

## Evaluation and Transport of Nitrogen and Phosphorus by River Indus at Kotri Barrage

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**Summary:** Water samples at Kotri barrage were collected during Jan 1994 to Dec. 1995 and analysed for nitrite, nitrate, ammonia, organic nitrogen, orthophosphate and condensed phosphate. The concentrations were multiplied with water discharges to obtain load of each ion including total nitrogen and phosphorus in the river Indus. The transport of nitrogen and phosphorus to Arabian sea and to irrigation channels at Kotri barrage were calculated. The variation in their concentrations with seasons and water discharge was noted. Nitrate nitrogen and condensed phosphate phosphorus were dominant and contributed 64% and 73% of total nitrogen and phosphorus transported.

### Introduction

The water quality in rivers is affected by change in vegetation, sediment balance, fertilizer use, industrialization and land utilization for forming and human settlements [1,2]. Quantification of water quality parameters are important in understanding the changes in water quality and possibilities of remedial actions [3].

The river Indus the largest within Pakistan in terms of length, water discharge and sediment yield, has changed considerably during the last 70 years, due to the construction of barrages and dams on the river. Guddu, Sukkur and Kotri barrages have been constructed on river Indus to divert the water flow to different channels for irrigation. Two huge dams have been constructed in the Indus river basin, Mangla on the Jehlum river and Tarbela on the Indus for hydro electric power generation.

River Indus is 2737 km long and originates in Hamalyas. After leaving Hamalayan mountains, it travels about 1000-1200 km in the plains before flowing to the Arabian sea. During it travels in the plains it is joined by several tributaries [4,5]. (Fig. 1).

Kotri barrage was constructed in 1956 and is 3000 feet long and is designed to pass a maximum flood of 24300 m<sup>3</sup>/S. It is situated about 200 km from Arabian sea. The barrage is used for regulating the flow of river Indus to irrigation channels, the surplus water is released to sea [4]. Some of which is used for lift irrigation on the side of river Indus and the remaining water drains down to sea. From 1981-

1985 Arain *et al.*, examined at Kotri barrage the transport of carbon and minerals by the river Indus to the Arabian sea [6-11], Tahir *et al.*, [12] have reported iron, zinc, nickel, copper and lead in Indus water using atomic absorption spectrometry. Akil and Khattak [13] have examined sulphate, nitrate, nitrite, ammonia, chloride, filterable residue, hardness and iron of river Indus water near Tarbela dam during 1968-69. Recently transport of residue (Total, filterable, nonfilterable, volatile and fixed) by the river Indus to irrigation channels and to Arabian sea have been reported [14]. Both nitrogen and phosphorus are important nutrients for fresh water and marine phytoplankton growth and production. The relationship between phosphorus and the biomass and species of fresh water phytoplankton communities is well established [15,16]. Nitrogen often acts in concert with phosphorus to regulate phytoplankton communities in fresh waters. Nitrogen may be more important than phosphorus in estuarine and marine communities [17,18].

In the present work two indicators of water quality: phosphorus (orthophosphate, condensed phosphate and total phosphate) and nitrogen (nitrate, nitrite, ammonia, organic nitrogen and total nitrogen) have been examined in river Indus and their transport to Arabian sea.

### Results and Discussion

The determination of nitrogen and phosphorus in different forms is important in understanding their variation in water body with biological activity

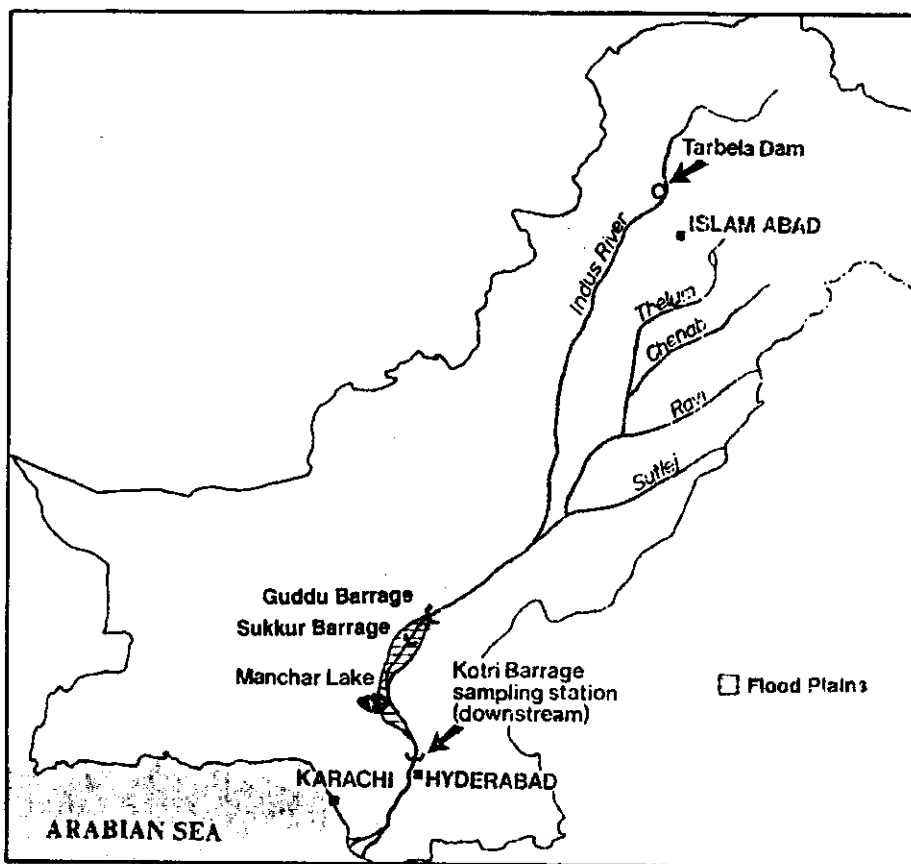


Fig. 1: Sketch map of Indus, showing sampling location at Kotri barrage near Hyderabad.

and water discharge due to seasonal changes. Total nitrogen was identified as organic, ammonia, nitrate and nitrite nitrogen which are biochemically interconvertible and are components of the nitrogen cycle. Oxidation of ammonia is termed as nitrification and reduction of nitrogen as denitrification. Total phosphorus was accounted as orthophosphate and condensed phosphate phosphorus.

#### *Organic nitrogen:*

The organic nitrogen is mostly present as proteinaceous material and the range of its variation at Kotri barrage was between 0.46 to 2.15 mg/L with average of 1.33 mg/L ( $n=24$ ) and contributed 25% of total nitrogen with higher concentration in lower water discharge during Dec. and Jan. and lower in higher water discharge during July and August (Fig. 2). In low water discharge and low water flow biological activity is maximum with the consumption of nitrate and formation of organic nitrogen.

#### *Ammonium nitrogen:*

Ammonium nitrogen contributed 14% of total nitrogen with mean concentration of 0.75 mg/L ( $n=24$ ), with overall fluctuation between 0.15-1.38 mg/L. Ammonium nitrogen concentration dropped to minimum in the months of rising water discharge in July-August and varied inversely with nitrite with correlation coefficient of  $r = -0.84$ . Phytoplankton are developed at the expense of nitrate, and is decomposed slowly producing ammonia nitrogen.

#### *Nitrate nitrogen:*

Nitrate nitrogen was most dominant contributing 64% of total nitrogen with mean concentration of 3.37 mg/L ( $n=24$ ) and over all variation during the study period was between 1.63 to 7.34 mg/L. The concentration are higher by a factor of 3.7 to 16.6 than the global mean of 0.44 mg/L [25]. Due to effective consumption of nitrate by biological

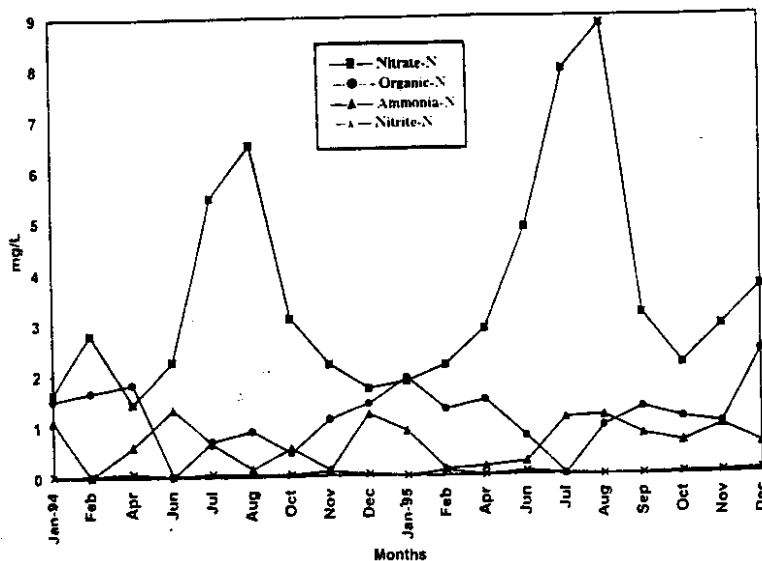


Fig. 2: Seasonal variation in concentration of nitrate, organic nitrogen nitrate, ammonia and nitrite nitrogen at River Indus at Kotri Barrage during Jan. 1994-Dec. 1995.

activity adsorption of nitrate on nonfilterable residue and settling down of the residues in low water flow, the nitrate concentration was minimum during Dec. and Jan. while during rising water discharge and high flow there is better mixing of water layers and the sediments, which may retard somewhat biological activity and extract the nitrate from the sediments and the soil bed in river basin. Thus maximum concentration was recorded in the months of July-August during peak water discharge (Fig. 2).

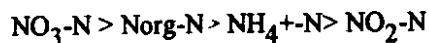
#### Nitrite Nitrogen:

Nitrite nitrogen contributed less than 1% towards total nitrogen, which reflects that it is unstable product of either nitrification of free ammonia or denitrification of nitrate. Its mean concentration was 0.04 mg/L with below detection limits to 0.09 mg/L and showed reciprocal relationship with ammonia, with correlation coefficient of  $r = 0.84$  (Fig. 2).

The level of total dissolved nitrogen which is the sum of all the nitrogen forms analysed ranged between 2.8 to 9.6 mg/L (Table-1) with mean concentration of 5.3 mg/L and followed a similar pattern of seasonal variation as nitrate, because nitrate nitrogen was the dominant form of nitrogen. The concentrations of different forms of nitrogen decreased in the following order:

Table-I: Assessment of Different Forms of Nitrogen and Phosphorus in mg/l at River Indus Kotri Barrage During Jan. 1994 to Dec. 1995

Name of the Form	Mean Values with Confidence Interval 95%	Extreme Values
Organic nitrogen	$1.33 \pm 0.24$	0.46-2.15
Ammonia-N	$0.75 \pm 0.20$	0.15-1.38
Nitrate-N	$3.37 \pm 0.79$	1.63-7.34
Nitrite-N	$0.037 \pm 0.015$	N.D-0.091
Total-N	$5.27 \pm 1.04$	2.8-9.65
Orthophosphatephosphorus	$0.048 \pm 0.032$	N.D-0.28
Condensed phosphate	$0.13 \pm 0.046$	0.036-0.38
Phosphorus		
Total acid Hydrolyz-able phosphorus	$0.18 \pm 0.06$	0.047-0.51



#### Phosphate-Phosphorus contents in River Indus

Orthophosphate: Orthophosphate-Phosphorus is a major nutrient responsible for biological activity in aqueous ecosystem even in small quantities [16]. Its concentration varied within below the detection limits to 0.27 mg/L with mean of 0.048 mg/L ( $n = 19$ ). Its proportion was 26.6% to total phosphorus with 29.57% during high flow of water (June to Sept) and 22.85% during low flow of water (October to May). Its variation with water discharge was as for nitrate, with maximum during July-August and minimum during Nov. to Jan. (Fig. 3).

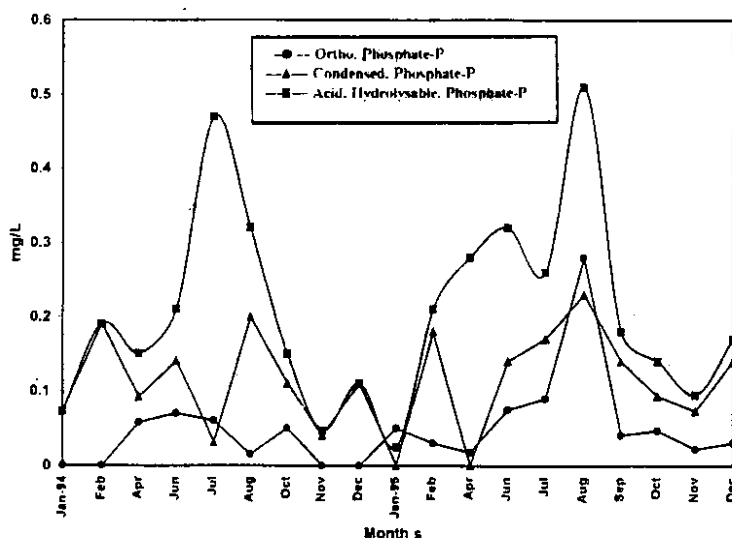


Fig. 3: Seasonal variation in concentration of orthophosphate condensed phosphate and acid hydrolyzable phosphorus at River Indus at Kotri Barrage during Jan.-1994 Dec. 1995.

#### Condensed phosphate-phosphorus:

The level of condensed phosphate phosphorus ranged between 0.036 to 0.38 mg/L, with a mean concentration of 0.12 mg/L, which is higher by a factor of 2.5 than orthophosphate and contributed 73.4% to total acid hydrolyzable phosphate. The seasonal variation was similar as for orthophosphate, with only difference that it was detected throughout the year.

#### Total acid Hydrolyzable Phosphate Phosphorus:

Total acid hydrolyzable phosphate phosphorus fluctuated between 0.047 to 0.5 mg/L with mean average of 0.18 mg/L. The seasonal variation in its concentration was similar to orthophosphate and condensed phosphate phosphorus as expected (Fig. 3).

The decrease in the concentration of phosphorus with discharge could be due to the consumption for biological production as for nitrate, but the presence of ferric oxide in the sediments is also considered to affect the phosphorus recycle, where phosphates are reversibly adsorbed from interstitial water by clay minerals, organic colloids and ferric oxide. Now in the month of July and August due to high rate of mixing of water with sediments, the possibility of release of phosphate to the water body

becomes higher. The effect is also enhanced because of decrease in dissolved oxygen due to high temperature in these months.

Inorganic nitrogen to inorganic phosphorus ratio by weight was also calculated. Inorganic nitrogen was derived by summing up the values of nitrate, nitrite and ammonia nitrogen, while acid hydrolyzable phosphorus produced the values for inorganic phosphorus. The average values of inorganic nitrogen and phosphorus during the study period provided N:P ratio of 23 and indicated that phosphorus was limiting the biological growth.

#### Nitrogen and Phosphorus Transport by River Indus at Kotri Barrage

The nitrogen and phosphorus transport by river Indus at Kotri barrage and to the sea depend upon water discharge up stream and down stream Kotri Barrage (Fig. 4) and total concentrations of nitrogen or phosphorus. The minimum monthly load of nitrogen carried was estimated to 950 tonnes/month in March and maximum of  $2.37 \times 10^5$  tonnes/month in August with total annual load of  $4.66 \times 10^5$  tonnes/year nitrogen during 1994. Similarly during 1995 minimum load of  $2.7 \times 10^3$  tonnes/month was observed in March and maximum load of  $2.72 \times 10^5$  in August, with annual load of  $5.94 \times 10^5$  tonnes/year. The coefficient of correlation

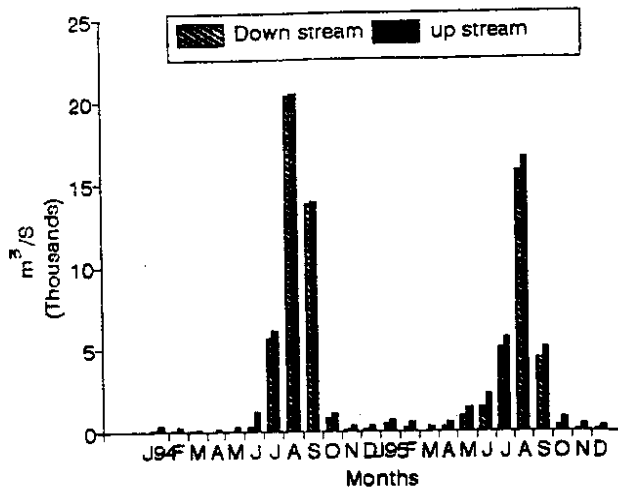


Fig.4 Monthly variation of water flow upstream and downstream of river Indus at Kotri barrage during 1994 and 1995.

of (r) of total nitrogen with water discharge was 0.88.

Total flux of nitrogen to Arabian sea was  $4.20 \times 10^7$  tonnes/year during 1994, while  $4.96 \times 10^7$  tonnes/year during 1995. The results of monthly transport of nitrogen indicates that  $2.35 \times 10^7$  tonnes/month and  $2.59 \times 10^7$  tonnes/month nitrogen transported to Arabian during August 1994 and 1995

respectively. There was no transport of nitrogen during March April 1994 and March 1995 (Fig.5).

Similarly total annual load of phosphate phosphorus on river Indus was calculated  $4.28 \times 10^4$  and  $2.12 \times 10^4$  tonnes/year during 1994 and 1995 respectively (Table 2). The maximum load of  $2.9 \times 10^4$  and  $1.31 \times 10^4$  tonnes/month were observed during August 1994 and 1995 respectively and minimum of 15.6 and 92.7 tonnes/month were recorded during February 1994 and Nov. 1995 respectively. The coefficient of correlation (r) of total phosphorus with discharge was obtained 0.68.

The transport of phosphorus down the Kotri barrage and the sea was estimated to  $4.05 \times 10^4$  tonnes/annum for 1994 and  $1.87 \times 10^4$  tonnes/annum for 1995 with maximum of  $2.95 \times 10^4$  and  $1.31 \times 10^4$  tonnes/month during Aug. 1994 and 1995 respectively. There was no water discharge down the Kotri barrage and the phosphorus transport to the Arabian sea during March and April 1994 and March 1995 (Fig. 5).

The results reflect that most of the transport of nitrogen and phosphorus along river Indus were recorded during the months of peak water discharge, which accounted for averagely 80% of nitrogen and phosphorus carried during July and August. After

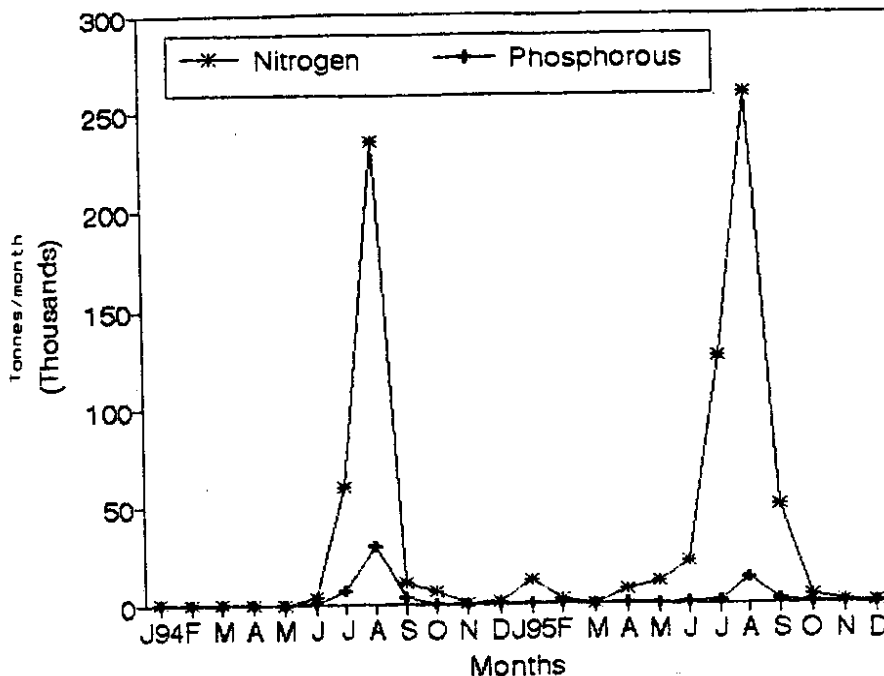


Fig.5 Transport of total nitrogen and phosphorus by river Indus down the Kotri barrage during 1994 and 1995.

Table-II: Total Flux of Nutrients (Nitrogen and Phosphorus) in Tonnes/Month on River Indus at Kotri Barrage and its Transport towards Arabian Sea During Jan. 1994 to December 1995

Month	Discharge (m <sup>3</sup> /S)		Nitrogen		Phosphorus	
	U/S	D/S	At River Indus	Arabian Sea	At River Indus	Arabian Sea
Jan-94	380.96	84.57	4315.15	958.0	72.08	16.00
Feb	308.00	23.48	4343.0	331.0	15.60	11.86
Mar	86.3	1.01	950.20	10.67	39.21	--
Apr	208.43	--	1512.48	--	31.20	--
May	363.40	--	3208.00	--	113.00	--
June	1186.77	289.76	15256.50	3725.20	938.70	240.61
July	6141.24	5614.37	69756.60	59806.60	7481.20	6839.20
Aug	20484	20321.64	236639.75	234917.26	29733.00	29497.20
Sept	13883.62	13792.82	112277.40	11154.10	3598.00	3575.10
Oct	1146.62	798.17	9616.00	6743.88	445.80	310.26
Nov.	402.32	73.17	3647.00	662.20	41.67	7.58
Dec.	386.51	116.28	4332.20	1305	110.20	33.15
Total Load tonnes/Y in 1994			465854.10	420002.71	42804.68	40530.76
Jan-95	692.31	480.76	17316.60	12025.15	448.61	311.53
Feb	539.50	216.06	7027.30	2816.00	265.70	106.37
Mar	332.04	--	3081.00	--	172.1	--
Apr	553.00	305.00	12685.37	6996.45	401.30	221.35
May	1461.00	938.00	18442.20	11840.40	871.00	559.20
June	2278.00	1471.60	34541.70	21486.25	1003.70	624.65
July	5696.00	5040.40	142030.00	125672.60	1771.00	1567.64
Aug.	16566.00	15792.00	272233.70	259514.35	13311.11	13098.50
Sept	5105.00	4397.00	58221.50	50147.00	2381.78	2051.46
Oct.	865.00	394.60	8856.20	4040.00	313.89	143.20
Nov.	490.00	103.40	6286.89	1321.53	92.71	19.48
Dec.	363.00	66.00	6049.90	1098.28	160.00	29.10
Total Load Tonnes/Y in 1995			586773.00	496957.00	21193.00	18732.70

U/S = upstream, D/S = Down stream Kotri barrage.

supplying the water for irrigation purposes 70 to 91% transport of nitrogen and phosphorus was observed down to Kotri barrage to the sea.

### Experimental

A water sample about 100 m upstream from the Kotri barrage was collected every four to six weeks from the boat by mixing 2 to 4 sub samples of equal volume from a vertical section. The water samples were collected within 3-9 inches from the surface of water. The samples were mixed well and a sample of 2.5 L was transferred to a clean glass bottle. Analysis of nitrogen and phosphorus was made immediately after collection of the sample. If prompt analysis was not possible, the sample was acidified to pH 1.5-2 with sulphuric acid (1N) and stored just above the freezing point. Nitrite was preserved by adding 40 mg/L HgCl<sub>2</sub> and stored at 4°C.

Nitrate, nitrite, ammonia and orthophosphate were determined by spectrophotometer. Nitrate was determined using brucine sulphate as derivatizing

reagent [19,20] or after reduction of nitrate to nitrite in a copperized cadmium column [21]. Both the methods gave a similar results. The batch samples of 1 and 2 were analysed using cadmium column reduction method but became of the ease of procedure using brucine sulphate as derivatizing reagent, all the remaining batch samples were analysed using brucine method. Nitrite was determined by diazotized sulphanilic acid with N-(1-naphthyl)ethylenediamine dihydrochloride [21]. The ammonia was determined by phenate method [21]. Organic nitrogen together with ammonia was determined by micro-Kjeldahl method [21,22] Subtraction of ammonia determined by the phenate [27] method from Kjeldahl nitrogen gave organic nitrogen. Orthophosphate was determined by reduction of phosphomolybdate to molybdenum blue with ascorbic acid. Acid hydrolyzable phosphorus was determined by persulphate acid digestion method, followed by estimation as for orthophosphate. Subtraction of orthophosphate from total acid hydrolyzable phosphorus gave condensed phosphorous [21]. Average monthly data on water discharge

were obtained from control room department of irrigation. Kotri barrage. The quantity of water discharge was calculated from the relation  $Q = A \times V$ ; where  $A$ =area and  $V$  = velocity of water. Area of the water body was obtained by multiplying average depth and breadth. The depth of the water was measured by sounding rod and velocity with velpot meter. In order to calculate the total load of nitrogen and phosphorus on river Indus and transport down stream Kotri barrage to Arabian sea, the amount in mg/L were multiplied with one to convert  $g/m^3$ . Total load in tonnes/month = concentration ( $g/m^3$ ) x av. water discharge (m/s) x  $60 \times 60 \times 24 \times 30 \times 0.00001$  = concentration ( $g/m^3$ ) x av. water discharge (m/s) x 2.592. The water discharge in cusec was multiplied by 0.028 to convert into m<sup>3</sup>/s [14].

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