Determination and Transport of Metal Ions in River Indus at Kotri Barrage

V.K. DEWANI, I.A. ANSARI AND M.Y. KHUHAWAR*
Dr. M.A. Kazi Institute of Chemistry,
University of Sindh, Jamshoro, Sindh, Pakistan

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Summary: Water samples from river Indus at Kotri barrage were collected at an interval of 4-6 week and analysed for sodium, potassium, calcium, magensium by flame atomic absorption spectroscopy (FAAS). Their average concentration ranged 5.6 to 93.4 mg/L. Copper, iron, nickel, cobalt, lead, manganese, cadmium and zinc were analysed by FAAS after preconcentration by solvent extraction. The average amount of metal ion (n=20) found were in the range of 4.0-560 ug/L. The variation in the metal contents with seasons were recorded. Transport of metal contents down the Kotri barrage to Arabian sea were also calculated.

Introduction

River Indus represent one of the major water distribution system in the South Asia along with Gangas, Brahmputra and Irrawady of India, Bangladesh and Burma. It is eleventh largest river in the terms of drainage, river discharge and sediment transport. It originates from Himalya mountains and upon leaving them. the river traverse across the broad Indus plains to nearly 1000-12000 k.m before flowing to Arabian Sea [1,2].

The river flow is highly variable and generally is low in winter, when snow melt and rain fall are low. High flow occurs in summer, when snow melts extensively and dominant monsoon rains augments many fold. The peak flow occurs from July to September, producing many floods, which spread the slit, enriching the soil for cultivation.

Kotri barrage is situated at 200 k.m from Arabian sea. It is 3000 feet long and is designed to pass maximum flood of 24500 m^3/Sec. The barrage is used for regulating the flow of river water to irrigation channels. During dry season the barrage gates are regulated to reduce the flow of Indus river to the sea. In wet season after supplying water to channels, the surplus water is released to the sea.

A number of studies have been reported on river Indus at Kotri barrage mainly determination and transport of carbon and minerals, residues, nitrogen and phosphorus along the river [3-9].

The determination of metal ions in natural water ways has immense importance, because the information would provide the status of nutrient in the water and would help to calculate the transport of metals. Sodium, potassium, calcium and magensium could easily be determined by flame atomic absorption spectrometry (FAAS). However, difficulties were encountered in the determination of Fe, Cu, Ni, Zn, Mn, Co, Cd and Pb because of their low concentration. Several preconcentration methods have been proposed such as ion exchange [10], coprecipitation [11], evaporation [12], freeze drying [13], flotation [14] and solvent extraction [15,16].

The solvent extraction procedures are easier and required preconcentration is achieved with a significant decrease in matrix effects. For simultaneous multielemental analysis based on preconcentration by solvent extraction, a number of chelating reagents are proposed. These includes diethyl dithiocarbamate [15,19-21], ammonium

*To whom all correspondence should be addressed.

It is a pleasure for me to dedicate our present article to Professor Dr. Atta-ur-Rahman on his 60th birthday.
Professor Atta-ur-Rahman is a dedicated researcher and educator, great thinker and able administrator. He has remained a source of aspiration for more than two decades for the scientific community of Pakistan, particularly for chemical research.
Among his admires are his students, co-workers, and national and international scientific community. He has gained wide recognition as the Minister of Science and Technology due to his wisdom and far sightedness in enhancing the role of scientific community of Pakistan in national development.
On behalf of my colleagues and our research group at University of Sindh, I wish Professor Rahman a happy 60th birthday.
Prof. M.Y. Khuhawar

pyrolidine dithiocarbamate (APDC) [20, 22-23], hexamethylene dithiocarbamate [24], pentamethylene dithiocarbamate [25], 8-hydroxyquinoline (oxine) [26], dithiozone [27], 5-(2'-carbomethyoxy-phenyl) azo-8-quinolinol [28] and 3-amino-3,5-di-2-pyridiyl-4H-1,2,4-triol [29]. A reagent or a mixture of two reagents have been used to complex as many of the required metals as possible prier to solvent extraction [30].

The present work examines 12 metal contents of river Indus at Kotri barrage during 1993-96. The metal contents were determined directly by FAAs and after preconcentration by solvent extraction using APDC and oxine as complexing reagents. The variation in the metal contents with water discharge and their transport to the sea was also examined.

Results and Discussion

The average results of major cations (Table I) indicates that calcium was dominant following by sodium, magensium and potassium in decreasing order. The % contribution of calcium, magneisum sodium and potassium calculated on the basis of milli equivalent was 44.63, 36.0, 17.95 and 1.29 respectively. Sodium indicated maximum % variation (8.2 - 37.7%) may be because of the exchange of sodium ions with sediments [6]. The total cationic concentration fluctuated between 7.1 to 19.55 meq/L and was higher by the factor of 2.84 than the upper level of the cations reported during 1982.83 at river Indus at Kotri barrage [4].

Table-I: Average Amounts of Major Cations (n = 32). Paranthesis Show Min-Mix. Values

Major Cations	Conc. meq/L
Na	2.16 (0.6-6.39)
K	0.14 (0.09-0.28)
Ca	4.7 (3.40-6.98)
Mg	3.85 (2.2-5.9)

B.D = below detection limit.

The seasonal variation of the cations was not uniform. Sodium attainded highest level in April and lowest during months of peak discharge (July-August). Calcium indicated a similar pattern. Magensium indicated maximum concentration in August and minimum in May 1993. The trends of variation of these cations during 1994 were not exactly similar, because of high water discharge in river Indus (About 4 times during peak months of 1994 than 1993) and conditions of flood. This resulted in rising concentration of the metals with peak discharge, possibly due to the dissolution of the cations from flooding regions (Fig. 1). Sodium adsorption ratio (SAR) was calculated to 1.41 with a range of 0.54 to 2.78 and indicates a suitable source for agriculture.

The eight elements Fe, Cu, Ni, Mn, Pb, Zn, Co, and Cd were examined quantitatively from June 1994 to March 1996 (n=20). The % recovery of each of the metal was exmained using analytical procedure and the average recovery (n=4) was observed within 88-100% with coefficient of variation within 1.2-3.4%. The average concentrations of Fe, Cu, Ni, Mn, Pb, Zn, Co and Cd observed, were 560, 36, 13, 52,

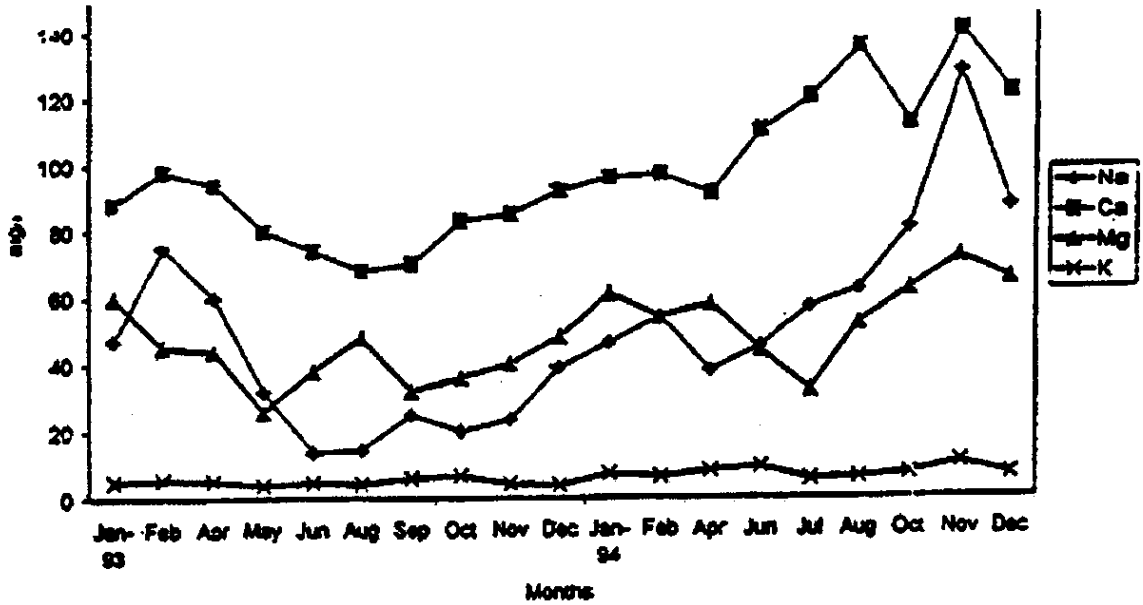

Fig.1: Seasonal profile of Na, k, Ca, Mg at river Indus at Kotri barrage during 93 and 94.

57, 60, 18 and 4 ug/L respectively (Table II). The concentration of iron was greater by a factor of 13-220 than other seven elements. The higher contents of iron could be due to the extraction of iron from the sediments at the adjusted pH 2-2.5 for preservation. The concentration of metals exhibited the following decreasing sequence.

Fe>Zn>Mn>Pb>Cu>Ni~ Co>Cd

Table-II: Average Concentration of Metal Ions (n=20) with Confidance Interval at 95% Paranthesis Show MIN.-MAX Values

METAL ION	CONC. ug/L
Fe	560±210 (280-800)
Cu	36.0±7.0 (18-75)
Ni	13.0±5.0 (3.0-27.0)
Mn	52±20 (27-81)
Pb	57±17 (29-98)
Zn	60±13 (40-85)
Co	18±3 (10-31)
Cd	4.0 ±1.2 (N.D-8)

B.D = below detection limit.

The influence of water discharge on the variation pattern of the metal contents was examined. It was observed that the concentration of iron and manganese started elevating during rising water stage from June. Copper, lead and zinc indicated maximum values in August, thereafter, their concentration dropped in following water stage.

The higher concentration of the metals with high water discharge could be due to the extraction or desorption of the metals from the sediments in rising water stage [31]. Similar results have been reported also from some other rivers of the world [32,33]. The observed results for metal analysis of river Indus at Kotri barrage are some what comparable with the reported results for river Nile (Egypt) [34].

The transport of the metals Fe, Cu, Ni, Mn, Pb, Zn, Co and Cd down the Kotri barrage were calculated based on the water discharge and concentration of metals in water analysed. The average monthly transportation of the metals are summarized in table III. The results indicate that iron transported highest value of 19778 tonnes during August and cadmium as lowest with 0.61/tonne during December.

Experimental

A water sample about 200 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 the 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 clean glass bottles. The unfiltered water sample (1 L) was acidified to pH 2.0-2.5 with sulphuric acid (1 N) and was used for the determination of metal contents.

Solvent Extraction Procedure

Well mixed sample (300 ml) was transferred to separating funnel and to it was added ammonium acetate-acetic acid buffer pH 4 (8 ml), followed by APDC (1.5 ml, 5% w/v in water), oxime (1.5 ml, 2% w/v in methanol) and MIBK (20 ml). The mixture was shaken well for 5-7 min. and layers were allowed to separate. Organic layer was collected and aqueous layer was added ammonia solution (2%, 5 ml) to

Table-III: Mean Monthly (n=3) Transport of Metal Contents from River Indus at Kotri Barrage to Arabian Sea 1994-1996.

	METAL IONS (TONNES/MONTH)							
MONTH	Fe	Cu	Ni	Mn	Pb	Zn	Co	Cd
JAN	527.5	34.0	12.2	49.0	53.6	56.5	17.0	3.76
FEB	191.3	12.3	4.4	17.7	19.5	20.5	6.1	1.4
MAR	101.6	6.5	2.4	9.4	10.3	11.0	3.3	0.7
APR	610.2	39.2	14.1	56.3	62.1	65.1	19.6	4.3
MAY	916.0	59.0	21.3	84.8	93.2	98.2	29.4	6.5
JUNE	1413	90.6	32.7	128.0	143.6	151.2	45.4	10.0
JULY	7407	459.4	172.0	687.6	753.8	793.5	238	52.6
AUG	19778	1271	460	1836	2012	2119	635.6	141.2
SEP	8918	573.3	207	827	907.7	955.6	286.4	63.5
OCT	634.5	40.7	14.0	59	64.6	68.0	20.4	4.5
NOV	95.3	6.1	2.2	8.8	9.7	10.2	3.0	0.65
DEC	88	5.6	2.0	8.1	8.9	9.4	2.8	0.61

adjust the pH to 9.2. APDC (0.5 ml, 5% w/v), oxime (0.5 ml, 2% w/v) and MIBK (20 ml) were added and the extraction was repeated. The combined extract was acidified with nitric acid (2.5 ml, 65%) and contents were shaken for 3-5 min. Doublly distilled water (15 ml) was added and contents were again shaken for 3-5 min. The aqueous layer was collected and the volume was adjusted to 25 ml. Metal contents of iron, cobalt, nickel, lead, copper, manganese, cadmium and zinc were evaluated from calibration curves prepared, following the same procedure with double distilled water (300 ml) containing 0-250 ug iron, cobalt, nickel, lead, 0-125 ug copper and manganese and 0-50 ug cadmium and zinc. Reagent blank was also prepared from doublly distilled water (300 ml) following the same extraction procedure.

Sodium, potassium, calcium and magnesium were determined in water samples after dilution. The metal contents were determined using Varian Spectr AA-20 atomic absorption spectropho-tometer. Air-acetylene flame with standard burner head was used at the conditions recommended by the manufacturer. The analyses were carried out in triplicate with delay time of 3 sec and integration time of 3 sec.

Average monthly data on water discharges were obtained from control room department of irrigation, Kotri barrage. The quantity of water discharge was calculated from the relation Q=AxV; where A=area and V=velocity of water. Area of the water body was obtained by multiplying average depth and breath. The depth of the water was measured by sounding rod and velocity with velpotmeter. The load of metal ions transported down stream of Kotri barrage to Arabian sea was calculated by multiplying the concentration in mg/L with a factor of one to convert to g/m^3. Total load in tones/month = concentration (g/m^3) x average water discharge (m^3/S) x 60x60x24x30x0.00001 = concentration (g/m^3) x av. water discharge (m^3/S) x 2.592. The water discharge in cusec was multiplied by 0.028 to convert into m^3/S. Sodium adsorption ratio (SAR) was calcualted using the relation: SAR = $Na^+/(Ca^{2+}+Mg^{2+}/2)$. The concentration of each ion are in milli equivalent

Conclusions

The work examines the metal contents of river Indus at Kotri barrage. The results are average of about 3 years. The metal contents were observed within the safe limits for human consumption, but iron contents are slightly on the higher side, may be due to the extraction from sediments, at pH (2.5) adjusted for the preservation of water samples.

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