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RESEARCH ARTICLE

SPATIAL AND TEMPORAL DISTRIBUTION OF VARIOUS FORMS OF NITROGEN IN DAL LAKE, KASHMIR HIMALAYA

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ABSTRACT

Inspite of innumerable conservation practices taken by management authorities over the past two decades, the ecological condition of the famous urban lake (Dal Lake) has deteriorated and it is getting enriched with plant nutrients (mainly N and P) and pollutants, getting slowly shallower and shrinking gradually in size. In this backdrop, an exhaustive study was undertaken from summer 2011 to spring 2013 to evaluate the present trophic status of the lake by determining nitrogen load from its catchment area, floating gardens and houseboats. The present research has shown that lake is marching towards hypertrophic condition mainly due to enhanced levels of nitrogen forms. Results from one-way ANOVA of nitrogen forms revealed that data was over all significant ($P<0.05$) with respect to Ammonia and Nitrite and insignificant ($p>0.05$) in case of nitrate. GLM was also applied to identify various predictors and factors. Regression analysis and Cluster analysis was also applied to ascertain the correlations between nitrogen forms and closeness among various sites respectively. The present study was an attempt to identify the sources and distributional pattern of nitrogen levels across seventeen sites of Dal Lake along spatial and temporal scales.

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INTRODUCTION

Nitrogen, one of the key plant nutrient is relatively found in higher concentration in polluted aquatic ecosystems (Vollenweider, 1968; Jin, 2015). Global nitrogen (N) cycle has been altered due to the influence of human activities (Galloway, 1998; Sullivan, 2014). Due to allocthonous addition of reactive N into aquatic ecosystems there has been considerable increase in N levels in many aquatic ecosystems (Galloway *et al*., 2004), which in turn has led to the alteration in species composition and ecosystem structure (Vitousek *et al*., 1997). In lakes, as in other aquatic ecosystems, N concentrations are affected by both external as well as internal inputs.

Besides in the water column, transformations of N at the sediment–water interface (SWI) are important, as sediments are storehouses of organic carbon and nitrogen, and often have steep redox gradients required for denitrification and other anaerobic processes (Wetzel 2001). According to the technical reports published by the J&K lakes and waterways development authority (Anonymous, 1998, 2000), 15 major drains find their way into the Dal Lake waters charged with 25 tons of nitrogen on an annual basis. Nitrogen occurs in numerous forms such as dissolved molecular nitrogen, a large number of organic compounds such as amino acids, amines, proteins, nitrates, nitrite and ammonium (Wetzel, 1983). Nitrogen is regarded as the primary limiting nutrient for phytoplankton biomass accumulation (Rabalais, 2002). The accumulation of Nitrogen in natural water bodies has become a common phenomenon which alters ecological process in many parts of the world due to intensive human activity. Increased nutrients along with altered nutrient ratios cause multiple and complex changes in aquatic ecosystems. Land use dynamics of the surrounding watershed is intimately connected with the

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concentration and the rate of supply of nitrate (Moore *et al.,* 2014). Both nitrate (NO_3-N) and ammonia (NH_4-N) concentrations are highly variable during lake seasonal cycles. For deep stratified lakes, nitrates higher during mixing events and usually decreases in late summer and fall. For the trophogenic zone of shallow lakes, both concentrations would be lower during periods of water column stability and they will increase during vertical mixing events.NH_4-N is generated by heterotrophic bacteria as the primary nitrogenous end product of decomposition of organic matter, and is readily assimilated by plants in the trophogenic zone (Wetzel, 2001). NO_3-N is the common form of inorganic nitrogen entering lakes from the drainage basin; in relatively aerobic waters nitrification prevails (Wetzel, 2001). When NO_3-N from external sources reaches lakes it is taken by autotrophs and bacteria, transformed in organic matter that on decay and food web transmission ultimately goes to the NH_4-N pool. Therefore, NH_4-N accumulates with respect to NO_3-N in relatively standing waters like those of lakes and reservoirs. In eutrophic and hypertrophic lakes, a large lake concentration of organic matter implies a large potential pool of ammonia. In more reductive media de-nitrification and nitrate reduction to ammonia would prevail (Stumm and Morgan, 1996). The removal of N from lakes is usually dominated by NO_3-N de-nitrification concomitantly with the oxidation of organic matter, but in highly productive surface waters, high pH would favor N release to the atmosphere as NH_3.

Nitrogen and Phosphorus are regarded as the most important nutrients in terms of the pollution of lakes. They form an important component of aquatic ecosystems particularly lakes and are essential for the growth of aquatic biodiversity. But due to their uncontrollable release in the water bodies due to human influence, undesired effects like blooming of toxic algae and water transparency reduction is bound to occur (Conley *et al*., 2009; Paerl *et al*., 2011). The concentration of Nitrogen is usually greater than Phosphorus in a Lake ecosystem and there will always be surplus nitrogen despite being used up by the primary producers(Dolman 2012).During the past few decades, phosphorus was considered as the primary limiting nutrient for the algal bloom (Schindler, 1974, 1977; Smith ,1982) irrespective of the fact that N limitation is a widespread and prevalent phenomenon in lakes (Elser, 1990; 2007).Nitrogen has therefore received comparatively less focus than phosphorus and more information is needed regarding the role nitrogen may play in abating eutrophication and in particular its impact on the taxonomic composition of freshwater algae (Lewis, 2008; Sterner, 2008).

MATERIALS AND METHODS

Study area

Dal Lake, the urban lake towards the North east of Srinagar city is a tectonic lake at an altitude of about 1,584 m above mean sea level. The lake lies between 34°6´N and 34°10´N latitude and 74°50´E and 74°54´E longitude. The lake is mainly fed by a large perennial inflow channel, Telbal nala, which drains the largest sub-catchment area of about 145 km^2 and contributes about 80% of the total inflow to the lake (ENEX, 1978; Zutshi and Vass, 1978; Trisal, 1987) as well as a number of small streams, viz., Peshpaw nala, Shalimar nala, Merakhsha nala, Harshikul, etc., around the shore line besides some contribution from groundwater. Of the total area of the lake, 1305 ha is water body, 749 ha is under floating garden or cultivation, 28 ha is under plantation/orchards and 315 ha under marshy conditions (Amin *et al.,* 2014). Being an urban type lake, municipal and domestic effluents have altered the surface-water composition of the Dal Lake, leading to increased eutrophication. Moreover, excessive sedimentation rates, enhanced by extensive soil erosion due to deforestation, and an encroachment by surrounding population have intensely reduced the lake volume (Jeelani and Shah, 2006). An exhaustive ecological study of the water body was conducted during 2011-2013, so as to gain an insight on the current trophic status of the lake by analyzing water samples from 17 sampling stations across Dal Lake representing both open-lake and nearshore locations (Fig.1).

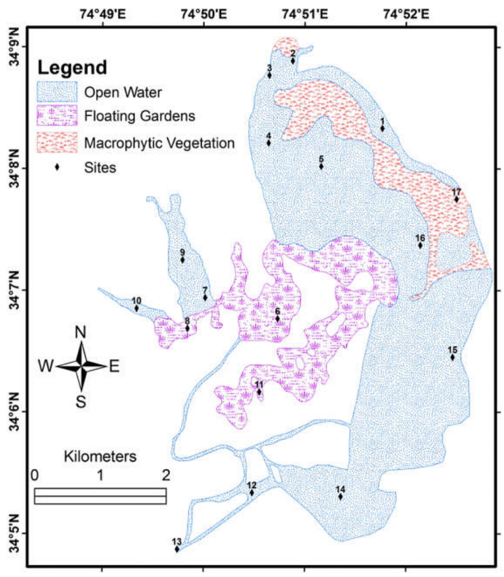

Fig. 1. Location of different study sites in the Dal Lake

Water Analysis

In order to have a detailed account of distribution of nitrogen forms and their sources, 17 sampling sites were selected across the length and breadth of Dal Lake for the collection of the field data. Water samples were taken at depth of 0.5 m below the water surface, stored at 4°C and analyzed for NH_4-N, NO_3-N and NO_2-N within a day. All analyses were conducted in triplicates. Water samples were analyzed in the laboratory adopting standard methods of APHA (2005).

Statistical Analysis

ANOVA was done with the help of SPSS 22. Cluster analysis and Pearson correlation was done by PAST software package.

RESULTS AND DISCUSSION

Ammonia

Results from one-way ANOVA of NH_4-N of water revealed that data was over all significant ($P<0.05$). Multiple comparison revealed that site 3 and site 10 were significantly

($F=3.75$, $p<0.05$) different from rest of the sites. Distribution of NH_4-N along 17 sites of Dal Lake in box plot showed that site 3 and site 10 had high levels of NH_4-N (Fig 2A). Low concentration for ammonical-nitrogen in the open water (Site 5, 9 and 14) of the lake has also been reported by Zutshi and khan (1988). NH_4-N recorded a gradual increase from summer towards autumn which gradually decreased towards winter with the slight peak in spring (Fig 3).

Higher level of NH_4-N in spring season (Fig 3D), was found again at site 10 in first year and site 3 in 2nd year. Higher concentration of ammonia at site 3 (lake inlet) may be due to the influx of sewage from the catchments through inlet and also due to nearby Habak STP.Site 10 (lake outlet) is marked by high concentration of ammonia which may be due to stagnation of water and outflow of nutrients. Site 3 and site 10 had lower level of Dissolved oxygen (Fig 2B).

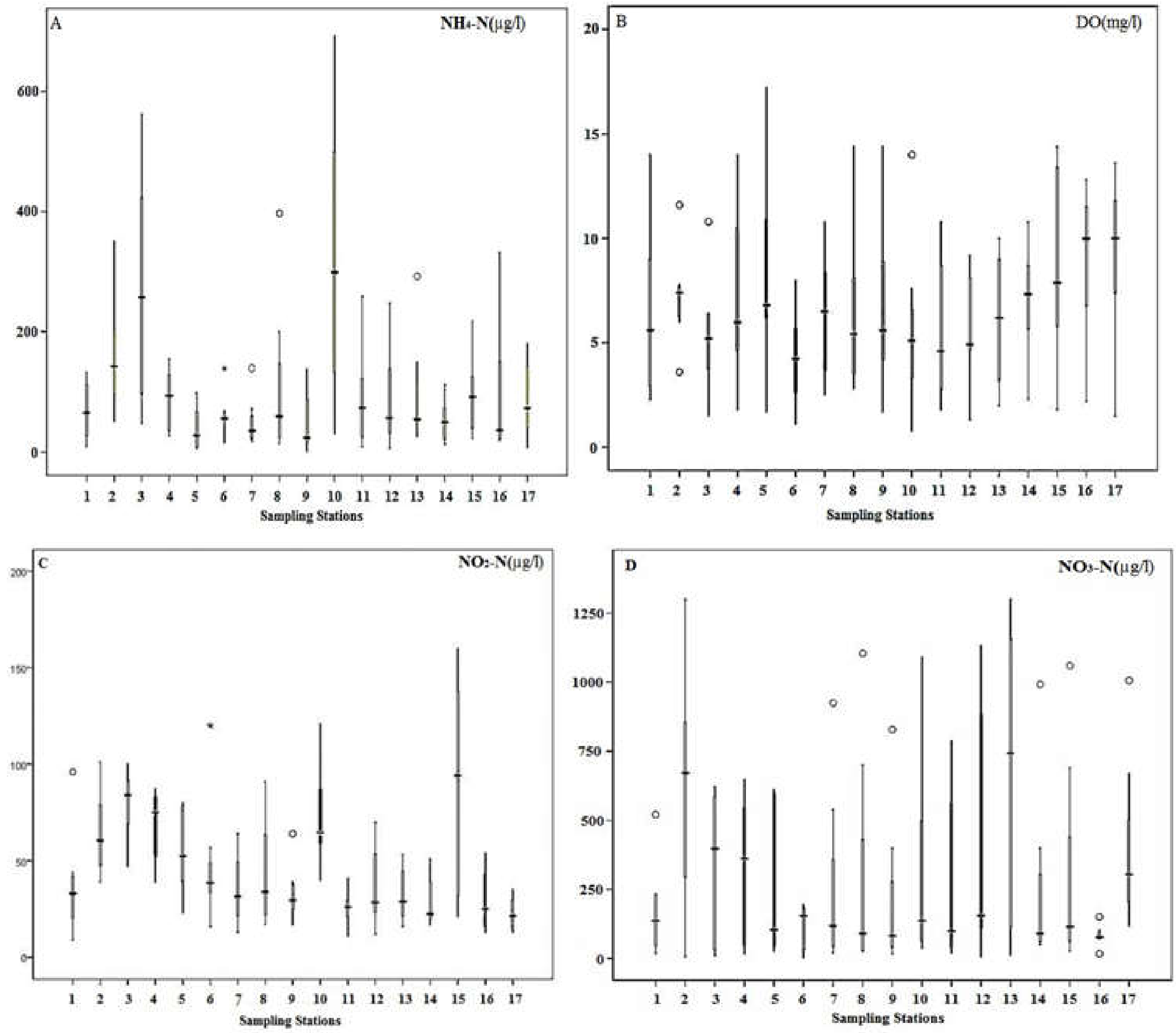

Fig. 2. Site wise distribution of ammonia (A), dissolved oxygen(B), nitrite(C) and nitrate (D). Units are in µg/l.

The reason for this may be the high decomposition rate during autumn season as the distribution of ammonia in freshwaters is highly variable and depends upon the extent of organic matter as much of ammonia arises as a primary product of the decomposition of organic matter (Wetzel, 2001). Low rate of decomposition in winter attributed to low NH_4-N level.

In summer season (Fig 3A), NH_4-N was higher at site 10 in the Ist year and at site 11 in 2nd year. Elevated levels of NH_4-N in autumn season (Fig.3B), was found at Site 10 for first year and at site3 for 2nd year. Higher level of NH_4-N in winter season (Fig 3C), was found at site 10 consecutively in both years.

At low Dissolved oxygen, nitrification of ammonia ceases (Stenstrom and Poduska, 1980), the absorptive capacity of the sediments is reduced, and a marked increase of the release of NH_4-N from the sediments then occurs that is why site 3 and 10 have higher levels of NH_4-N. An elevated level of NH_4-N at Site 11which is adjacent to floating garden experiences heavy inflow of agricultural fertilizers and sewage from the nearby locality (Kandmohalla).

Nitrite

Results from one-way ANOVA of nitrite revealed that data was over all significant ($P<0.05$).

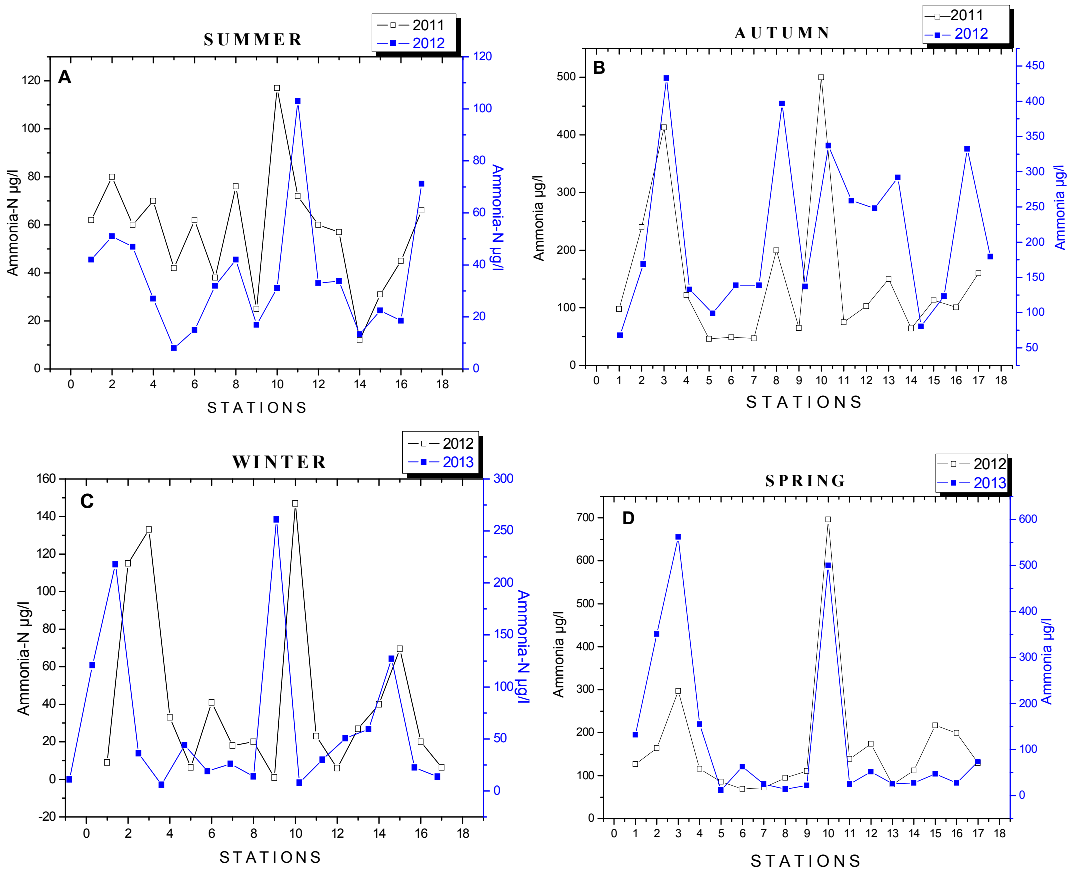

Fig.3. (A-D) Corresponds to Ammonical nitrogen concentration in Summer (A), Autumn (B), Winter (C) and Spring (D) at different sampling stations

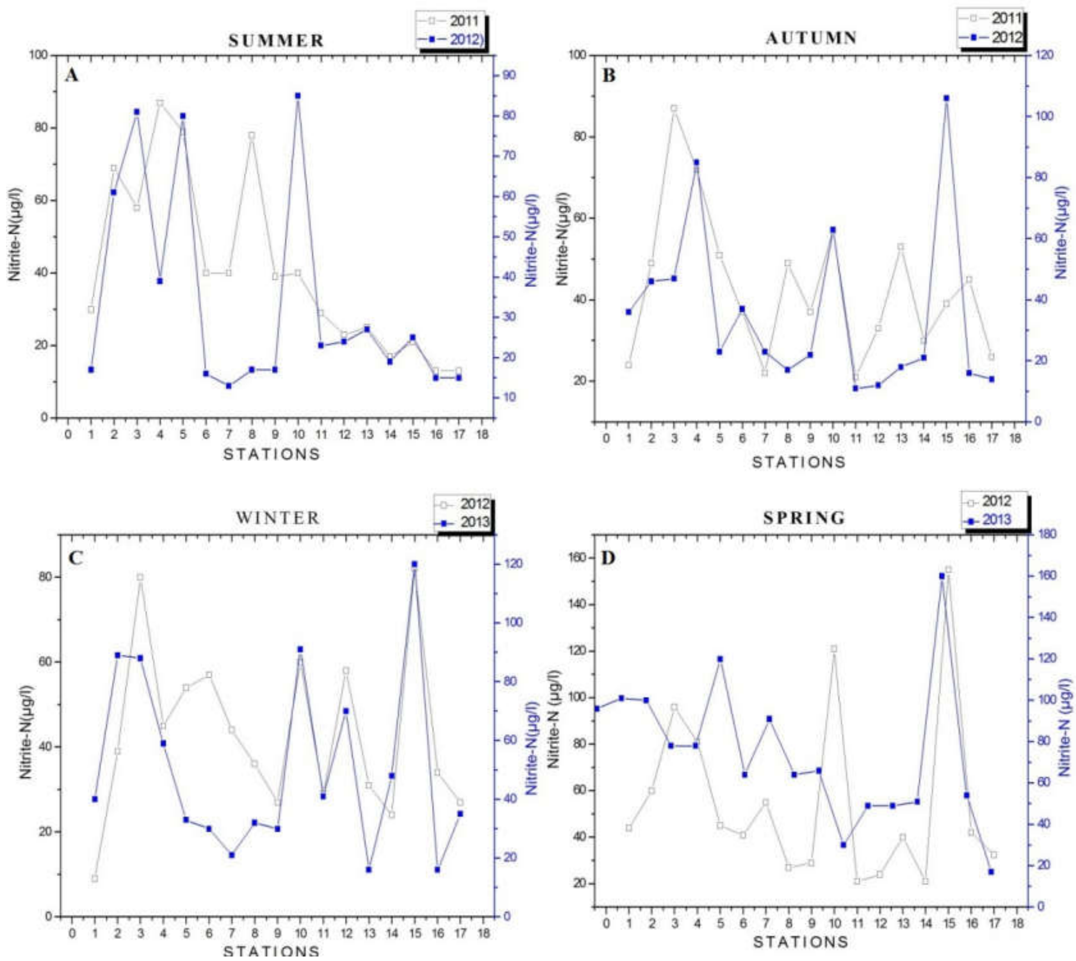

Fig. 4. The values of nitrite nitrogen (NO_2-N) in summer (A), autumn (B), winter (C) and Spring (D) at different sampling stations

Multiple comparison (Tukey HSD) of nitrite revealed that site 15 was significantly ($F=5.9$, $p<0.05$) different from rest of the sites excluding sites 2, 3 4, 5, 10, 15. Nitrite was recorded higher at site15 followed by site10 (Fig 2C). This may be due to outflow of effluents from STPs present at both the sites. Exceptional high values in different seasons may be attributed to the large influx of nutrients from surrounding catchment area. Nitrite is the product of intermediate oxidation state of N produced, both in the oxidation of NH_4 to NO_3 and in the reduction of NO_3. It is an intermediate compound in N cycle and is unstable. The low concentration of NO_2-N is in consonance with its insignificant role in the environment and also with its short residence time in water (Malhotra and Zanoni, 1970).Temporal distribution of nitrite along seventeen sites is shown in Fig 4.

The seasonal dynamics of NO_3-N in the dal lake was similar to the findings of Kaul *et al.* (1980), Lanzik *et al.* (1999) and Buhvestova *et al.* (2011) who attributed lower nitrogen levels during summer to the consumption of NO_3-N by phytoplankton, aquatic plants and denitrification processes in the sediments. In winter the nitrogen concentration rose once again most likely due to the remineralisation resulting in increased losses from the sediments into the water and lower biological activity in the lake.

High nitrate in winter are also due to release of nitrate from dense macrophytes. In summer nitrate is absorbed by extensive vegetation as soon as it is synthesized. In fall when die back of vegetation's occurs, nitrate is released (Bass and Potts, 2011).

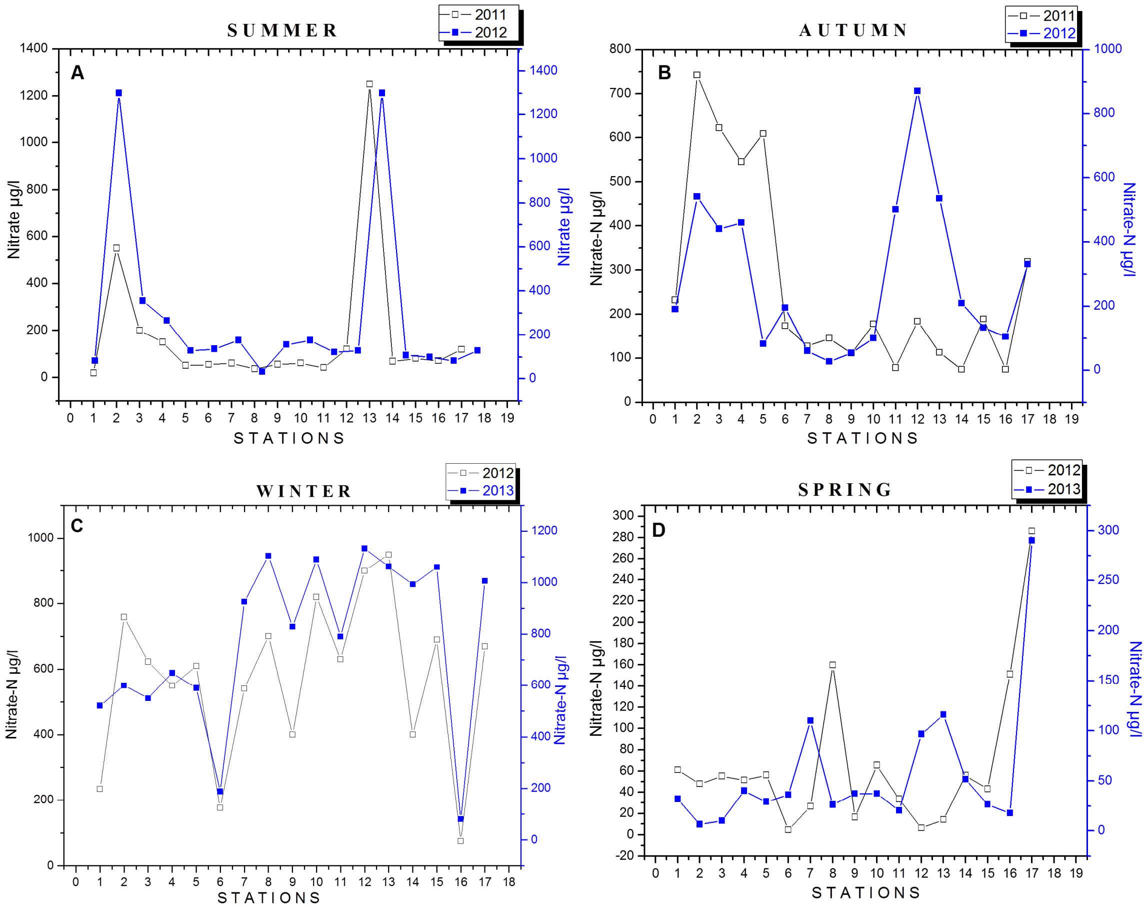

Fig. 5. The values of nitrate nitrogen (NO_3-N) in summer (A), autumn (B), winter (C) and spring (D) at various sampling locations

Nitrate

Data was over all non-significant ($F=1.1$; $p>0.05$).Nitrate-nitrogen showed non-significant variation between the sites in different basins. Increased level of NO_3-N during summer season in both years was reported at site 13(Fig 5A). Peak values of NO_3-N during autumn season were observed at site 2 in Ist year and at site 12 in 2nd year (Fig 5B).In winter season, nitrate was higher at site 13 for the first year and at site 12 in 2nd year(Fig 5C).Higher value of nitrate-N was found for both years at site 17 during spring season (Fig 5D). An analysis of the results carried out on seasonal basis revealed that NO_3-N in the water exhibited peak values during winter and autumn.

The higher level of Nitrate-nitrogen at site 2, Lake Inlet (Fig. 2D) may be attributed to the inflow of agricultural run-off from the catchment area, bringing in nitrate rich fertilizers (Wani and Subla, 1990).High level of NO_3-N at Site 12 can be due the raw sewage emanating from houseboats.

Site 13 (lake outlet$_{2)}$ is marked by high concentration of NO_3-N which may be due to stagnation of water and outflow of nutrients. As site 17 is characterized by the process of deweeding of aquatic macrophytes, an important sink for nitrates is eliminated. Hence this site is having more nitrate concentration.

Table 1. Generalized Linear Model showing the effect of season, site and year on the ammonia concentration in Dal Lake

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	3041116.238	1	3041116	8.867602	0.043998
Year	735.2494118	1	735.2494	0.021197	0.895011
Site	1519672.707	16	94979.54	5.964651	0.0001
Season	902301.1188	3	300767	6.120537	0.039338
Year * site	70309.29559	16	4394.331	0.600379	0.867718
Year * season	112833.6718	3	37611.22	5.138664	**0.003665**
site * season	904736.1162	48	18848.67	2.575215	**0.000682**
Year * site * season	351324.5632	48	7319.262	500.4724	**0.000**

Significant values are in bold

Table 2. Generalized Linear Model showing the effect of season, site and year on the Nitrate concentration in Dal Lake

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	25983502.55	1	25983503	5.191916	0.093824
Year	441244.8459	1	441244.8	2.814466	0.194407
Site	5940673.866	16	371292.1	1.900101	0.048361
Season	13636240.8	3	4545414	14.20657	0.000393
Year * site	534256.7147	16	33391.04	0.966468	0.505648
Year * season	473807.8583	3	157936	4.571289	**0.006776**
site * season	9435122.935	48	196565.1	5.689367	**0.0001**
Year * site * season	1658378.224	48	34549.55	1319.653	**0.0001**

Significant values are in bold.

Table 3. Generalized Linear Model showing the effect of season, site and year on the Nitrite concentration in Dal Lake

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Intercept	606217.9	1	606217.9	42.36383	0.001854
Year	621.0331	1	621.0331	0.219525	0.676085
Site	107577	16	6723.562	8.355894	0.000199
Season	32418.31	3	10806.1	3.258042	0.156634
Year * site	8386.404	16	524.1503	0.716622	0.763467
Year * season	9108.746	3	3036.249	4.151181	**0.010769**
site * season	48572.01	48	1011.917	1.3835	**0.132161**
Year * site * season	35108.07	48	731.418	780.1792	**0.00001**

Significant values are in bold

It was also found that nitrogenous wastes emanating from houseboats at site 12 contributes large amount of NO_3-N in to the lake as compared to the houseboats placed at site 7 (Fig. 2D). Floating gardens at site 11 releases more NO_3-N in to the lake than the floating gardens at site 6. However, houseboats are found to be the main source of NO_3-N with in the lake than the floating gardens.

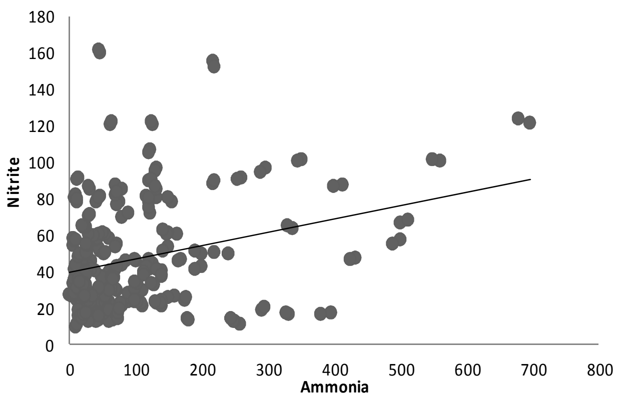

Fig. 6. The concentration of ammonia in Dal in 2011-2012 plotted against Nitrite in different months ($y = 0.0729x + 39.498$, $R^2 = 0.08$, rp=0.3, p=0.001)

General Linear Model

The general linear model is a statistical linear model. It can be written as

$Y = XB + U$ (Christensen, 2002)

Where Y is a corresponds to multivariate measurements, X is a matrix that might be a design matrix, B is a matrix containing parameters that are usually to be estimated and U is a matrix containing errors.

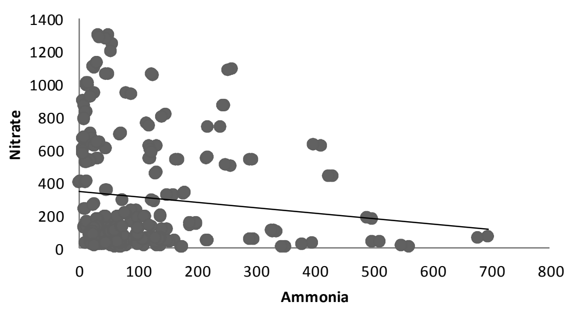

Fig. 7. The concentration of ammonia in Dal in 2011-2012 plotted against Nitrate in different months($y = -0.3348x + 344.48$, $R^2 = 0.0135$, rp=-0.116, p=0.056)

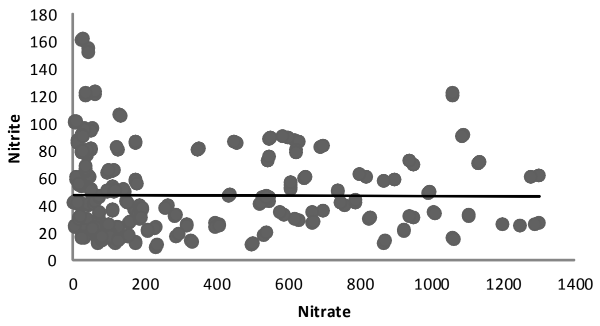

Fig. 8. The concentration of Nitrate in Dal in 2011-2012 plotted against Nitrite in different months (y = -0.0004x + 47.327, R² = 2E-05, rp=-0.004, p=0.94)

The general linear model is a generalization of multiple linear regression model to the case of more than one dependent variable. The results of GLM with reference to Ammonia (Table 1) showed that site (p=0.0001) and season (p=0.04) were important factor which influenced the ammonia concentration, whereas there was no effect of year (p=0.86) on the ammonia concentration. The combined effect of year and site (year * site, p=0.86) showed no major change in the alteration of amount.

However, joint effect of season with year and site influenced the concentration of ammonia. In general all three factors i.e. year, site and season were important factors for the distribution of ammonia concentration (p=0.0001). With reference to Nitrate level (Table 2), site (p=0.04) and season (p=0.00) were important predictors besides cumulative effect of year*season (p=0.006), site*season (p=0.0001) and year*site*season (p=0.0001). On applying GLM on Nitrite concentration (Table 3) in the lake, Site (p=0.0001) and year*season (p=0.010) were prominent factors.

Regression Analysis

Results of regression analysis revealed significantly weak positive correlation between ammonia and nitrite (Fig.6) and significantly week negative correlation between ammonia and nitrate(Fig.7). There was insignificant correlation between nitrate and nitrite (Fig.8).Negative correlation(r=-0.48) was found between NH_4-N and NO_3-N, as inter conversions through the processes of ammonification and de-nitrification occurs in the Lake (Table 4). NH_4-N are usually low in oxygenated waters as negative correlation (r=-0.17) was found between ammonia and Dissolved oxygen. At low Dissolved oxygen, nitrification of ammonia ceases, the absorptive capacity of sediment is reduced, and a marked increase of the release of NH_4-N from the sediment then occurs.

Cluster analysis

Cluster analysis revealed that Site 12 and Site 16 were grouped in upper cluster (90 % similarity) in the dendrogram with respect to NH_4-N (Fig9D); 90% above similarity was found between Site 13 and Site 16 with respect to nitrite concentration (Fig 9C); highest similarity between Site 10 and Site 15 with respect nitrate (Fig 9B) and Site 16 and site 17 showed highest similarity in terms of DO (Fig 9A).

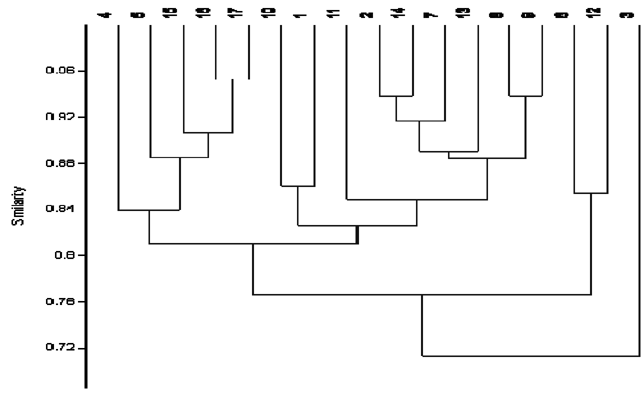

Fig. 9A.

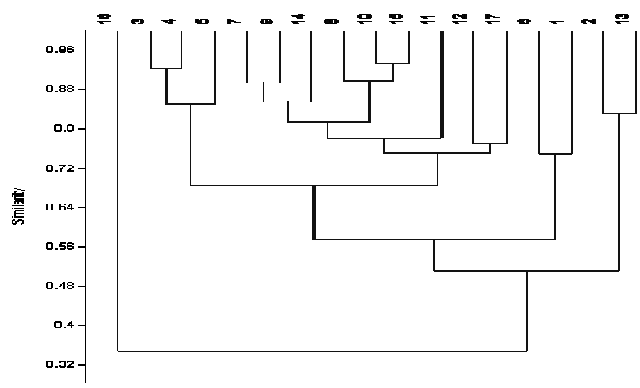

Fig. 9B.

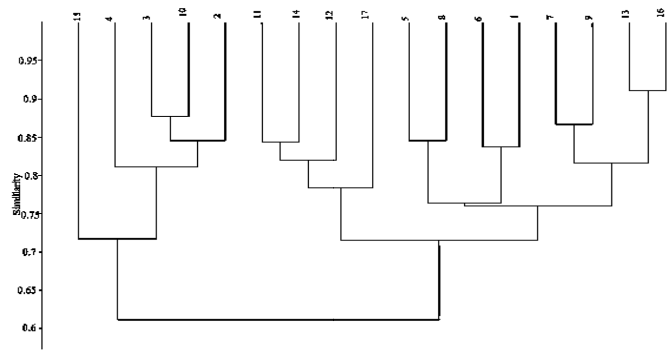

Fig. 9C.

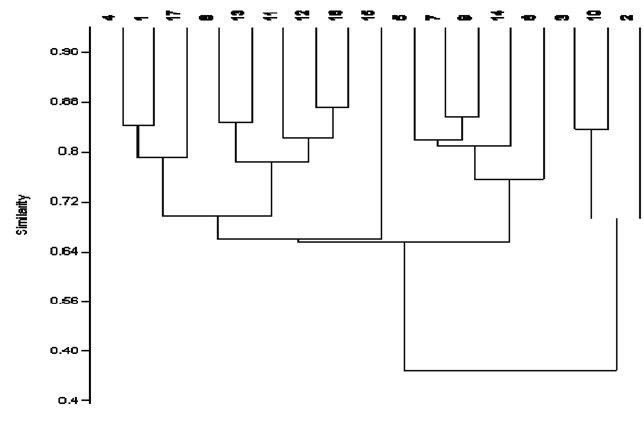

Fig. 9D.

Fig. 9. Cluster analysis of sampling stations with respect to DO(A), nitrate(B), nitrite (C) and ammonia(D)

Conclusion

It was concluded that enhanced levels of nitrogen in Dal lake waters is due to huge influx of effluent (raw sewage) from houseboats and adjoining residential areas. Stagnation of water and low rate of flushing also lead to anoxic conditions and high concentration of ammonia. Floating gardens emerged as potent sources of nitrogen due to heavy inflow of agricultural fertilizers and sewage from the nearby localities. Appreciable nitrite was found in the vicinity of STPs. Macrophyte harvesting at some of the sites lead to nitrate upsurge, as aquatic plants are an important sink for nitrates. Overall houseboats and floating gardens were the main contributors of ammonia and nitrates with in the lake and war footing efforts are needed to plug these sources.

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