

Spatial Variability and Associated Risk Assessment of Nitrate and Ammonium Concentration in Hail Haor Wetland, Northeastern Bangladesh

Humyra B. Murshed¹, Arafat Rahman^{1*}, M. J. Uddin¹ and Muhaiminur Rahman²

¹*Department of Soil, Water and Environment, University of Dhaka, Dhaka 1000, Bangladesh.*

²*Department of Geography and Environment, University of Dhaka, Dhaka 1000, Bangladesh.*

Authors' contributions

This work was carried out in collaboration among all authors. Author AR designed the study, conducted sample collection, managed the laboratory analyses, guided and corrected the paper. Author HBM wrote the protocol, performed all statistical analyses, managed the literature reviews and wrote the first draft of the manuscript. Author MR drew all maps. All authors read and approved the final manuscript.

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ABSTRACT

Nitrate-nitrogen and ammonium-nitrogen concentration were evaluated to assess the current nutrient condition of an ecologically as well as economically important wetland of Bangladesh. The contamination condition of surface water nitrate and ammonium of Hail Haor wetland was assessed to understand its probable risk to human health using the water samples collected from total-fifty monitoring stations, 25 each for two different seasons within 2018 to 2019. Nitrate concentration was measured using the spectrophotometer by colorimetric method, whereas ammonium was quantified using the micro Kjeldahl's distillation method. Statistical and geo-spatial analysis revealed an extensive understanding of the temporal and spatial variability as well as possible source identification of the nutrients in the studied area. Medium to a low level of nitrate ranging from 0.95 up to 9.25 mg/L and high ammonium with values from 0.32 up to 1.92 mg/L was a sporadic trend observed in wetland water, with low water season having more concentration than

*Corresponding author: E-mail: arafat.du.edu@gmail.com;

that of wet high water season. Hazard quotients (HQ) obtained from wetland water for four individual age groups recognized wetland water to be safe for consumption ($HQ < 1$) based on its nitrate level. Wetlands can provide valuable ecosystem services, conserve the native and exotic wetland inhabitants and mitigate flood along with their purifying properties of nutrient removal to lessen the public health concerns about nitrate-nitrogen in drinking water. Therefore, appropriate rein in measures, incentivizing water use efficiency, and continuous monitoring of water quality will ensure safety for wetland habitats, also may aware of the risks or opportunities associated with using wetland water for both drinking and agricultural use.

Keywords: Nitrate; ammonium; source identification; health risk assessment; wetland.

1. INTRODUCTION

Nitrate and ammonium are a chief nitrogen-bearing element of water, found mainly in an agricultural zone as a consequence of the excessive use of synthetic fertilizer and animal manure [1]. In 2001, Environmental Protection Agency (EPA) reported that the nitrate itself is not a direct toxicant but contributes a health hazard because of its conversion to nitrite which reacts with blood hemoglobin to cause methemoglobinemia. The escalated concentration of nitrate-nitrogen in drinking water threatens the water quality, concurrently augments the risk of blue baby syndrome (methemoglobinemia), cancer, thyroid disorders, spontaneous abortions, and also diabetes [2,3]. Moreover, the recovery of nitrate and ammonium polluted water requires expensive treatment involving a series of physical, chemical, and biological processes [4]. Therefore, continuous monitoring and subsequent mitigation measures for the prevention of nitrate and ammonium pollution, produced by either natural processes or exploitative human interventions, have become a pervasive concern globally.

Wetlands around the world have a distinctive feature of continuous hydrological connectivity to the aquatic ecosystem and bordering uplands. Though a relatively small portion of the earth's surface is occupied by freshwater wetlands, their significance outreaches their area [5]. An extensive formation of hydrological and biogeochemical activity of wetlands help in the transmission and retention of nutrients, carbon, and other solutes, which consequently render valuable ecosystem services, for instance, removal of reactive nitrogen, carbon sequestration, sorption of phosphorus and storage, also sediment retention [6,7]. Wetlands are known as the "kidney" of a watershed [8,9] for their role in nutrient removal from water through the denitrification process to improve the water quality [10-13]. Previous studies suggest

that wetlands can provide ecological services, restore the riverine and wetland inhabitants and mitigate flood along with their filtering properties of nutrient removal to lessen the public health concerns about nitrate-nitrogen in drinking water [14].

Hail Haor wetland, a prominent freshwater reservoir in the Sylhet basin located in north-eastern region of Bangladesh, is a bowl-shaped large shallow permanent reservoir surrounded by low hills on three sides. Generally, this county receives approximately 2600- 3800 mm of rainfall during monsoon with a fluctuating temperature of below 10°C in low water season to above 35°C in the high water season; and its spatial and temporal distribution is uneven [15]. It is qualified as wetlands of international importance based on the Ramsar convention and supports vulnerable, endangered, or critically endangered plant and animal species or threatened ecological communities in their life cycles, or provides refuge during adverse conditions regarding the biogenic region. Other than being the habitat ground of rare resident and migratory waterfowls, Hail haor has pronounced economic importance for its fisheries and agricultural activity. The Haor region of Bangladesh provides support to major commercial and subsistence fisheries, the temporally flooded plain is accountable for 18% of the total rice production, ample aquatic vegetation secure rich grazing for livestock, and is a source of fertilizer, fuel, and food for the regional community [16]. Henceforth, aim of the conducted study was to investigate the levels of nitrate and ammonium in the water of Hail Haor wetland and compare the obtained results with national and international guidelines including potential health impacts assessment.

Plenty of studies has been conducted on wetland restoration, water quality improvement, carbon sequestration, wildlife protection, fishery resources, and agricultural activity for the wetlands of Bangladesh [5,16-19]. However,

appraisal of nutrient status and associated health risk assessment in Haor wetland, especially the Hail haor had never been done before. Thus, the present investigation might be considered as a benchmark study for monitoring nitrate and ammonium levels, which will comprehensively help to understand the nutrient status of wetland water, identify risk outbreaks and feasible extenuation measures, and speculate fruitful wetland attributes for nutrient removal.

2. METHODOLOGY

2.1 Salient Features of the Study Area

Being comprised of the anticline between the Balishara and Barshijura hills to the east and the Satgaon hills to the west, incorporated with saucer- or bowl-shaped large tectonic depressions, Hail Haor wetland is an ecologically important wetland sanctuary located in Sreemongol and Moulavi Bazar Sadar Upazilla (Upazilla denotes an administrative subunit of districts which is locally named) under Moulavibazar District, in northeastern of Bangladesh. Coordinates lie between Latitude: 24°25' N to Longitude: 91°40' E. Field sampling area belongs to the agro-ecological Zone of AEZ-22 (Northern and Eastern Piedmont Plain) under Meghna basin of the Bengal delta and in terms of climatologically, it enjoys a sub-tropical monsoon climate including a very flat and low topography. Generally, the wet season extends to cover approximately 14,000 ha, whereas the dry season is typically shrinking to 4,000 ha area on an average [20,21]. Its natural depressed seasonal-perennial basin water originates from the surrounding hills, approximately 85% of the catchment lies in Bangladesh and 15% in India and covering watershed of about 600 km² (237 mi²). This swampy land is deeply inundated almost half of the year. The catchment area contains villages and farmlands, pineapple gardens, rubber plantations, lush tea estate, and remnants of natural forest including Lawacharra National Park. Areas above flood level are intensively cropped (2–3 crops/year) with dominantly Boro rice cultivation. The local people have encroached most area of Hail haor in recent years for expansion of agriculture by converting haor lands into agricultural field especially paddy fields, imposing alarming threat to this wetland resultantly, and there has been excessive harvesting of fish and other aquatic resources and deteriorating the water quality of Hail Haor as well. Moreover, the water bodies are converted to small fishing blocks by artificial

embankments and roads, resultantly a declining fish population along with waterfowls. The Forest Department has constructed a center for the protection of moribund waterfowls from hunting and poaching.

2.2 Water Samples Collection and Preparation

Dealing with the more variable weather condition in Hail Haor wetland area, water samples were collected during July 2018 (moderate flow of water midst wet season; mentioned as high water season) and April 2019 (low flow of water at the end of winter season; named as low water season). According to envisage open water and its watershed, samples were collected from fifty random points in this natural open water wetland ecosystem. A replicated sample was taken into account for each sampling point. The latitude and longitude values were recorded by a GPS tracker (Germin-62s, USA) and were applied to represent the sampling sites map. The map of the studied sites was drawn up by using ArcMap 10.3 software developed by Environmental Systems Research Institute (ESRI) exhibited in Fig. 1.

Water samples were collected at each point in the midstream at a depth of approximately 20 cm below the surface water by grab method. Necessary steps were instituted to prevent microbial decomposition of organic and inorganic materials existent in water samples. High-density polyethylene bottles (washed with tap water, kept immersed in 3% HNO₃ acid water, rinsed with sufficient amount of deionized water, and finally, air dried) were used for sample collection and preserved in a refrigerator at 4°C until laboratory analysis. After sampling, the bottles were screwed carefully and marked with the respective identification number.

2.3 Sample Analyses

Before chemical and instrumental analysis, every sample was filtered through a nylon membrane filter (Whatman, pore size 0.8 μm, diam. 47 mm). Ammonium-N (NH₄⁺-N) content of water was analyzed by micro Kjeldahl's distillation method [22]. Nitrate-N (NO₃⁻-N) content was determined by colorimetric method [23] using a fixed absorbance in a UV-VIS spectrophotometer (Model: HACH DR 5000 UV-VIS). The UV Absorption (nm) Spectroscopy method is probably the simplest, so long as studied samples did not contain appreciable

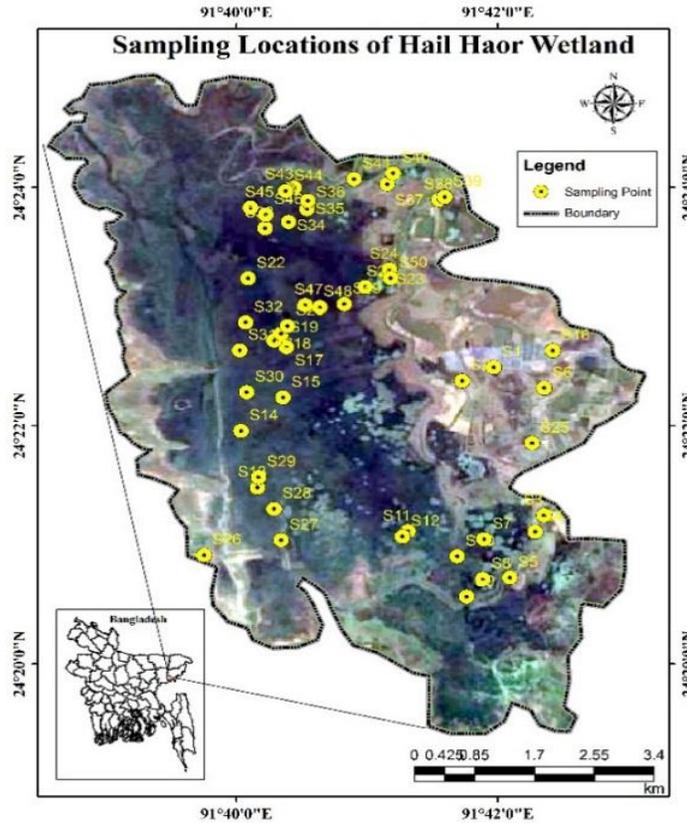


Fig. 1. Map exhibiting surface water sampling sites of 50 locations in both seasons in hail haor wetland area, Bangladesh

concentrations of organic matter and $[\text{NO}_3^-] > 10$ mg/L. Regarding maintaining good accuracy and precision of the results, Ammonium-N ($\text{NH}_4^+\text{-N}$) and Nitrate-N ($\text{NO}_3^-\text{-N}$) analysis was done as soon as possible after sample collection and all the reagents used for analytical purposes were of analytical grade (Merck, Germany). Water samples were analyzed in the laboratory of the Department of Soil, Water, and Environment under University of Dhaka. The collected data were compiled and tabulated in proper form and were subjected to further statistical analysis.

2.4 GIS and Statistical Analysis

Geospatial maps of nitrate and ammonium ion concentration and hazard quotient of nitrate for four individual age groups are derived using ArcGIS-10.3 software developed by ESRI. Inverse Distance Weighting (IDW) interpolation was drawn to observe the distribution pattern of individual ion concentration and risk status in geospatial maps. IDW is an interpolation method that shows the spatial distribution of values of

variables from the sampling site which is assigned and indicated by geographic coordinates. 25 sampling locations for each season and a total of 50 locations for nitrate risk are integrated with IDW geostatistical procedure to get a spatial distribution map of nutrients to identify the potential risk-prone zones.

Microsoft Excel-2016 and IBM-SPSS V. (25) were used to perform statistical analysis. Pearson correlation method was used to determine the nitrate-ammonium correlation. Hierarchical cluster analysis was carried out to classify the wetland according to their nutrient status and geospatial location seasonally. Ward's method of linkage was used, with the squared Euclidean distance, as a measure of similarity, to determine the distance between clusters [24].

2.5 Human Health Risk Assessment Model for Nitrate

Human health risk assessment is the process of evaluating the nature, extent, frequency, and

duration of exposure along with the likelihood of adverse health effects in a human, who may be exposed to any chemicals in a contaminated environment, now or in future. Since there is scant evidence of the carcinogenic health risk of Nitrate through ingestion, only non-carcinogenic effects due to long term exposure were quantified in present study according to the US Environmental Protection Agency health risk assessment model in terms of hazard quotient (HQ) [25]. The exposure routes of the contaminants in water include direct ingestion, dermal contact, and inhalation [26,27]. HQ can be calculated by comparing the average daily dose (ADD) contacted through the ingestion of contaminants from each exposure way with the corresponding reference dose (RfD), which is 1.6 mg/kg/day for nitrate [26,27] using Eq. (1),

$$HQ_{\text{nitrate}} = \text{ADD}_{\text{ing}}/\text{RfD} \quad (1)$$

$$\text{ADD}_{\text{ing}} = (C_w * \text{IR} * \text{EF} * \text{ED})/(\text{BW} * \text{AT}) \quad (2)$$

where ADD_{ing} defines the average daily dose (mg/kg/day); C_w is the concentration of nitrate from wetland (mg/L); IR is the ingestion rate of water (L/day); EF is the frequency of exposure (days/year); ED is the duration of exposure (year); BW is the body weight (kg); AT is the average exposure time (days) [25-28]. Table 1 contains the parameters used in the quantification of the Hazard quotients of nitrate for the four age-based consumer groups of water. In Eq. (2), the exposure duration is set to be the total time of water use for drinking purpose with an exposure frequency of 365 days. Therefore, the product of exposure frequency and duration is divided by average time, the quotient is equal to one [27,29]. Equation (2) can be simplified:

$$\text{ADD}_{\text{ing}} = (C_w * \text{IR})/\text{BW} \quad (3)$$

The calculation of ADD_{ing} is carried out using eq.(3) into four age categories namely infant (<2 years old), children (2- 6 years old), teenagers (6- 16 years old) and adults (> 16 years old), thus four hazard quotients for each nitrate concentration of any location is obtained.

HQ provides a single effective value for comparison of health risks. An estimated value of $\text{HQ} < 1$ demonstrates an insignificant risk of non-carcinogenic effects to the exposed individual, whereas $\text{HQ} \geq 1$ means that it may render health risk impact [26-29].

3. RESULTS AND DISCUSSION

3.1 Concentrations of Nitrate and Ammonium in Surface Water

In north-eastern region of Bangladesh, Hail Haor wetland of Srimongol is located in a highly seasonal domain. Though, Nitrate-nitrogen patterns in this wetland are roughly similar in both the 'High water season' of June through November and 'Low water season' of winter and summer. In the present work, analyzed results as mean (of high-water season 2018 and low water season 2019 from Hail Haor wetland are presented along with their descriptive statistics in Table 2. Nitrate concentration in the high-water season or the wet season rise from a low value of 1.02 mg/L to about 8.78 mg/L, and similarly in the dry low water season concentration of nitrate ranged from 0.95 to 9.25 mg/L. However, the mean concentration of the wet season was slightly lower than that of the dry season.

The mean nitrate concentrations of the wet and dry season were 4.71 mg/L and 4.83 mg/L, respectively with a standard deviation of 2 and 3.15 mg/l. The extensive administration of synthetic fertilizer, animal manure to the agricultural land, increased use of nitrogen-fixing organisms, run-off from the nearby hills and fossil fuel combustion produces a significant amount of nitrate-nitrogen in the environment [31]. An increased concentration of nitrate in streams and rivers, as well as wetlands, have grave repercussions for both men and their surroundings, including deteriorated regional drinking water quality, deleterious eutrophication, and the development of hypoxic zones (dissolved oxygen < 2 mg/L) [11-12,26]. There is a general tendency for nitrate concentrations in shallow water to increase as a result of enhanced nutrient run-off; this may ultimately lessen their utility as potential sources of public water supply [32]. World Health Organisation (WHO) standard of nitrate for inland surface water is 50 mg/L and for drinking purpose is 10 mg/L (maximum contaminant level) based on the presence of microbial contamination and subsequent gastrointestinal infection; whereas EPA recommended value is 50 mg/L for surface water [32,33]. Almost all the samples showed a low concentration of nitrate compared to the permissible limit for drinking with a highest value of 9.25 mg/L in dry season sampling station S46. Nitrate concentration ranged from 1.02 – 8.78 mg/L and 0.95 – 9.25 mg/L in high and low water seasons respectively.

Table 1. Parameters applied for health exposure assessment in water

Parameter	Risk exposure factors	Values for groups				Unit	References
		Infants	Children	Teenagers	Adults		
Nitrate	C _w	-	-	-	-	mg/L	
	IR	0.08	0.85	2.0	2.5	L/day	[30]
	BW	10	15	50	78	kg	[29]
	RfD	1.6	1.6	1.6	1.6	mg/ kg/day	[27]

Table 2. Mean (± SD) of nitrate and ammonium concentration in mg/L and their descriptive statistics in high water season July 2018 and low water season april 2019

High water season			Low water season		
Sample ID	Nitrate	Ammonium	Sample ID.	Nitrate	Ammonium
S1	6.42±0.04	0.78±0.01	S26	1.12±0.04	0.32±0.02
S2	6.86±0.03	0.95±0.02	S27	3.05±0.11	0.7±0.02
S3	6.32±0.09	0.69±0.03	S28	3.02±0.04	0.82±0.01
S4	6.58±0.01	0.57±0.02	S29	2.98±0.04	0.5±0.02
S5	7.69±0.07	1.02±0.07	S30	1.84±0.07	0.92±0.01
S6	8.78±0.07	1.12±0.02	S31	2.45±0.01	1.02±0.02
S7	6.78±0.02	0.61±0.01	S32	2.76±0.01	1.01±0.02
S8	4.72±0.01	0.41±0.03	S33	1.78±0.01	0.63±0.02
S9	6.31±0.04	0.62±0.02	S34	2.31±0.01	0.88±0.04
S10	5.45±0.01	0.58±0.08	S35	2.15±0.08	0.93±0.03
S11	6.19±0.01	0.82±0.02	S36	1.05±0.07	1.05±0.04
S12	6.1±0.04	0.93±0.05	S37	0.98±0.17	0.52±0.05
S13	3.81±0.11	0.61±0.02	S38	0.95±0.08	1.1±0.01
S14	3.65±0.04	0.65±0.01	S39	8.94±0	0.92±0.03
S15	3.43±0.06	0.79±0.09	S40	9.15±0.01	1.21±0.04
S16	3.78±0	0.77±0.02	S41	8.58±0	0.89±0.02
S17	3.64±0.01	0.82±0.02	S42	8.57±0.07	1.69±0.02
S18	3.96±0.06	0.78±0.05	S43	7.73±0.07	1.52±0.01
S19	3.32±0.06	0.41±0.03	S44	5.56±0.04	1.02±0.03
S20	3.19±0.04	0.52±0.04	S45	6.62±0.01	1.32±0.04
S21	3.17±0.08	0.42±0.06	S46	9.25±0.01	1.92±0.01
S22	2.63±0	0.63±0.02	S47	7.8±0.01	1.54±0.01
S23	2.17±0.11	0.4±0.02	S48	8.98±0.1	1.85±0.06
S24	1.76±0.01	0.86±0.03	S49	5.8±0.06	0.92±0.04
S25	1.02±0.13	0.79±0.01	S50	7.33±0.03	1.36±0.01
Min	1.02±0.13	0.4±0.02	Min	0.95±0.08	0.32±0.02
Max	8.78±0.07	1.12±0.02	Max	9.25±0.01	1.92±0.01
Mean	4.71±2.0	0.7±0.19	Mean	4.83±3.15	1.06±0.42

Ammonium (NH₄⁺) content of the Hail Haor wetland varied from 0.40- 1.12 mg/L in high water season, and 0.32- 1.92 mg/L in the low water season. A wide range of ammonium concentration was observed in the dry low water season where almost 98% of the values exceeded the maximum admissible limit for drinking and pisciculture is 0.5 and 1.2 mg/l, stated by ECR [34]. In terms of surface water regulation for freshwater fish, the permissible limit is 1.0 mg/L for total ammonium [32]. Wet season concentration is less than the dry season even though only 16% (4 sampling station) of the

25-sampling station had ammonium concentration within the permitted limit.

Nitrogen, biologically available forms includes nitrate, nitrite, or ammonium in water reservoir can cause eutrophication which can prevent oxygen from entering into the water, generating it hypoxic and forming a dead zone for fish and other habitats [31]. As the investigated area is largely dominated by eutrophication site, it may originate and influence the seasonal nitrate and ammonium variability in this water reservoir.

Ammonium-nitrogen is widely known as a leading source of nitrogen for paddy rice in anaerobic conditions [35]. Lately, many shreds of evidence on the significance of nitrate on the acquisition of nitrogen in the rhizosphere of waterlogged paddy rice have come to light [36]. Hail Haor wetland is one of the major haors of Bangladesh, representing rice crop cultivation as the main cropping pattern. NH_4^+ content may also be added in water through the extraction from submerged soil sediments of rice field. In the wetland, nitrates denitrify as nitrogen gas in the atmosphere upon absorbed by the plant. So, Nitrate-N is efficiently withdrawn by aquatic biomass from wetland surface waters. Eutrophication throughout the Hail haor enunciates the nutrient status of the water and possible occurrence of vast denitrification of nitrate from water. NH_4^+ and temperature being the prominent environmental gradients for the phytoplankton; concentrations of nitrates, an oxidized form of nitrogen is more appropriate for heterotrophic bacteria [37]. Through surface runoff, most of the Ammonium-N enters into this wetland. Generally, plants absorb ammonium or volatilization occur converting ammonium into nitrogen gas. Ammonium can also be changed into nitrate-nitrogen form through nitrification. However, nitrate removal from surface water by wetland plants occurs more readily than the ammonium [38]. Comparatively, the low concentration of nitrate and high concentration of ammonium in our study proves that.

3.2 Geospatial Distribution of Nitrate and Ammonium

Nitrate and ammonium concentration measured in high water season-2018 and low water season-2019 were demonstrated spatially using the Inverse Distance Weighting (IDW) interpolation method in Figs. 2 and 3. Although their concentrations found in wetland water are within the standard limit for inland surface water and beneficial for agricultural use [32], distinct regional variation is observed in the spatial distribution maps. It can be seen that nitrate

concentration in the southeastern marginal area of wetland is relatively higher than the northwestern zone in high water season. Also, nitrate concentrations from low water season showed similar characteristics of having a high concentration in the north-eastern wetland region near hills and residential areas than the region from the deep wetland. High concentrations of nitrate can be attributed to the Direct encounter of surface run-off containing residues of synthetic or organic fertilizers used in adjacent tea gardens. Besides, sewage discharge and livestock manure from the nearby residential area also contribute to the high concentration in the marginal area in both seasons [31]. The central region of the wetland encompassing the shallow permanent reservoir, on the other hand, exhibits a very low concentration of nitrate regardless of the seasonal variation. Denitrification of nitrate into gaseous nitrogen by aquatic biomass may be behind the low concentration found in deep wetland areas. Some of the sampling sites where basin depression is the maximum, extremely low concentration of nitrate was found.

The ammonium concentration distribution map (Fig. 3) revealed a slightly different pattern. Ammonium concentration throughout the wetland has a greater value than the drinking water permissible limit, but not exceeding the standard limit for inland surface water [32,34]. High ammonium concentration in both seasons may be attributed to the carbon sequestering characteristic of wetland leading to high organic load since the residual part of the wetland crops have never been removed from the water. The higher concentrations that observed near the locality as sewage and liquid manure from the marginal area discharged into the wetland through these sampling sites [31,39].

3.3 Pearson Correlation

The correlation analysis results of nitrate and ammonium with pH in both high and low water season are shown in Table 3.

Table 3. Pearson correlation coefficient for nitrate and ammonium concentration of hail haor wetland

	High water season			Low water season		
	pH	Nitrate	Ammonium	pH	Nitrate	Ammonium
pH	1	-.612*	-0.246	pH	1	-.495*
Nitrate		1	.442*	Nitrate	1	.716**
Ammonium			1	Ammonium		1

** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed)

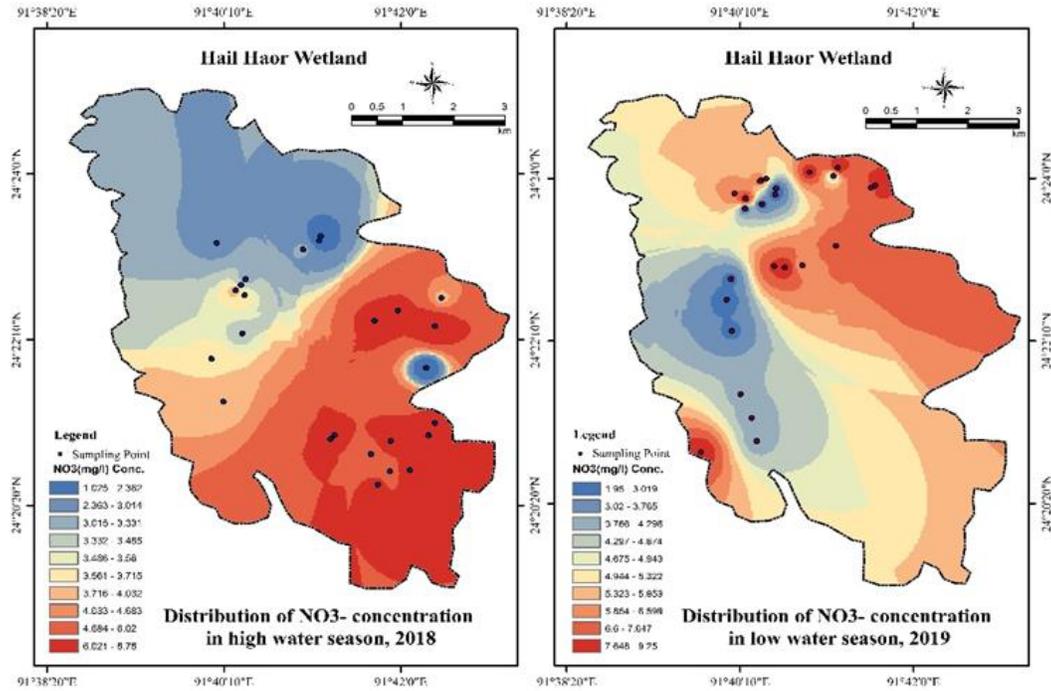


Fig. 2. Spatial distribution of nitrate concentration and variation of changes in high and low water season at hail haor wetland

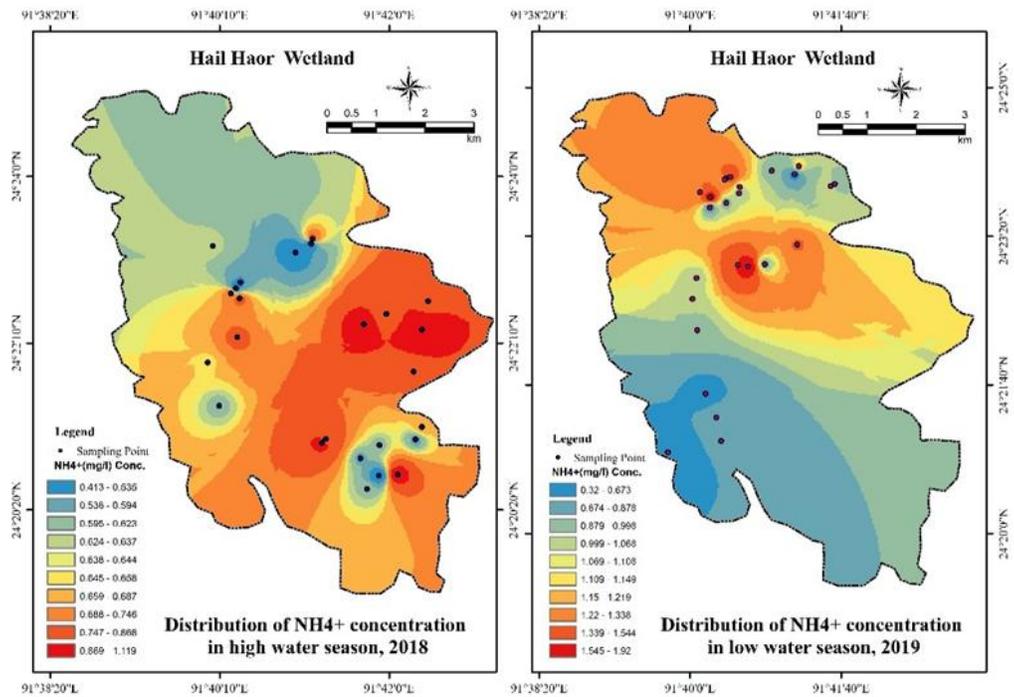


Fig. 3. Spatial distribution of ammonium concentration and variation of changes in high and low water season at hail haor wetland

From the table, it is found that pH has a distinct negative correlation with both nitrate and ammonium regardless of temporal variation. In high-water season, pH showed a significant negative correlation with nitrate ($r = -0.612$, $**P < 0.01$), but no remarkable correlation with ammonium. Similarly, in low water season pH has significant negative correlation with both nitrate ($r = -0.647$, $**P < 0.01$), and ammonium ($r = -0.495$, $*P < 0.05$). Nitrate showed a significant positive correlation with ammonium in both high water season ($r = 0.442$, $*P < 0.05$), and low water season ($r = 0.716$, $**P < 0.01$). From the correlation analysis, it can conclude that nitrate and ammonium have an inverse linear correlation with pH value of the water from Hail Haor wetland, meaning with a greater concentration of nitrate or ammonium in water, the pH levels decline and vice versa. The synergistic relation of nitrate and ammonium can also be understood from this correlation.

3.4 Cluster Analysis

Cluster analysis (Fig. 4) allowed us to classify the sampled system sites and determine the similarities of wetlands according to their nitrate and ammonium concentration. The resulted dendrogram grouped all 25 sampling locations in three statistically significant groups in high water season: G1 (sites 1 to 12), G2 (sites 13 to 21), and G3 (sites 22 to 25) at $(D_{link}/D_{max}) * 25 < 5$. Cluster 1 comprises mostly sampling stations from the east side of the wetland where fisheries are common land-use practices. Nitrate and ammonium concentration in this site are

comparatively greater here ranging from 4.72-8.78 mg/L and 0.41- 1.12 mg/L respectively, making this cluster the most polluted region of Hail haor wetland in high water season. Being in the periphery of the wetland region this clustered sited are more susceptible to anthropogenic contribution to pollution. Cluster 2 corresponds to the deeply flooded area of Hail haor, where nitrate and ammonium concentration is in a moderate range. Though eutrophication is common throughout the Hail haor, Cluster 3 comprises of sampling location, where heavy eutrophication was observed during sampling time.

Cluster analysis for low water season yielded a dendrogram that grouped all 25-sampling location into three statistically significant groups: G1 (sites 26 to 38), G2 (sites 39 to 42, 46 to 48, and 50) and G3 (sites 44, 45, 49) at $(D_{link}/D_{max}) * 25 < 5$. Cluster 1 encompasses the center region of the shallow permanent reservoir of Hail haor wetland. Low concentration of nitrate ranging from 0.95-3.05 mg/L and moderate pollution of ammonium varied from 0.32 to 1.1 mg/L is a characteristic feature of this cluster. Cluster 2 comprises the marginal zone of wetland which is surrounded by low hills. Runoff from nearby tea gardens may be the reason behind a high concentration of nitrate and ammonium varying from 7.33 to 9.25 mg/L and 0.89 to 1.92 mg/L respectively in this cluster. Heavy eutrophication was also observed in these clustered areas during sampling in the low water season. Cluster 3 consists of only 3 sampling stations with a moderate level of nitrate and ammonium.

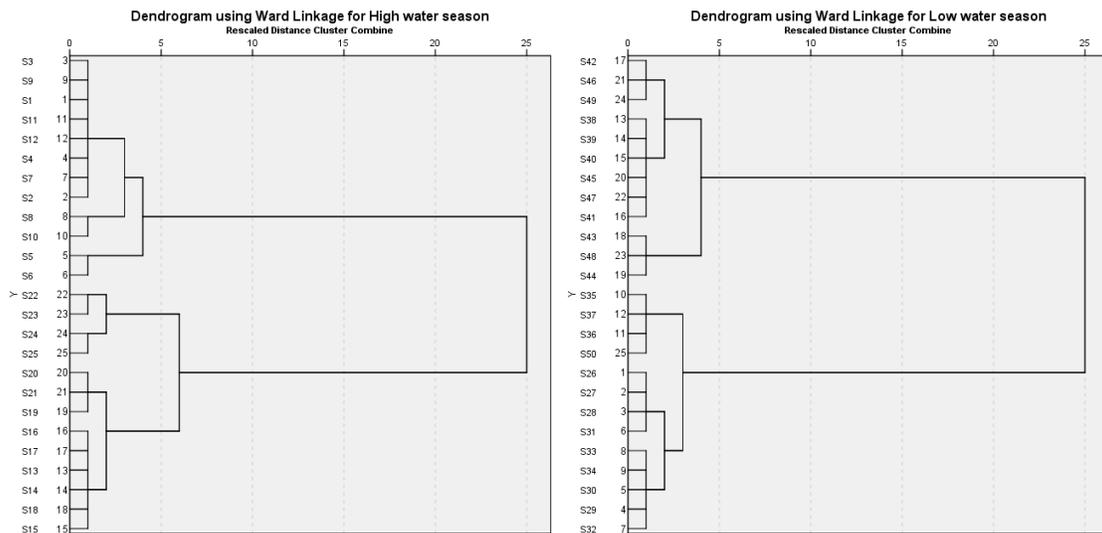


Fig. 4. Dendrogram of cluster analysis for high and low water season

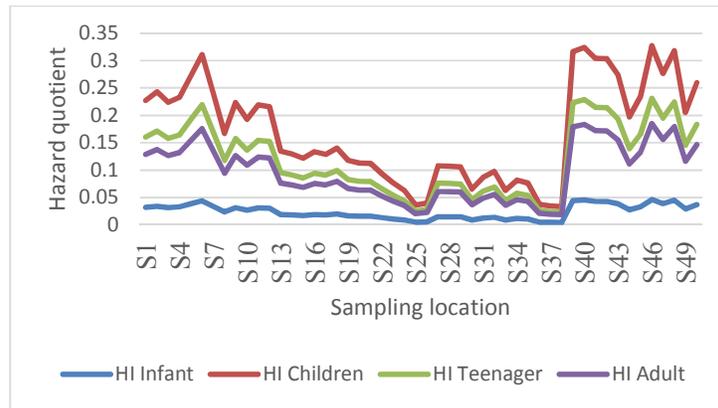


Fig. 5. Hazard quotient (HQ) values for nitrate in hail haor wetland

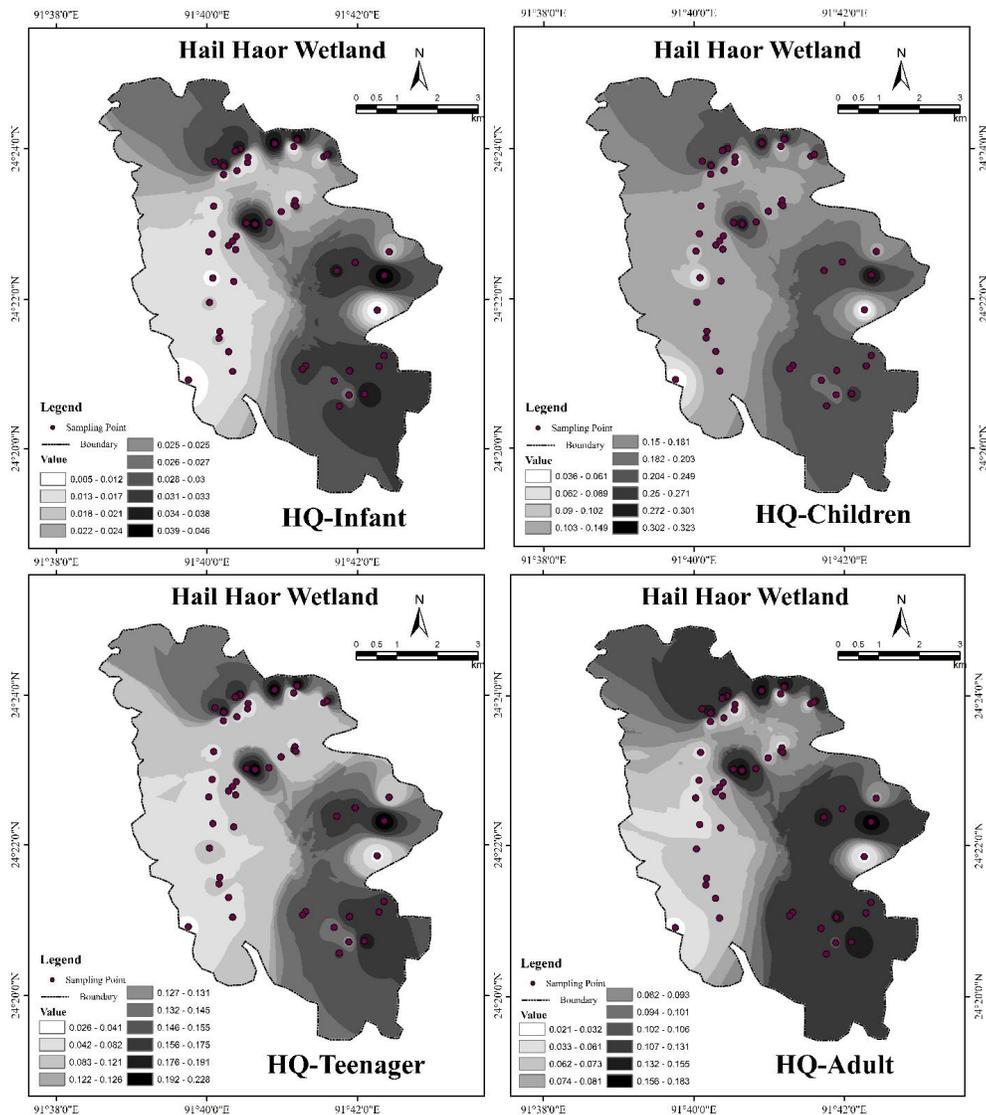


Fig. 6. Hazard quotients for Hail haor wetland water for Infants, children, teenagers and adult

3.5 Human Health Risk Assessment

Assessment of health risk has been broadly used in research associated with human health. The wetland region of the northeast part of Bangladesh is mostly inhabited by impoverished and disadvantaged groups of people, who lack access to basic services of water supply. The situation is exacerbated by flash floods, a prime threat to crop areas. Habitually, from May to October the wetland area is flooded. The majority of tube-wells get submerged at the high-water season and flood periods engendering a severe scarcity of pure drinking water [15]. Moreover, groundwater in Moulvibazar, where Hail haor wetland is situated, is highly contaminated with arsenic exceeding the Bangladesh standard by 33% and WHO guideline value 60% [40], leaving no choice but to drink wetland water risking the health of the Haor community. The presiding human health risk related to nitrate through the ingestion of nitrate-containing drinking water is considered to be an induction of methemoglobinemia by nitrate-derived nitrite [29-32,41].

To quantify the health risk in the wetland water samples, nitrate concentrations are taken to estimate the non-carcinogenic risk in the wetland water. The most important exposure route for nitrate in surface water occurs through ingestion contact route. The average daily dose, ADD value for our dataset varied from 0.008- 0.074 (mean 0.038), 0.05- 0.52 (mean 0.27), 0.04-0.37 (mean 0.19), and 0.03-0.29 (mean 0.15) mg/kg/day for infants, children, teenagers and, adults, respectively. The Non-carcinogenic risk of nitrate in drinking water of the study area was computed using the hazard quotient (HQ) following the methodology developed by the USEPA [25]. Possible health risks to four age groups comprising infants, children, teenagers and, adults, from the consumption of nitrate-containing drinking water are assessed in this study. Fig. 5-6 represents the result of the hazard quotient from the wetland in all seasons graphically and in a form of geospatial distribution, respectively. The finding showed the HQ for the four age groups ranged from 0.004 to 0.04, 0.034 to 0.33, 0.02 to 0.23, and 0.02-0.19 with the mean value of 0.02, 0.17, 0.12, and 0.09, respectively. Thus, human exposure to nitrate through direct ingestion relates to the following chronology: children > teenagers > adults > infants. However, all the HQ obtained from Hail Haor are well below the marginal range of risk. Generally, an estimated value of $HQ < 1$

represents an insignificant risk of non-carcinogenic effects, whereas $HQ \geq 1$ incentivizes harmful health impact [26-29]. In the viewpoint of non-cancer health risk assessment, an insignificant danger of non-carcinogenic risk was found, meaning drinking wetland water is safe considering its nitrate concentration.

4. CONCLUSION

The detected level of nitrate and ammonium content from the wetland water in both high and low water seasons exhibited spatial variability since surface water has a great influence from surface run-off, uptake of nutrients by phytoplankton and also the nitrification-denitrification processes. Unlikely exceedances of nitrate concentration were satisfactory within the WHO guidelines, but ammonium concentration in most parts of the wetland contravened the desirable limit. Correlation analysis introduced the synergistic relationship between nitrate and ammonium. Besides, cluster analysis classified the studied area optimally, including identifying natural and anthropogenic source contributions. Hazard quotient for all the four-age groups suggesting the wetland water is safe from nitrate pollution and its danger. Consequently, the augmented ammonium concentration in wetland may become an opportunity for rice cultivation in a natural condition. Moreover, a relatively low concentration of nitrate can validate the nitrate removing attribute of wetland, which can be an incentivized management practice for wide-scale nitrate removal from watersheds to improve water quality. Benchmark data on nitrate and ammonium concentration from Hail Haor, a basin region of Bangladesh, can aid in understanding the water quality of a tropical wetland and contribute to further studies of wetland conditions on a global basis. Henceforth, continuous monitoring of nitrate and ammonium status and their associated hazard quotient will ensure wildlife safety, uninterrupted agricultural practice, and is essential to safeguard from any undesirable health issues caused by them.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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