Evaluation of Metal Contents in Phulleli Canal and Hyderabad City Sewage by Flame Atomic Absorption Spectrophotometer

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

(Received 15h June, 1998, revised 18th March, 1999)

Summary: Samples from Phulleli canal and sewage water being added to this canal while passing through Hyderabad city was monitored for metal contents using flame atomic absorption spectrophotometer (FAAS). Twelve sampling stations were selected, 7 from Phulleli canal and 5 from sewage water. Samples were collected at the interval of 6-8 weeks during 1993-95. Sodium(I), potassium(I), calcium(II) and magnesium(II) were determined after appropriate dilution and their average amounts were within the range of 5.8 - 173.0 µg/L in Phulleli canal and 43 - 527 µg/L in Hyderabad sewage, whereas copper(II), cobalt(II), cadmium(II), iron(II), manganese(II), nickel(II), lead(II) and zinc(II) were determined by complexation with ammonium pyrrolidine dithiocarbmate (APDC) and 8-hydroxyquinoline (oxine) followed by extraction in methyl isobutyl ketone (MIBK). After back extraction, metal contents were determined in aqueous phase. Their values varied within 4-130 µg/L and 6.5 - 380 µg/L, expect, iron whose values varied upto 930 - 1360 µg/L and 830 - 2670 µg/L in Phulleli canal and sewage water respectively. Variation in metal contents with the water discharge in the Phulleli canal and sewage water added was determined to evaluate the distribution of metal contents in Phulleli canal.

Introduction

Phulleli canal originates from river Indus at Kotri barrage and passes through Hyderabad city with population of about 2.0 million. Most of the sewage of Hyderabad city and industrial effluents ends on either side of Phulleli canal. It travels about 20 km from Hyderabad city, followed by 70 km to provide water for agricultural purposes and source of surface water in the region. The description about the Phulleli canal and the impact of sewage and industrial effluents on the variation of chemical oxygen demand and residues in Phulleli canal has been reported [1]. Recently a preliminary results of metal contents of Phulleli canal have been presented [2].

For the determination of metals in water the major cations, sodium(I), potassium(I), calcium(II) and magnesium(II) are conveniently determined by flame atomic absorption spectrophotometer (FAAS), but as copper(II), cobalt(II), cadmium(II), iron(III), nickel(II), manganese (II), lead(II) and zinc(II) are generally present in trace amounts (below 1 ppm) therefore it requires to be concentrated prior to measurement. A number of preconcentration methods are reported including ion exchange [3], coprecipitation [4], evaporation [5], freeze drying [6] and liquid - liquid extraction [7,8]. Liquid - liquid

extraction methods are considered to be superior, because of simplicity and low blank levels. For simultaneous multielemental analysis a number of complexing reagents are reported eg diethyl dithiocarbamate [7,9-14] ammonium pyrrolidine dithiocarbamate (APDC) [12,15-18] hexamethylene pentamethylene dithiocarbamate [19] dithiocarbamate [20] 8-hydroxyquinoline (oxine) [21,22] and dithiozone [23,24]. Sturgeon et al., [25] have reported preconcentration procedure for the determination of cadmium(II), lead(II), iron(II), manganese(II). cobalt(II), chromium(III), nickel(II) in coastal sea waters by graphite furnace spectrophotometer absorption atomic preconcentration, employing solvent extraction technique with APDC and oxine into methyl isobutyl ketone (MIBK). The trace metals are further extracted in 1.5 M nitric acid. A slightly modified procedure of Sturgeon et al., [25] has been used for the determination of copper, cobalt, cadmium, iron, manganese, nickel, lead and zinc using FAAS in canal and sewage water samples to evaluate variation in the metal contents with water discharges in Phulleli canal. This paper also examines the concentration of metal ions present in micro and semi micro level to evaluate the extent of pollution in Phulleli canal and city sewage in comparison with the national and international standards.

^{*}To whom all correspondence should be addressed.

Table-1: Average amount of major metal ions in Phulleli canal with confidence interval at 95% (n=12)

			Sampling	station			
Metal ion mg/L	1	3	5	7	9	11	12
mg/L Na ⁺¹	47.7 ± 20.68 (13-147)	103.2 ± 85.6 (21-641)	80.6 ± 53.7 (16-394)	73.6 ± 52 (18-383)	102 ± 46 (23-353)	77 ± 33.66 (19-384)	.75 ± 30.5 (15-363)
K*1	5.8 ± 0.90 (3.8-11.3)	13.1 ± 8.44 (4.1-153.2)	14.6 ± 9.79 (4.7-56.2)	13.5 ± 9.62 (4.5-59.4)	21.16 ± 10 (6.2-73.7)	15 ± 11.8 (5.3-71.5)	12.8 ± 7.9 (5.1-55.6)
Ca ⁺²	91.2 ± 11.27 (61-180)	167.6± 84.5 (70-585)	151.7 ± 64 (73-450)	133 ± 47.68 (68-370)	173 ± 39.6 (95-325)	135.4 ± 36.8 (78-350)	130.3 ± 41.25 (72-325)
Mg ⁺²	50.7 ± 8.7 (19-62)	107.3 ± 70.4 (28-440)	90.4 ± 54 (23-54)	77.7 ± 41.4 (22-270)	95.8 ± 33.4 (25-255)	75 ± 30.5 (22-240)	71.5 ± 33.6 (21-235)

Parentheses show min - max values

Table-2: Amount of average major metal ions in sewage water with confidence interval at 95% (n=12)

		Sampling Station			
Metal ion mg/L	2	4	6	8	10
mg/L Ca ⁺²	488 ± 40.7 (390-660)	201 ± 23.1 (143-245)	234 ± 16.5 (193-290)	245 ± 20.5 (203-320)	296 ± 66.82 (160-600)
Mg ⁺²	380 ± 74.25 (221-770)	109 ± 27 (28-250)	142 ± 26.4 (61-245)	153 ± 31 (66-275)	168 ± 62 (57-400)
Na⁺	527 ± 103.4 (283-924)	153 ± 31 (68-262)	203 ± 43 (114-438)	237 ± 45 (123-404	342 ± 112 (148-760)
K ⁺¹	72.5 ± 27 (34-135)	56.3 ± 11 (27-91)	64.4 ± 10 (45-105)	52 ± 6.2 (35-72)	43 ± 14.1 (20-49.5

Parentheses show min - max values

Results and Discussion

In order to examine quantitatively metal ion contents in Phulleli canal and sewage water ending in Phulleli canal a number of samples were collected and analysed for metal contents. The average results of analyses of sodium(I), potassium(I), calcium(II) and magnesium(II) with confidence interval at 95% and range at each sampling station for Phulleli canal (Table-1) indicate that average concentration were observed for calcium(II) 91.2 - 173.0 µg/L. magnesium(II) 50.7 - 107.0 µg/L, sodium(I) 47.7 -103.0 μ g/L and potassium(I) 5.8 - 21.2 μ g/L. The concentrations are in order Ca > Mg > Na > K. The average results in Table-2 for sodium(I), potassium(I), calcium(II) and magnesium(II) for sewage water indicate slightly different pattern with Ca > Na > Mg > K with concentration of calcium(II) within 201 - 488 mg/L, sodium(I) 153 - 527 mg/L, magnesium(II) 109 - 380 mg/L and potassium(I) 43 -72.5 mg/L. Sodium is the constituent of diet and passes through intestine, leads to increase the sodium concentration in sewage water. The high concentration of calcium in Phulleli canal and sewage water may be due to rocky bed right from the river Indus and around Hyderabad city, where some of the calcium carbonate dissolves, as a result calcium concentration rises.

The higher concentration of sodium(I), calcium(II) and magnesium(II) in sewage are increasing the concentration of Phulleli canal water as added with maximum at sampling station 9 (Fig. 1), because of addition of the large amount of the sewage from Darya Khan pumping station (Table-3). In order to examine the effect of variation in the water discharge in Phulleli canal on the concentrations of the metal ions, the concentration of sodium(I), potassium(I), calcium(II), and

Table-3: Average quantity of waste water and the % contribution of waste water from different sewage sampling stations discharged into Phulleli canal

Waste water station	*Average quantity discharged m³/day	% contri- bution of the total discharged
Jacob Tank Canto ment board waste	13944 ± 1397	6.18
Kali Mori open drain	56376 ± 2232	25
Open drain near old power house	42323.44 ± 3229.82	18.76
Darya Khan Panhwer pumping station	96441 ± 4151	42.75
Site area pumping station near Nara Jail	13500 ± 1963.4	5.98
Other sources	3000 ± 855-	1.33
Total	225584.44	100

*Mean of 12 determinations

[±] Confidence interval at 95%

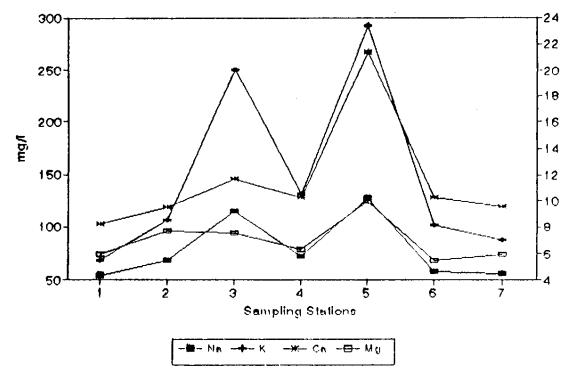


Fig. 1: Variation of sodium, potassium, calcium and magnesium along phulleli canal during March 1995. Sampling station near (1) Akhund Village (3) CIA Centre (5) Shakhipir Road near Liaquat Colony (7) Bhatti village near Fateh Textile Mills (9) Darya Khan village (11) Pono Koli village (12) Hosri bridge near Behar Colony.

magnesium(II) recorded during the months of March and August are indicated in (Fig. 1,2). Their concentrations were highest in March compared to that of August. During the month of August owing to the higher water discharge in Phulleli canal (Table-4) the metal ions are diluted including sewage water added, resulting the decrease in their concentrations. However in month of March they are diluted to lesser extent due to low water discharge in Phulleli canal, with the result that their concentrations are observed on higher side.

Phulleli canal water is mostly used for agricultural purposes, thus sodium absorption ratio (SAR) [26] was calculated, SAR ratio was observed within 3.3 to 5.6 and indicate a reasonable water quality for agricultural purposes.

Transition metal ions Cd(II), Cu(II), Fe, Co(II), Mn(II), Ni(II), Pb(II) and Zn(II) were determined in Phulleli canal and sewage water samples. The metal ions were determined by FAAS.

Table-4: Mean monthly water discharge in old Phulleli canal

Month Year	Mean Discharge (m³/S)
August 1993	240
September -	173.6
October	113
November	64.37
December	4.1
January 1994	53
February	54
March	21.7
April	62.1
May	87.0
June	240
July	181
August	154
September	18.34
October	83
November	92
December	67
January 1995	38
February	75
March	77
April	6.6
May	128
June	224
July	212
August	233

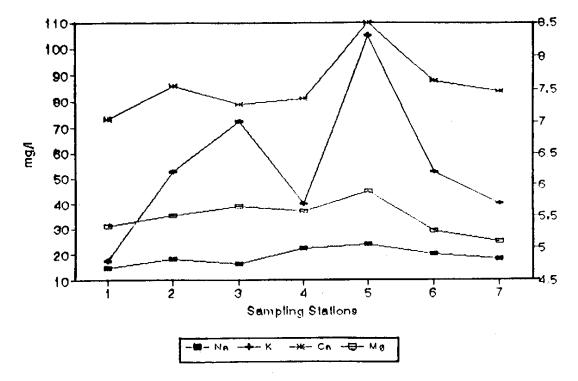


Fig. 2: Variation of sodium, potassium, calcium and magnesium along phulleli canal during August 1995. Sampling station near (1) Akhund village (3) CIA centre (5) Sakhipir Road near Liaquat Colony (7) Bhatti village near Fateh Textile Mills (9) Drya Khan village (11) Pono Koli village (12) Hosri bridge near Behar Colony.

Preconcentration by solvent extraction procedure was examined. Different complexing reagents and extraction procedures were checked. A mixture of APDC and oxine as complexing reagents was added and two extractions at pH 4 and 9.2 were carried out with MIBK for the quantitative transfer of metal ions from aqueous to organic phase. The metal ions were back extracted and determined in aqueous phase. The instrument was calibrated using 5 standard solutions of known concentration of metal ions and metal ion solutions after solvent extraction were recorded as samples, to calculate % recovery of each metal ion. The average % recovery (n = 4) was observed within 88 - 100%, with coefficient of variation (C.V) within 1.2 -3.1% (Table-5).

The results of average concentrations of Cd, Cu, Fe, Co, Mn, Ni, Pb and Zn with 95% confidence interval with range, consisting of minimum and maximum values for Phulleli canal and sewage water (Table-6 and 7) indicate that the concentration of the metal ions in sewage water is higher than

Table-5: % Recovery of metal ions by preconcentration (n=4)

mg/L	Amount Added mg/L	Amount Found mg/L	% Recovery	C.V%
Fe ⁺²	2.0	1.94	97	2.7
Fe ⁺² Cu ⁺² Pb ⁺² Cd ⁺² Zn ⁺² Ni ⁺²	1.0	0.95	95	1.2
Pb ⁺²	2.0	1.84	92	1.38
Cd ⁺²	0.4	0.37	94	1.48
Zn ⁺²	0.4	0.36	91	2.1
Ni ⁺²	2.0	1.86	93	1.6
Mn ⁺² Co ⁺²	1.0	0.88	88	3.1
Co ⁺²	2.0	1.8	90	2.8

Phulleli canal. Therefore as Phulleli canal travels along Hyderabad city, their concentrations increase and reach a maximum value at sampling station 9. Thereafter their concentrations gradually decrease, may be due to the flocculation action of the sediments and adsorption at the water pH within 7.6 - 8.5 [27] with the result that the metal ions concentration in Phulleli canal is slightly higher at the point of exit from Hyderabad city than the entry point.

Table-6: Amount of trace metal ions at different sampling along the phulleli canal (n=12)

	Sampling Station						
Concen- tration (µg/L)	1	3	5	7	9	11	12
Fe ⁺¹	930 ± 250 (410-1550)	908 ± 480 (430-2000)	1260 ± 490 (350-2.750)	1110 ± 430 (390-3060)	1360 ± 510 (350-3120	1041 ± 390 (270-2500)	970 ± 280 (410-1650)
Cu ⁺²	34 ± 7.5 (17-70)	45 ± 15 (18-73)	55 ± 27 (20-180)	47 ± 12 (29-66)	59 ± 21 (33-98)	51 ± 17 (27-87)	46 ± 11 (20-76)
Ni ^{+2*}	12 ± 5.0 (2-25)	018 ± 8.0 (3-41)	21 ± 9 (6-60)	19 ± 8 (4-41)	34±9.5 (7-57)	25.4 ± 9.1 (5-47)	20 ± 7.5 (5-37)
Mn ⁺²	046 ± 8.5	92 ± 41	88 ± 44	96 ± 50	130 ± 48	105 ± 54 (41-290)	108 ± 49
Pb ⁺²	(21-68) 55 ± 17	(30-260) 68 ± 22	(35-270) 80 ± 27	(38 - 310) 74 ± 25	(57-270) 110 ± 32	89.4 ± 27	(53-310) 71 ± 19
Zn ⁺²	(27-98) 68 ± 13 (49-110)	(23-130) 79 ± 32 (40-140)	(38-185) 110 ± 42 (42-260)	(35-181) 89 ± 31 (35-270)	(45-172) 130 ± 63 (40-430)	(35-120) 98 ±43 (38-277)	(33-130) 81 ± 35 (31-240)
Co ⁺²	018 ± 3.1 (10-030)	23 ± 5 (11-35)	26 ± 4.3 (9-39)	24 ± 6.3 (8-48)	33 ± 5.1 (20-46)	29 ± 6.1 (10-48)	(31-240) 22 ± 4.7 (21-45)
Cd ⁺²	4± 1.2 (3-10)	5.5 ± 1.3 (3-10)	6 ± 1.2 (4-15)	5.2 ± 1.0 (3-11)	7.3± 1.3 (5-12)	6.6 ± 1.4 (5.7-12)	6.1 ± 1.5 $(4-12)$

Mean values, ± Confidence interval at 95% Parentheses show min - max values

Table-7: Chemical assessment of metal ions at different sewage stations (n=12)

	Sampling Stations					
Concentration (mg/L)	2	4	6	8	10	
Fe ⁺²	0.83 ± 0.31	1.23 ± 0.48	2.76 ± 1.31	1.11 ± 0.51	2.11 ± 0.35	
	(0.66-1.75)	(0.56-2.35)	(0.68-7.05)	(0.4-1.92)	(0.95-3.12)	
Cu ⁺²	0.059 ± 0.012	0.17 ± 0.11	0.19 ± 0.12	0.10 ± 0.029	0.15 ± 0.41	
	(0.05-0.11)	(0.065-0.35)	(0.085-0.55)	(0.045-0.13)	(0.055-0.35)	
Ni ⁺²	0.030 ± 0.007	0.054 ± 0.017	0.084 ± 0.22	0.051 ± 0.015	0.079 ± 0.02	
	(0.007-0.048)	(0.009-0.09)	(0.01-0.13)	(0.009-0.094)	(0.021-0.15)	
Mn ⁺²	0.27 ± 0.11	0.25 ± 0.09	0.38 ± 0.08	0.18 ± 0.034	0.40 ± 0.17	
	(0.079-0.5)	(0.068-0.48)	(0.09-0.62)	(0.078-0.27)	(0.071-0.71)	
Pb ⁺²	0.087 ± 0.022	0.13 ± 0.05	0.15 ± 0.04	0.094 ± 0.033	0.16 ± 0.06	
	(0.05-0.14)	(0.065-0.48)	(0.07-0.33)	(0.066-0.022)	(0.08-0.38)	
Zn ⁺²	0.097 ± 0.035	0.24 ± 0.08	0.36 ± 0.15	0.18 ± 0.13	0.16 ± 0.062	
	(0.05-0.24)	(0.09-0.39)	(0.16-0.82)	(0.055-0.67)	(0.06-0.31)	
Co ⁺²	0.035 ± 0.008	0.045 ± 0.008	0.044 ± 0.009	0.043 ± 0.007	0.063 ± 0.039	
	(0.015-0.057)	(0.022-0.085)	(0.018-0.075)	(0.03-0.058)	(0.047-0.091)	
Cd ⁺²	0.0065 ± 0.0018	0.0085 ± 0.002	0.011 ± 0.0025	0.009 ± 0.0014	0.0135 ± 0.0035	
	(0.004-0.014)	(0.006-0.018)	(0.008-0.019)	(0.005-0.012)	(0.009-0.02	

Mean values, ± Confidence interval at 95%
Parentheses show min - max values

The results of analyses of metal contents in sewage water (Table-7) also indicate that their concentration increases along Hyderabad city and reach maximum in sewage water (sampling station 6) coming from the middle of Hyderabad city, which is thickly populated and, where cottage industry is located.

The average concentration of metal ions along Phulleli canal observed were iron 0.93 - 1.3 mg/L, zinc(II) 68 - 130 μ g/L, manganese (II) 46 - 139 μ g/L, lead(II) 55 - 100 μ g/L, copper(II) 34 - 59

μg/L, cobalt(II) 18 - 33 μg/L, nickel (II) 12 - 34 μg/L, and cadmium (II) 3 - 6 μg/L. Similarly the sewage water indicated slightly different pattern with average metal concentrations of iron 0.82 - 2.76 mg/L, manganese(II) 270 - 400 μg/L, zinc(II) 97 - 360 μg/L, lead(II) 87 - 160 μg/L, cobalt 35- 44 μg/L, nickel(II) 30 - 84 μg/L, and cadmium (II) 6.5 - 18 μg/L.

The effect of water discharge in Phulleli canal on the metal contents was also examined here. During the month March when water discharge was

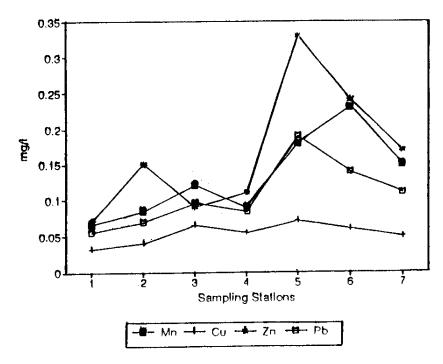


Fig. 3: Variation of concentration of manganese, copper, zinc and lead along phulleli canal during March 1995. Sampling station near (1) Akhund village (3) CIA centre (5) Sakhipir Road near Liaquat Colony (7) Bhatti village near Fateh Textile Mills (9) Drya Khan village (11) Pono Koli village (12) Hosri bridge near Behar Colony.

low and during August when water discharge was high were selected. It was observed that during August their concentrations were higher as compared to March (Fig. 3 and 4). In August due to high flow a large amount of sediments are carried with water [2], thus it may be metal ions are extracted from the sediments due to better mixing in the water body as it travels along Phulleli canal and rises the metal contents on the higher side. During March due to low flow and low water discharge, the sediments settle down in the bottom of the canal. Thus it may be due to the adsorption action of sediments during settling, the concentrations of the metal ions are observed lower in March.

Now comparing the results for metal contents of sewage water and National Environmental Quality standards effluents Government of Pakistan [27] iron concentration only crosses the limits (Table-8).

Comparing the results for metal analyses with the permissible limits of EEC for surface water (Table-9) it indicates that the concentration of

Table-8: Comparison of observed results of metal ions in sewage water with NEQS (National Environmental Quality Standards) EPA, Pakistan.

Concen-	Observed values	NEQS for untreated	
tration	on Minimum Maximum		Muncipal and Liquid
(mg/L)			Industries effluents
(mg/L) Cu ⁺² Pb ⁺²	0.04	0.4	1
Pb ⁺²	0.04	0.38	0.5
Cď ⁺² Ni ⁺²	0.00	0.02	0.1
	0.01	0.15	1
Fe ⁺²	0.40	7.0	2
Mn ⁺²	0.07	0.71	1.5
Zn ⁺²	0.04	0.82	5
Total	0.21	2.48	2

manganese, zinc, lead, and iron cross the limits and the concentrations of calcium, magnesium, sodium and potassium touch the maximum limits recommended by EEC [28].

Experimental

Twelve samples, seven along Phulleli canal and five from sewage water, before entering in Phulleli canal were collected (Fig. 5). Along Phulleli

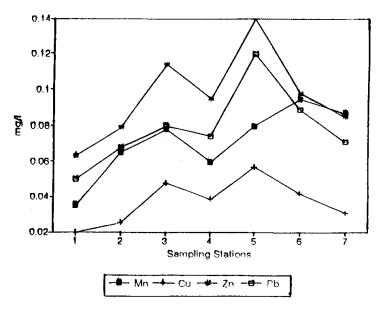


Fig. 4: Variation of concentration of manganese, copper, zinc and lead along phulleli canal during August 1995. Sampling station near (1) Akhund village (3) CIA centre (5) Sakhipir Road near Liaquat Colony (7) Bhatti village near Fatch Textile Mills (9) Drya Khan village (11) Pono Koli village (12) Hosri bridge near Behar Colony.

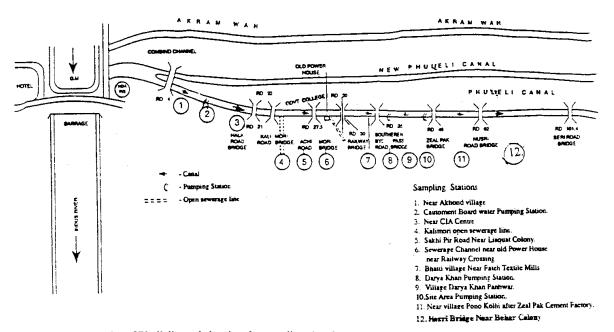


Fig. 5: Map of Phulleli canal showing the sampling sites from Phulleli canal and sewage water of Hyderabad

Table-9: Comparison of the observed results of metal ions in Phulleli canal water with EEC (European Economic Community) standards for surface water.

		ed values of leli canal	EEC standards for surface water		
Concen- tration (mg/L)	Minimum	Maximum	Normal value	Max:Permi- ssible Limit	
Ca ⁺² Mg ⁺² Na ⁺¹ K ⁺¹ Fe ⁺²	60	585	100	_	
Mg ⁺²	19	440	30	50	
Na ⁺¹	13	641	20	175	
K*1	3.8	73.7	10	12	
Fe ⁺²	0.4	3.11	-	0.3	
Cu ⁺² Ni ⁺²	0.03	0.07	0.1		
Ni ⁺²	0.02	0.05	_	0.05	
Mn ⁺²	0.04	0.28	0.02	0.05	
Zn ⁺²	0.05	0.33	-	0.1	
Pb ⁺²	0.04	0.19		0.05	
Zn ⁺² Pb ⁺² Co ⁺²	0.02	0.05			
Cd ⁺²	0.00	0.01			

canal sample (1) was collected near Akhund village, the point of exit of Phulleli canal from Kotri barrage before the entry of any sewage water. Four samples were collected from the canal in between the entry points of sewage water. Sample (6) was collected near village Pono Koli where it reaches Hyderabad city limits and last sample was collected from Hosri bridge near Behar colony about 5 - 6 km away from Hyderabad city (Table-10).

Grab sampler was used for the collection of the samples from sewage lines [29]. However due to extremely high pressure it was not possible to collect a cross section of the flow or from the middle of the flow, but was possible to penetrate a few cm in the flow of water and sample was collected. Two to four sub samples from Phulleli canal were taken from the middle of the bridges, where it was not possible the sample was collected 3 - 4 m from the side of canal. Periodical sampling was made at an interval of 6 - 8 weeks and this practice was made 12 times.

Sample was transferred to 2.5 L prewashed glass bottle rinsed with the sample several times. The sample was filtered through 0.45 μ m glass fiber filter (Gelman Sciences Australia) and was acidified with nitric acid to pH 2-3.

Solvent extraction procedure

To separating funnel containing 300 ml double distilled deionized water was added standard metal ion solution in the range 0-250 µg iron, cobalt,

Table-10 Sampling sites from Phulleli canal and sewage water

S.No. of Sampling Station	Location of Sampling Station	Distance (meters) of Sampling Station from Kotri Barrage
1.	Near Akhond Village	762.0
2.	Cantonment Board	2286.0
	Waste pumping Station*	
3.	Near C.I.A. Centre	4724.4
4.	Kali Mori open sewerage line near Govt. College*	6401.0
5.	Saki Pir Road Near Liaquat Colony	7925.0
6.	Sewerage Channel Near Old Power House*	9296.4
7.	Bhatti Village Near Fateh Textile Mills	10973.0
8.	Darya Khan Panhwer pumping Station*	11582.4
9.	Near Village Darya Khan Panhwer	12901.6
10	Site Area pumping Station Near Nara Jail*	13411.2
11.	Near Village Pono Kolhi after Zeal Pak Cement Factory	15240.0
12.	Hosri Bridge Near Behar Colony	21336.0

*(Asterisks) indicate sampling station from sewage water.

nickel, lead, 0-125 µg copper and manganese and 0-50 µg cadmium and zinc and was added ammonium acetate acetic acid buffer pH 4 (7 - 8 ml. 1M), followed by APDC (1.5 ml, 5% w/v), oxine (1.5 ml, 2% w/v) and MIBK 20 ml. The mixture was shaken well for 5-7 min and the layers were allowed to separate. Organic layer was collected and to aqueous layer was added ammonia solution (2%) (5 ml) to adjust the pH to 9.2. APDC (0.5 ml, 5% w/v), oxine (0.5 ml, 2% w/v) and MIBK (20 ml) were added and the extraction was repeated. The combined extract was added nitric acid (2.5 ml, 65%) and contents were shaken for 3-5 min. Water double distilled deionized (15 ml) was added and was again shaken for 3-5 min. The aqueous layer was collected and the volume was adjusted to 25 ml. The water samples were analysed following same procedure. The amount of metal ions were evaluated from the calibration curve, containing known amounts of metal ions. Reagent bank was also prepared from double distilled deionized water (300 ml), following same extraction procedure.

Sodium, potassium, calcium and magnesium were determined in water samples after appropriate dilution. The metal contents were determined using

Varian Spectra AA-20 atomic absorption spectrophotometer Air-acetylene flame with standard head was used at the conditions. recommended by the manufacturer. The analyses were carried out in triplicate with delay time 3 seconds and integration time 3 seconds.

Average water discharge in Phulleli canal was obtained from the records of control room Kotri barrage. Quantity of water discharge of sewage was calculated using the relation

$$Q = \{(BxD)x[\frac{S}{T}]\}$$

Where B = Breadth of the drain

D = Depth of drain

S = Specified distance in drain

T = Time taken by water for specified distance

For trapezoid shaped drain Q was calculated from the relation

$$Q = \left[\left\{\left(\frac{T+B}{2}\right)xD\right\}x\frac{S}{T}\right]$$

Where

T = Top width of water level

B = Bottom width of drain

Time of flow of water over a specified distance and the depth and width of the channel were calculated at the site. For the sewage ponds where the motors are lifting the waste water and introducing into the canal the discharge was estimated from the capacity of motors and average operating hours of motors.

References

- V.K. Dewani, I.A. Ansari and M.Y. Khuhawar, Scientific Sindh Annual Res.J., 2, 45-55 (1994).
- V.K. Dewani, I.A. Ansari and M.Y. Khuhawar, preconcentration and determination of Metal contetns in Hyderabad city Sewage and Phulleli Canal. Proc. 3rd Natl. Symp. Modern trends in Contemporary Chem 24th to 26th Feb. (1997)

- 21-24.
- D.G. Berge and J.E. Going, Anal. Chim. Acta, 123, 19 (1981).
- J.Q.K. Song, F.F. Xu, Lihua Jianyan Huacu Fence, 29, 179 (1993).
- C. Boutron and S. Martina, Anal. Chem., 51, 140 (1979).
- A. Hall and M.C. Godinoho, Anal. Chim. Acta, 113, 369 (1980).
- Y. Shijo, M. Mitsuhashi, T. Shimu, S. Sakurai, Analyst, 117, 1929 (1992).
- F. Vemon and C.D. Wani, Anal. Proc. (London), 30, 442 (1993).
- K.W. Bruland, R.P. Franks, G.A. Knauer and J.H. Martin, Anal. Chim. Acta, 105, 233 (1978).
- 10. S. Sugimae, Anal. Chim. Acta, 121, 331 (1980).
- 11. C.W. Mcleod, A. Otsuki, K. Okamoto, H. Haraguchi and K. Fuwa, Analyst, 106, 419 (1981).
- 12. P.J. Satham, Anal. Chim. Acta, 169, 149 (1985).
- 13. A. Le Bihan and J.Y. Cabon, Talanta, 37, 1119 (1990).
- 14. Y. Shijo, T. Shimizu, T. Tsunoda, I. Shiguan, M. Suzuki, Anal. Chim. Acta, 242, 419 (1991).
- 15. I. Dellien and L. Persson, Talanta, 26, 1101 (1979).
- 16. S.C. Apte and A.M. Gunn, Anal. Chim. Acta, 193, 147 (1987).
- 17. S. Sachsenberg, T. Klenke, W.E. Krumbein, E. Zeeck, Anal. Chem., 342, 163 (1991).
- 18. W. S. Bradshaw, A.J. Gascoign and J.B. Headridge, Anal. Chim. Acta, 197, 323 (1987).
- 19. H. Tao, A. Miyazaki, K. Bansho and y. Umezaki, Anal. Chim. Acta, 156, 159 (1984).
- 20. D.R. Babu, P.R. Naidu, Talanta, 38, 175 (1991).
- 21. L. Elei, M. Soylak and M. Dogan, Fresenius, J. Anal. Chem., 342, 175 (1992).
- 22. H.F. Hemandez, Meina, J. Escriche, J.V. Martin Prats, Analusis, 14, 181 (1986).
- 23. R.G. Smith and H.L. Windom, Anal. Chim. Acta, 133, 39 (1980).
- 24. M.J. Ashworth and R.H. Farthing, Int. J. Envign. Anal. Chem., 10, 35 (1981).
- 25. R.E. Sturgeon, S.S. Berman, A. Desaulniers and D.S. Russel, Talanta, 27, 85 (1980).
- 26. F. Voutsinou Taliadouri, Microchem. Acta, 119, 243 (1995).
- Govt. Pak. Environmental and urban Division,

- The Gazette of Pakistan, Part II, Islamabad August 29, 1993.
- 28. H.H. Rump and H. Krist, "Laboratory, Manual for the Examination of water, Waste water and soil," VCH Vertagsgesells-chaft, mbH,
- Germany 2nd ed. 156 (1992).
- M.A.H. Framon (Ed) Standard methods for the examination of water and waste water, 15th Ed. American Public Health Assoc. Washington, 1981.