018	1.041	2.751	1.930
		SD	1.11	0.86	0.555	0.429	0.69	0.729

This model describes the conversion of particulate organic nitrogen (PON) to dissolved organic nitrogen (DON) and the transformation of ammonium (NH_4^+) to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-) during decomposition.

Model 3: LPON→LDON→NH4+→NO2-→NO3-

This model focuses solely on labile fractions of particulate and dissolved organic nitrogen for decomposition analysis.

- Labile PON (LPON) decomposes to labile DON (LDON).
- LDON undergoes mineralization and nitrification to inorganic nitrogen species (NH_4^+, NO_2^-, NO_3^-).

$$d(LPON)/_{dt} = -k_{LPON}(LPON)$$

$$d(LDON)/_{dt} = k_{LPON}(LPON) - k_{LDON}(LDON)$$

$$d(NH_4^+)/_{dt} = k_{LDON}(LDON) - k_{NH_4^+(2)}(NH_4^+)$$

$$d(NO_2^-)/_{dt} = k_{NH_4^+(2)}(NH_4^+) - k_{NO_2^-(2)}(NO_2^-)$$

$$d(NO_3^-)/_{dt} = k_{NO_2^-(2)}(NO_2^-)$$

The rate of change of the concentration of a substance equals the product of the rate constant k_{LDON} and the difference between the concentration of the substance and the concentration of its reactant, both raised to the power of four.

The rate of change of nitrogen dioxide with respect to time is equal to the sum of the products of the rate constant and the concentration of nitric oxide plus and nitric oxide minus, respectively.

The rate of change of nitrogen dioxide with respect to time is equal to the product of the rate constant and the concentration of nitrogen dioxide squared.

For model 3, we hypothesized that only the labile PON would be broken down into labile DON, and subsequently, only labile DON would be converted into NH_4+ → NO_2- → NO_3-.

3. Results

3.1. Basic water characteristics during sampling periods

The precis of water first-rate parameters of the studied rivers in Bangladesh is provided in desk 1. Overall, the rivers displayed barely acidic to impartial pH values, starting from 6.7 to 7.1, with little version throughout websites. impartial to barely alkaline situations are typical of tropical rivers, often prompted via watershed geology and biological interest (Chapman, 1996; Wetzel, 2001). the steadiness of pH indicates a buffering potential of these rivers, that's critical because pH influences the solubility and decomposition fees of nitrogen. natural depend decomposition normally accelerates in alkaline situations because of more suitable microbial interest (Wei et al., 2021), while acidic waters might also sluggish microbial enzymatic methods (Zhao et al., 2020). The EC values of all the studied rivers ranged from 124-225 µS.cm-1 with an average of 163 µS.cm-1. The electrical conductivity (EC) values of the studied rivers ranged from 124 to 225 µS cm^{-1}, with an average of 163 µS cm^{-1}, showing notable differences among the various sampling sites. Dissolved oxygen (DO) levels were higher in colder months and showed a relative decline during the summer season. The chemical oxygen demand (COD_{mn}) ranged from 3.2 to 5.2 mg O_2 L^{-1}. COD values were particularly low in the Jamuna and Kharkharia Rivers compared to the other rivers, which may reflect local geological inputs or agricultural runoff. These findings are consistent with previous studies indicating that EC often reflects both anthropogenic influences and watershed characteristics (Simeonov et al., 2003). Among the inorganic nitrogen species, nitrate (NO_3^-) generally predominated in the rivers, while ammonium (NH_4^+) represented only a small fraction. The NO_3^-

Table 2. Mean concentrations of TON, PON, DON, labile (L) and refractory (R) forms of PON and DON in the study rivers; concentration unit is $mg.m^{-3}$

Rivers	Sample date	TON	PON	LPON	RPON	DON	LDON	RDON
Dhapa	2016-06-15	1752	883	599	420	869	352	517
	2016-08-23	2087	1242	966	603	845	127	718
	2016-11-14	1273	273	208	65	1000	376	624
	2017-02-10	1398	756	641	115	642	272	371
Punorbhava	2016-06-15	2758	1798	899	899	960	546	414
	2016-08-23	1675	758	359	399	918	626	292
	2016-11-14	1368	583	392	191	785	553	232
	2017-02-10	1988	1188	814	373	800	399	401
Atrai	2016-06-15	1915	1015	761	254	900	623	277
	2016-08-23	1763	603	348	255	1160	769	391
	2016-11-14	1620	668	359	309	953	600	353
	2017-02-10	1575	598	349	249	978	667	310
Jamuna	2017-03-08	1830	1035	417	618	796	492	304
	2017-05-20	1062	410	123	287	652	113	539
	2017-07-18	1173	193	197	107	981	101	880
	2017-10-22	1790	773	410	601	1017	328	689
Kharkharia	2017-03-08	1787	1032	504	528	737	471	267
	2017-05-20	1264	529	338	191	735	410	325
	2017-07-18	1117	404	178	226	713	465	248
	2017-10-22	1176	499	258	242	677	382	295
	Mean	1619	762	456	347	856	434	422
	Median	1648	712	376	271	857	438	362
	SD	410	380	246	211	141	186	181

concentrations in the Dhapa River were significantly higher than those in the Punorbhava, Atrai, and Jamuna Rivers ($p < 0.05$), whereas no significant difference was observed between the Dhapa and Kharkharia Rivers. The DIP concentrations had been low in all rivers except the Punorbhava River, wherein better levels may indicate factor-source pollutants or sediment launch beneath specific hydrological situations (Dodds & Smith, 2016). The low DIP availability shows a ability phosphorus limitation for primary manufacturers, as observed in many tropical river structures (Vanni et al., 2011). It has been reported that dissolved organic nitrogen (DON) concentrations in rivers vary from around 3 μM N in low-productivity, oligotrophic waters to approximately 100 μM N in highly productive, eutrophic rivers (Berman & Bronk, 2003). DON is regularly derived from algal and phytoplankton exudates and performs an important position in nitrogen cycling (Bronk et al., 2007). the release of DON through algae and phytoplankton is frequently the supply of a extensive amount of the DON commonly discovered in streams (Jørgensen, 2009).

3.2. Source and baseline concentrations of PON and DON

Riverine organic matter originates from soil, plant residues Hedges *et al.,* 1992), and microbial inputs. Its influx and composition vary with longitudinal transport and seasonal changes. In the studied rivers, PON and DON concentrations showed high variability (Table 2). No clear pattern was observed for particulate and dissolved organic matter, although seasonal trends were evident. For instance, storm events altered DOM concentrations across rivers. The mean PON and DON concentrations were 762 mg m^{-3} and 856 mg m^{-3}, respectively (Table 2). Water temperature strongly regulates biological processes Brown *et al.,* 2004), with warmer conditions enhancing microbial activity and accelerating litter decomposition compared to colder seasons Ferreira *et al.,* 2006; Englert *et al.,* 2015).

In aquatic ecosystems, nitrogen occurs in both organic and inorganic forms. The ON, including DOM and PON, often dominates (Seitzinger, 2002). The ON derived from plants, algae, and microbes can transfer to higher trophic levels through food webs, while bacteria and fungi decompose detrital PON and DON (Wetzel 2001). Microbial degradation or animal excretion releases ON as ammonium (NH_4^+) or, less frequently, as urea, which is subsequently hydrolyzed to NH_4^+ in water. Inorganic N forms in aquatic systems include dissolved N_2 gas, NO_3^-, NO_2^-, NH_4^+, and NH_3. At pH values below 9.3, typical of most aquatic habitats, NH_4^+ predominates. For instance, NH_4^+ concentrations are ~10-fold higher than NH_3 at pH 8.3, and ~100-fold higher at pH 7.3 (Emerson 1975). Microbial processes play a key role in transforming inorganic N species. Denitrification and dissimilatory nitrate reduction convert NO_3^- to NO_2^- and further to N_2, mediated by heterotrophic and denitrifying bacteria that utilize organic matter as an energy source while reducing NO_3^- or NO_2^- as electron acceptors (Knowles 1982). Because respiration with NO_3^- yields less energy than with O_2, denitrification occurs primarily under low-oxygen or anoxic conditions, such as in the hypolimnion of stratified lakes, estuarine bottom waters, and aquatic sediments. In natural ecosystems, denitrification represents the major sink for reactive nitrogen (Howarth, 2014).

3.3. Conversion of total organic nitrogen (TON)

The decomposition coefficients of total organic nitrogen (TON) were estimated using Model 1, resulting in a mean k_{ton} value of 0.025 day^{-1} (Table 3). Microbial activity is influenced by both the source and biochemical composition of the organic matter, and from a trophic perspective, the consumption of dissolved organic matter (DOM) and particulate organic matter (POM) may vary depending on their biochemical characteristics. Microorganisms produce enzymes primarily under nutrient-limited conditions (Koch, 1985), as enzyme synthesis requires both nitrogen and energy. Conversely, when assimilable nutrients are abundant, microbial enzyme production may decrease, leading to reduced decomposition of organic matter (Moorhead & Linkins, 1997). A negative correlation is commonly observed between enzymatic activity and nutrient availability. (Sinsabaugh & Moorhead, 1994).

3.4. Conversion of particulate organic nitrogen (PON)

We calculated the decomposition coefficients of TON using model 1, and the average kTON value came out to be 0. Day 1, row 025 (Table 3). The origin and chemical makeup of OM influence the functioning of microorganisms. From an ecological perspective, the intake of DOM and POM by various species could differ based on their distinct chemical structures. Microbes manufacture enzymes exclusively in situations where nutrients are limited (Koch, 1985) due to their connection with nitrogen and energy. Despite the presence of assimilable resources, microorganisms might reduce enzyme production, thereby aiding in the inhibition of organic matter decomposition (Moorhead & Linkins, 1997). Enzymatic activities frequently show a negative relationship with nutrient concentrations (Sinsabaugh & Moorhead, 1994).

Particulate matter plays a central role in the conversion of organic matter. Moreover, enzymatic proteins in dissolved form can be adsorbed onto particulate material, forming catalytic aggregates that contribute to organic matter transformation and nutrient regeneration. Microorganisms utilize the POM pool when nitrogen-rich compounds are insufficient to meet bacterial demands (Siuda & Chróst, 2002). During aerobic decomposition, enzymes are typically specific to certain compound groups (Furlan & Pant, 2005), and individual compounds may be efficiently degraded by particular microorganisms (Canfield et al., 1994). This study focused exclusively on aerobic decomposition, and it is acknowledged that decomposition rates may differ under anaerobic conditions; however, anaerobic conditions were not observed in the rivers examined. In Model 2 (PON → DON → NH_4^+ → NO_2^- → NO_3^-), the average k_PON value for the study rivers was 0.028 day^{-1} (Table 3). In contrast, the average k_LPON value calculated by Model 3 (LPON → LDON → NH_4^+ → NO_2^- → NO_3^-) was approximately three times higher than the k_PON estimate from Model 2.

3.5. Conversion of Dissolved organic matter (DON)

The Dissolved organic matter (DOM) generally exhibits higher decomposition rates than particulate organic matter (POM), indicating its preferential degradation in aquatic systems. DOM comprises a diverse mixture of compounds with varying degrees of lability. Recalcitrant fractions of DOM may persist for extended periods, whereas labile components can be decomposed within minutes (Carlson, 2002). Organic matter decomposition rates in aquatic environments are closely connected to the fluxes of both dissolved organic matter (DOM) and particulate organic matter (POM) (Siuda & Chróst, 2002). The production of DOM is largely driven by primary production processes, such as phytoplankton exudation and zooplankton grazing. However, dissolved organic nitrogen (DON) is often not readily bioavailable to certain aquatic organisms due to its complex molecular structure. The decomposition of DON converts high-molecular weight compounds into low-molecular weight forms, enhancing their bioavailability to a wide range of aquatic organisms, including algae, bacteria, bacterioplankton, cyanobacteria, and phytoplankton (Pehlivanoglu & Sedlak, 2004; Loh et al., 2011). Low-molecular weight DON compounds, such as ammonium, amino acids, humic substances, and urea, can be easily assimilated by these organisms (Bronk et al., 2010; Bushaw-Newton & Moran, 1999; Wigner et al., 2006). While some phytoplankton species can utilize DON directly, most algae primarily rely on readily available inorganic nitrogen forms in aquatic systems. Consequently, bacterial metabolism often plays a critical role in converting DON into forms accessible to algal communities.

In addition to microbial processing, photochemical reactions driven by solar or artificial radiation can transform the labile fraction of DON into simpler compounds. However, a portion of DON remains resistant to degradation and is considered refractory. The fraction susceptible to photochemical degradation is referred to as photodegradable DON (PDON). Upon exposure to light, PDON is converted into more labile compounds, enhancing its availability to aquatic organisms (Bronk et al., 2010; Bushaw-Newton and Moran, 1999; Moran and Zepp, 1997; Koopmans and Bronk, 2002; Vaihtalo and Zepp, 2005). Despite extensive research, the relationship between biologically degradable DON (BDON) and PDON remains poorly understood. The complex molecular composition of DON complicates predictions of its fate and behavior in aquatic environments. Furthermore, external environmental factors—including water residence time, microbial community composition, substrate complexity, temperature, pH, and dissolved oxygen—significantly influence the biomineralization of DON.

In Model 2 (PON → DON → NH_4^+ → NO_2^- → NO_3^-), the mean DON decomposition rate constant (kDON) was 0.187 d^{-1} (Table 4). In contrast, Model 3 (LPON → LDON → NH_4^+ → NO_2^- → NO_3^-) yielded mean and median LDON decomposition rate constants (kLDON) of 0.451 d^{-1} and 0.440 d^{-1}, respectively. The decomposition coefficient estimated by Model 3 was therefore more than twice that obtained from Model 2. Despite this difference, kDON remained substantially higher than kPON, reflecting the simpler biochemical structure of DON and its rapid conversion to dissolved inorganic nitrogen (DIN)

Table 4. Mean decomposition rates of different N fractions using decomposition model 3.

Rivers	Site		K_{LPON}	K_{LDON}	$K_{NH4(2)}$	$K_{NO3(2)}$
Dhapa	Kornai		0.075	0.435	0.624	0.973
	Kantoji		0.093	0.417	0.664	0.915
	Birgonj		0.087	0.463	0.649	0.889
	Noshipur		0.085	0.456	0.646	0.954
Punorbhava	Sreekrishnapur		0.116	0.491	0.650	0.947
	Kokoidanga		0.091	0.438	0.625	0.913
	Hotathpara		0.089	0.477	0.669	0.987
	Kanchanghat		0.081	0.426	0.682	0.938
Atrai	Bhusirbondor		0.121	0.494	0.642	0.960
	Madargonj		0.104	0.491	0.735	0.984
	Chibuk		0.087	0.486	0.675	0.969
	Boidesirhat		0.088	0.401	0.680	0.918
Jamuna	Rostomnagor		0.095	0.418	0.687	0.983
	Manmathpur		0.082	0.420	0.557	1.031
	Khorakhai		0.094	0.442	0.673	1.038
	Dokanipara		0.098	0.505	0.674	0.898
Kharkharia	Belaichandi		0.082	0.429	0.652	0.852
	Kutipara		0.081	0.422	0.590	0.952
	Paurasabha		0.073	0.428	0.622	0.960
	Candipur		0.091	0.482	0.571	0.934
		Mean	0.091	0.451	0.648	0.950
		Median	0.088	0.440	0.651	0.953
		SD	0.012	0.032	0.042	0.045

The unit of the decomposition rate is on per day basis. n = 80

In oligotrophic environments, DON represents a preferred substrate for microbial loop energetics (Stepanauskas and Leonardson, 1999). Microbial communities, particularly bacteria, commonly assimilate low-molecular weight compounds such as amino acids, short-chain peptides, and monosaccharides in aquatic systems. Among organic matter fractions, proteins are considered the most labile, and their decomposition plays a key role in the regeneration of inorganic nitrogen species, including NO_3^-, NO_2^-, and NH_4^+ (Stepanauskas and Leonardson, 1999).

3.6. Degradation of NH4+ and NO2-

In Model 2 (PON → DON → NH_4^+ → NO_2^- → NO_3^-), the mean and median ammonium transformation rate constants, $kNH_4(1)$, were 0.492 d^{-1} and 0.474 d^{-1}, respectively. In contrast, Model 3 (LPON → LDON → NH_4^+ → NO_2^- → NO_3^-) yielded higher rates, with mean and median values of 0.648 d^{-1} and 0.651 d^{-1}, respectively. In both models, the transformation of NO_2^- to NO_3^- occurred more rapidly than the conversion of NH_4^+ to NO_2^-, with NO_2^- oxidation rates approximately twice those of NH_4^+ oxidation.

The production of NH_4^+ from DON results primarily from enzymatic degradation and deamination processes (Pantoja et al., 1997). Under conditions of limited NH_4^+ or NO_3^- availability, DON can be mineralized to NH_4^+ and/or urea, thereby providing a nitrogen source for phytoplankton and bacterial communities (Berman, 1997).

3.7. Distribution of labile versus refractory nitrogen fractions

Microbial activity depends strongly on the availability and composition of individual constituents within both particulate and dissolved organic matter (POM and DOM). The relative proportions of labile and recalcitrant nitrogen forms varied substantially among sampling sites and rivers (Figure 2). Labile particulate organic nitrogen (LPON) accounted for 42-67% of total PON in the studied rivers. Lower LPON proportions were observed at sites with higher concentrations of inorganic nitrogen, suggesting a potential inhibitory effect on extracellular enzymatic activity.

With respect to dissolved organic nitrogen, the labile fraction (LDON) ranged from 31-67%. The mean contributions of LPON and LDON were 56% and 50%, respectively. The lability of organic matter is a primary factor controlling the partitioning between labile and recalcitrant organic nitrogen pools (Taylor et al., 2003). The protein-to-carbohydrate ratio is commonly used as an indicator of organic matter quality, as proteins are generally more labile than structurally complex carbohydrates such as cellulose and chitin (Cividanes et al., 2002). However, protein aging and the tendency of proteins to associate with refractory carbohydrates and phenolic radicals can result in their incorporation into more refractory pools. Consequently, a high protein-to-carbohydrate ratio does not necessarily suggest high nutritional value, consistent with

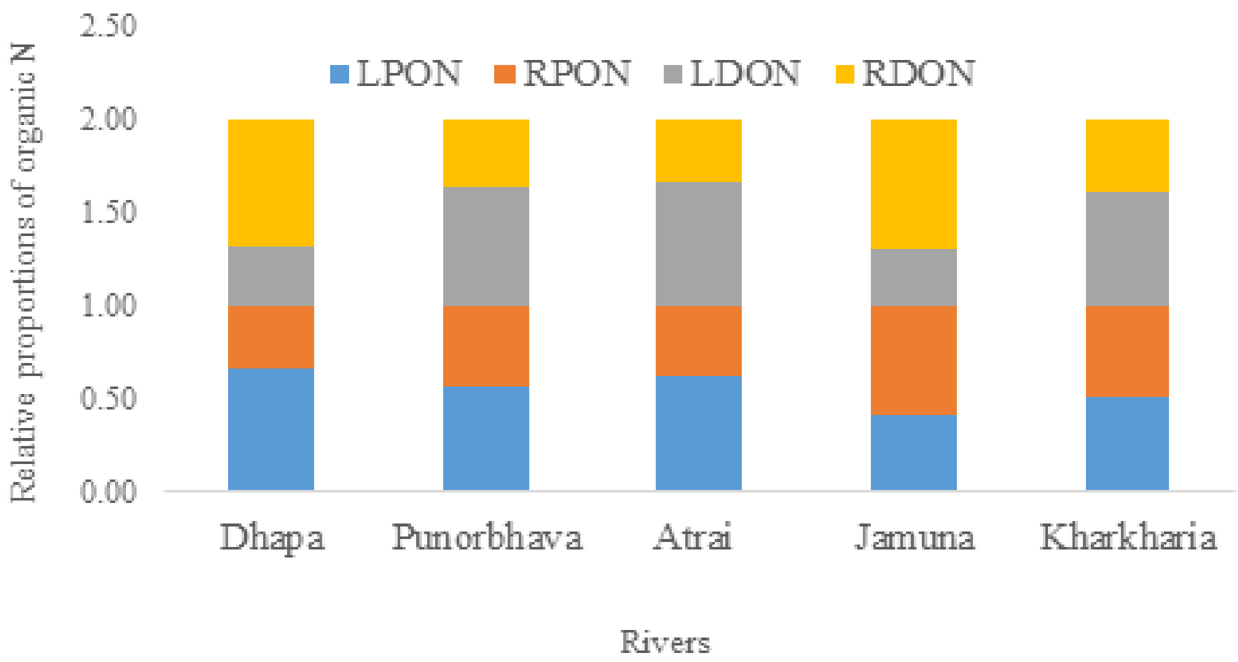

Figure 2. Relative proportions of labile (LPON, LDON) and refractory (RPON, RDON fractions of PON and DON in the study rivers

previous findings reported (Covazzi Harriague et al., 2007).

3.8. Model-based representations of organic matter decomposition

Nitrogen (N) fractions were quantified using operationally defined methods, with dissolved inorganic nitrogen species (NH_3, NO_2^-, and NO_3^-) serving as the primary analytical basis. Dissolved organic nitrogen (DON) was calculated as the difference between dissolved total nitrogen and dissolved inorganic nitrogen, and its accuracy therefore depended on the precision of inorganic N measurements.

Prediction uncertainty may arise from errors associated with the measurement of individual N fractions. Discrepancies between measured and modeled values can result from multiple factors, including sampling procedures, analytical techniques, and operator variability, none of which are explicitly represented in the model simulations. Consequently, minor deviations between observed and predicted data are considered acceptable.

Water temperatures in Bangladesh typically range from approximately 18-30 °C during the summer and fall below 15 °C in winter, while river flow velocities vary substantially with seasonal hydrological conditions. In this study, water samples were incubated at 20 °C; however, elevated temperatures may influence microbial community composition and metabolic activity. Temperature-dependent decomposition rates can be expressed as $k_{20} \times \theta$^(T−20), where θ is the temperature compensation coefficient (1.05) (Cole and Wells, 2011). The modeled results showed good agreement with calibration outcomes. In addition, differences between aerobic and anaerobic conditions may affect decomposition rate coefficients; nevertheless, simulation results indicate that these coefficients remain relatively stable and within acceptable ranges.

4. Conclusion

The degree of prior decomposition experienced by Organic matter serves as a key indicator of its subsequent reactivity. Despite the absence of explicit representation of individual microbial groups in the models, the governing equations remain effective in quantifying the decomposition rates of organic and inorganic nitrogen. Decomposition rates varied among sampling sites, rivers, and study periods. Such variability in the decomposition of different nitrogen fractions may explain observed differences in initial inorganic nitrogen concentrations among rivers and among sites within the same river.

Although some variability was associated with a limited subset of samples, these results indicate that the decomposition rate coefficients can be assumed to remain nearly constant, making them suitable for inclusion in river water-quality simulations. The eleven linked differential equations applied in this study offer a reliable approach for estimating the decomposition of both organic and inorganic nitrogen in marine systems

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7. Conflict of Interest

The authors declare no conflict of interest.

8. Authors' Contribution

Conceptualization, Md. Jahidul Islam; data curation, Md. Jahidul Islam and Md. Shazadur Rahman; formal analysis, Md. Jahidul Islam and Mohammad Sohidul Islam; investigation, Md. Jahidul Islam and M. Abdullah Al Mamun; methodology, Md. Jahidul Islam, Md. Mominul Islam, and Muhammad Asad; project administration, Md. Jahidul Islam; resources, Mohammad Sohidul Islam and A.K.M.M. Hossain; software, M. Abdullah Al Mamun and Mohammad Sohidul Islam; supervision, Md. Jahidul Islam, A.K.M.M. Hossain, and Md. Shazadur Rahman; validation, Md. Jahidul Islam and Mohammad Sohidul Islam; writing, original draft, Md. Jahidul Islam, M. Abdullah Al Mamun, Md. Shazadur Rahman, and Mohammad Sohidul Islam; writing, review & editing, Md. Jahidul Islam, M. Abdullah Al Mamun, Md. Shazadur Rahman, Mohammad Sohidul

Islam, Celaluddin Barutcular, Ayman El Sabagh, and Mohammad Sohidul Islam; funding acquisition, Md. Jahidul Islam; visualization, Mohammad Sohidul Islam. All authors have read and agreed to the published version of the manuscript.

9. SDGs Addressed

This study addresses SDG 6 (Clean Water and Sanitation) by improving understanding of nitrogen transformation processes critical for river water quality modeling and nutrient pollution management. It also supports SDG 14 (Life Below Water) by providing insights into nutrient cycling that help mitigate eutrophication and protect aquatic ecosystems.

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