

## Sediment Analysis of Sewage Contaminated Canal

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**Summary:** Sediments of sewage contaminated Fuleli canal was sampled before and after addition of sewage for over 25 k.m. and analysed for loss on ignition, pH, conductance, organic carbon, water soluble chloride, sulphate, carbonate, phosphates, Na, K, Ca and Mg. The sediments were also examined for total (Fe, Cu, Ni, Mn, Zn, Pb, Co and Cd) and bioavailable (Fe, Mn, Cu and Zn) metal contents.

The sediments showed alkaline character and contained wide range of variation in soluble salts. The major cations and total metal contents indicated following decreasing pattern Ca > Mg > Na > K; Fe >> Mn > Zn > Ni > Cu > Pb > Co > Cd.

The bioavailable metal contents crossed the safe limits for the use of sediments of contaminated portion of the canal for agricultural purposes.

### Introduction

The sediments reflect condition of overlying water and the analysis of sediments have gained importance due to increase in environmental pollution [1]. A number of studies have been carried out where an increase in concentration of metal ions have been observed in the sediments of receiving water due to the addition of sewage water, industrial effluents or mining activity within the region [2-9]. The present work reports the variation in metal contents of a major irrigation canal within the region (Hyderabad, Sindh, Pak.) contaminated by the addition of city sewage.

### Results and Discussion

The results of analysis for % moisture contents, pH, conductance, % organic matter, % of carbon from organic matter contents, chloride, sulphate, phosphate phosphorous, carbonates, calcium, magnesium, sodium and potassium are summarized in Table- I. The results are reported as average values (n=12) with confidence interval at 95% and range in terms of minimum and maximum values.

The variation in moisture contents was between 3.67 to 43.7% with maximum at station 3, may be because of high organic matter and Clay [10]. The % of organic matter and carbon contents throughout the study area fluctuated between 2.3 to 20.5% and 0.45 to 11.0% respectively with highest average recorded at station 3 (Table 1). It may be

because of addition of organic compounds rich sewage above the station 3. The sediments on the average were observed slightly alkaline, with total fluctuation in pH values were between 6.74 to 9.4. There was some decrease in pH as travelled from station 1 to 7 due to the addition of sewage. The conductance was low at station 1 (442  $\mu\text{S}/\text{cm}$ ) but increased sharply and remained high with average values within 839-1889  $\mu\text{S}/\text{cm}$  due to the addition of sewage water. Chlorides and sulphates also followed a similar pattern with average values of 57.0  $\mu\text{g}/\text{g}$  chloride and 188  $\mu\text{g}/\text{g}$  sulphate at station 1. The values increased in the range 64.6-787.65  $\mu\text{g}/\text{g}$  and 551-1229  $\mu\text{g}/\text{g}$  respectively under the influence of sewage water within sampling stations 2 to 7. Sulphate being the highest oxidized form of sulphur was observed higher in concentrations in sediments may be because of aerobic environment present at sediment than sewage. The carbonate contents of sediments varied within 133 to 1400  $\mu\text{g}/\text{g}$ . The elevated concentration of the carbonate was apparent after the entry of sewage water from station 2 to 7, but the variation of carbonate in between the two samples was within narrow margin. The phosphate contents in the sediment at station 1 on the average was 20.06  $\mu\text{g}/\text{g}$ . A significant varying levels of phosphates contents was noted in the waste water affected area of canal. The station 5 contributed to the maximum mean concentration of 77.6  $\mu\text{g}/\text{g}$  of the phosphate phosphorous. Other stations also indicated higher concentrations of phosphates by factor 2.3 to 3.8 than station 1.

Table-I: Variation in Physio-Chemical Composition of Sediments at Different Sampling Stations along the Fuleli Canal

Parameter	Sampling Stations						
	1	2	3	4	5	6	7
% Moisture contents	10.21± (3.67-16.1)	15.75±3.31 (6.5-22.8)	24.15±5.20 (15.2-43.7)	19.7±3.81 (12.25-24.5)	22.3±4.2 (14.75-39.12)	14.86±2.95 (9.11-21.12)	16.7±2.85 (8.7-23.1)
pH	8.47±4.3 (7.76-9.4)	8.17±0.41 (7.56-8.73)	2.81±0.50 (7.28-9.27)	8.19±0.43 (7.48-8.72)	8.02±0.48 (6.74-8.83)	8.27±0.69 (6.83-9.22)	8.0±0.6 (7.17-8.76)
Conductance $\mu\text{S/cm}$	442±211 (248-895)	1889±1062.5 (340-4200)	839±359.6 (378-1750)	975±303.6 (415-1640)	1306±356.8 (959-2050)	1097.6±370 (368-1602)	928±328 (401-1420)
% Organic matter	3.36±1.05 (2.3-5.6)	6.22±1.89 (3.26-13)	11.88±2.56 (3.85-20.5)	9.1±1.83 (5.4-17.2)	10.13±2.11 (4.8-19)	8.2±1.75 (5.2-15.2)	7.11±1.75 (4-16.5)
% Carbon (from COD)	0.68±0.23 (0.5-0.85)	2.95±0.95 (1.1-7.3)	4.85±1.40 (1.3-10.7)	3.45±1.21 (1.4-9.8)	4.11±1.21 (1.41-11)	2.62±0.86 (1.5-6.1)	3.11±1.01 (1.2-8.4)
Chloride $\mu\text{g/g}$	57.08±31.15 (16-127)	788.65±610 (43-2484)	87.34±74.4 (30-190)	64.56±39 (23-149)	103±58.4 (30-245)	98±45 (32-195)	73.65±35 (25-140)
Sulphates $\mu\text{g/g}$	188±129.4 (30-316)	1229±873 (146-2970)	567±416 (85-1872)	551±363 (206-1394)	1079±583 (455-2400)	917±507 (207-2012)	871±675 (200-2449)
Phosphates $\mu\text{g/g}$	20.06±17.28 (4.5-68.5)	52.67±28.7 (5.7-106)	72±54.5 (13.1-197)	46.5±24.7 (13.6-92)	77.6±33 (9.5-151)	66.25±27.35 (12-112)	54.34±27.6 (22-102)
Carbonates $\mu\text{g/g}$	216±68.6 (137-400)	355.7±128 (133-600)	389±198 (168-833)	400±338 (208-1400)	435.6±194 (212-800)	528.3±276.5 (162-900)	479.75±292 (191-1200)
Ca $\mu\text{g/g}$	283.8±95 (100-440)	1075±766 (280-2060)	608±519 (120-2040)	610±368 (122-140)	103±703 (340-3200)	1212±793 (310-3110)	1022±750 (300-2960)
Mg $\mu\text{g/g}$	107±58 (40-280)	232±144 (85-470)	162±100 (100-460)	177±81 (60-320)	367±215 (117-790)	322±129 (80-460)	240±98 (80-400)
Na $\mu\text{g/g}$	109±34 (27-140)	460±283 (123-580)	125±76 (80-210)	119±64 (60-180)	150±68 (100-323)	161±85 (86-444)	148±75 (81-297)
K $\mu\text{g/g}$	9.72±1.78 (5-10.7)	22.86±10.6 (10.6-46)	14.64±7.8 (8.5-31)	19.48±9.5 (7.5-40)	30.6±12 (9-48)	29.2±11 (11-39)	27.2±10.7 (8-34.4)

Average values with confidence interval at 95% parenthesis values are Min-Max Range.

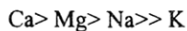
### Major Cations

Calcium was dominant throughout the study area with lowest value of 283.8  $\mu\text{g/g}$  at station 1. Among polluted sediments from station 2 to 7, the calcium contents were more than 1000  $\mu\text{g/g}$  which reflect the presence of abundant amount of salts of this element in sewage. The insoluble form ( $\text{CaCO}_3$ ) in water settled down in sediments.

The magnesium distribution in sediments closely paralleled those of calcium with highest mean concentration of 367  $\mu\text{g/g}$  recorded at station 5 and lowest of 107  $\mu\text{g/g}$  at station 1. The positive correlation between calcium and magnesium with regression coefficient ( $\gamma = 0.91$  to 0.80) at most of stations indicated that calcium and magnesium might be from the same source.

The sodium contents in the sediments ranged between 27-580  $\mu\text{g/g}$  with highest mean value of 460  $\mu\text{g/g}$  at station 2 and exhibited identical variation pattern as that of chlorides (Table-I).

The potassium throughout the investigation period in the entire study stretch of the canal was observed lowest and fluctuated between 5-48  $\mu\text{g/g}$ . The analysis of the major cations revealed the following decreasing concentration sequence in sediments.



### Total Heavy Metal Contents

The sediments of canal were rich in mobile elements and poor in cadmium contents. The deposition of mobile elements caused other elements to accumulate.

### Iron

The existence of iron above 1900  $\mu\text{g/g}$  at the sewage unaffected area (Station 1) indicated lithogenic origin. The concentration of iron did not indicate a significant variation from station 2 to 7, but was higher by a factor 1.2 to 1.3 within polluted

sediments. Thus the lithogenic factor of iron is further augmented by anthropogenic activities within the canal.

The clear distinction of iron in sediments during the different water flow levels was not obvious, but some higher concentration of iron was noted in the months of high water discharge (July-August) (Figure 1). High water flow resulted in greater mixing and penetration of water in sediments and brought iron rich contents by migration movements to the surface and deposited at sediment water interface [11]. Alternatively organically rich sediments are reduced layers, which contained lower concentration of iron than organically poor sediments [12]. At stations 2 to 7, some distinction between oxidized layer (prevailing in the months of high discharge) and reduced layer in the months of low water discharge (organically rich sediments) could be made, which accounts for the existence of higher concentration in July and August.

#### Manganese

The enrichment of manganese in sediments like iron reflected lithogenic factor. The fluctuations in the manganese contents were within 218-700  $\mu\text{g/g}$ . These variation could be partly due to the secondary impacts of sewage water and partly due to the possible variation [13]. The average concentrations of manganese in the sediments of stations 2 to 7 were higher by factor 1.4 to 1.6 than station 1.

The seasonal variation was like iron with higher contents noted during rising water stage and lower during following stage.

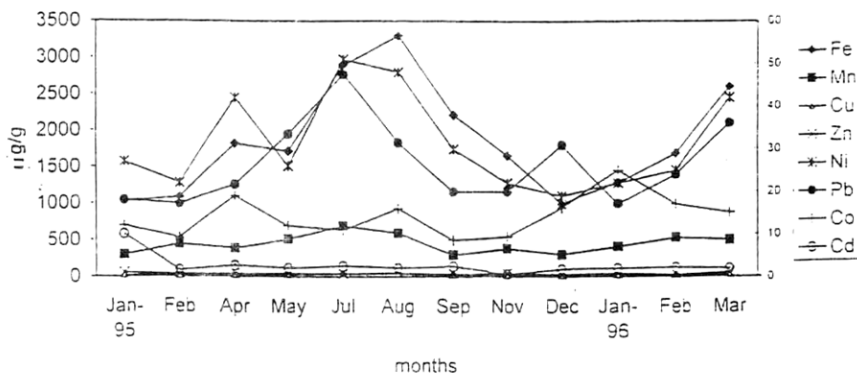


Fig.1: Seasonal profile of metal contents (Fe, Mn, Cu, Zn, Ni, Pb, Co and Cd) in the sediments at sampling station 3 of Fuleli canal.

#### Copper

The copper across the investigated area varied from 10  $\mu\text{g/g}$  to 57.5  $\mu\text{g/g}$  with highest average concentration of 38.25  $\mu\text{g/g}$  contributed by station 5. There was no regular seasonal variation, but slightly higher levels of copper were noted during high flow, may be because of sorption on clay and Fe/Mn oxides at relatively higher pH [14].

#### Zinc

Zinc indicated fluctuating behavior in between the stations and concentration varied from 24 to 103.5  $\mu\text{g/g}$  with highest average of 76.4  $\mu\text{g/g}$  at station 5 as for copper. Zinc did not indicate a distinct pattern of variation with respect to the water discharge.

#### Nickel

Lowest nickel contents of 24.2  $\mu\text{g/g}$  was estimated at station 1 before the addition of sewage water. A uniformity in the concentration was noted from 2 to 7 with the exception of station 6 where nickel average contents rose to 43.25  $\mu\text{g/g}$  possibly due to inputs of sewage water from industrial units (vegetable ghee using nickel as catalyst) situated in locality of station 6. Nickel did not exhibit a clear variation profile relating with the water flow stages.

#### Lead

The lowest mean contents of lead 12.6  $\mu\text{g/g}$  was observed upto station 4. Thereafter was a sharp rise in concentration at station 5 to 121  $\mu\text{g/g}$ , because lead extraction was being carried out in the vicinity of station 5 along the canal [15]. The impact was also

noticeable at station 6 and 7 where lead concentration was slightly below 80 µg/g. Lead did not indicate clear variation in relation to the discharge of water at station 1 to 4, but at station 5, highest concentration was observed during lowest water discharge (Dec. and Jan.) while in rising water stage (July-August) a decline in lead contents in the sediments was noted. This could be attributed to the fact that usually high flow rates could have flushed the contaminated sediments down stream and partially replaced them with the material from relatively unpolluted water flowing in the canal.

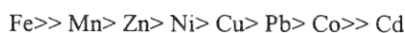
#### Cobalt

Cobalt contents in sediments was significantly lower than the other metal ions which is related to its lower contribution by sewage water draining into canal. The highest mean concentration of 18.1 µg/g was observed at station 3 and lowest mean of 11.4 µg/g was determined at station 1. Clear seasonal profile for cobalt concentration was not observed.

#### Cadmium

The trace level of cadmium was detected in sediments of canal. The concentration in the study area was below 3.0 µg/g.

The investigation of the total metal contents in the sediments revealed the following decreasing order.



#### Bioavailable Metal Contents in Sediments

The extractable trace metal contents of Fe, Mn, Cu and Zn (nutrients) in sediments were determined by DTPA test (diethylenetriaminopenta acetic acid) to access the possibility of mobilization of metal ions if used for land fill for agricultural purposes.

#### Iron

The iron contents in sediments of station 1 ranged within 16-30 µg/g. Its range within the polluted region was 9-88 µg/g and crossed the safe limits of 0.11-40.0 µg/g [16].

#### Manganese

Average manganese contents in entire course of study was between 10.2 to 33.2 µg/g and was within the normal range (2.8- 41.0 µg/g) for plant growth. However individual values for manganese contents ranged 6.8-54 µg/g and crossed the safe limits [16].

#### Copper

The average values 1.7-4.4 µg/g were within the safe limits (0.3-6.0 µg/g), but over all observed range 0.54-7.7 µg/g did cross the limits at some points.

#### Zinc

Zinc is an important micronutrient. On the average 1.1-5.5 µg/g are within the limits (0.2-5.9

Table-II Total Metal Contents (Mean with 95% Confidence Interval and Extreme Values in Paranthesis) in Bottom Sediments Of Fuleli Canal n=12

Sampling Station	Concentration of Metals in µg/g							
	Fe	Mn	Cu	Zn	Ni	Pb	Co	Cd
1	1927±619.7 (1012-3425)	319±59 (218-487)	18.5±3.6 (10-22.5)	34.8±4.6 (24-51.5)	24.2±6.5 (10-42.5)	12.6±3.9 (5.0-22.0)	11.4±2.7 (6.25-17.5)	1.27±0.35 (N.D-2.1)
2	2412.5±668 (1050-3580)	480±71 (312-595)	27.7±7.6 (16.5-45)	46.8±5.6 (33-58.7)	31.29±7.1 (16-48.7)	20.77±4.3 (10.1-30.5)	14.65±3.1 (10-18.5)	1.87±0.43 (0.75-2.87)
3	2397±687 (1064-3620)	444±89 (300-695)	28.25±5.6 (17-43)	57.7±7.1 (35-67.7)	36.2±7.85 (18.5-51)	26.7±6.8 (17-47.5)	18.1±3.78 (11.5-25)	2.1±0.41 (0.75-2.9)
4	2405±670 (1060-3690)	499±90.4 (306-680)	31.45±5.8 (18-47.5)	66.2±8.75 (31.5-80)	35.2±7.6 (17-54)	24.2±5.6 (13.8-38.5)	17.6±3.4 (9.5-26)	1.95±0.42 (0.78-2.85)
5	2474±698 (1075-3860)	510±97 (290-700)	38.25±8.7 (20.5-57.5)	76.4±11.3 (43-103.5)	(38±7.4) (20.5-53)	121±70.5 (48.8-450)	16.1±2.95 (10-24)	2.2±0.47 (0.8-2.95)
6	2431±679 (1037-3710)	458±71 (350-620)	32.5±5.7 (21.5-45)	69.4±7.44 (40-88.5)	43.25±9.3 (22-63)	78.8±25.5 (37-136)	16.5±3.11 (7.5-23)	1.91±0.43 (0.7-2.7)
7	2383±678	469±80.6	34.1±6.8	71.2±7.9	37±7.11	74.6±50.3	15.2±3.31	1.76±0.43

$\mu\text{g/g}$ ) but the individual value within stations 2 to 7 crossed the safe limits (Table 2).

The study of the bioavailable metal contents suggested that the sediments of the canal may not be recommended for agricultural purposes.

## Experimental

Fuleli canal takes off from river Indus from the eastern side of Kotri barrage and passes through Hyderabad city with a population of about 2 million. It receives most of the sewage and industrial effluents while it passes through Hyderabad city and then travels an approximate distance of 80 km to provide water for agricultural purposes. Seven samples were collected to cover approximate distance of 22 km. Sample (1) was collected near Akhund village (Point of exit of canal from the barrage before entry of any sewage), four samples were collected from the canal (2) near CIA Centre (3) Sakhi Pir road, Near Liaquat Colony (4) Bhatti Village near Fateh Textile Mills, (5) Village Darya Khan Panhwar in between two point of source of sewerage lines. Last two samples were collected from the canal (6) after Zeal Pak Factory near village Pono Kolhi and (7) Hosri barrage near Behar Colony, where the canal leaves the city limits. The exact description about Fuleli canal and sewage added is reported elsewhere [15].

The samples were collected with Ekman-Berg dredge bottom sampler at the sediment water interface. The samples were collected in polyethylene bags and were transferred to the laboratory for analysis. The sampling scheme was repeated every 5-7 weeks during 1995-1997.

Moisture contents and loss on ignition were determined with a air dried sample (5-10 g) at  $105^\circ\text{C}$  and  $550\pm 50^\circ\text{C}$  for 2 hr. Air dried sediments (50 g) was shaken with water (1:2 w/v) on mechanical shaker for 30 min. The filtrate was used for measurement of chloride, carbonate and sulphate by titrimetry and spectrophotometry [17,18]. The phosphates phosphorous was extracted with Trongs reagent [19] [ $\text{H}_2\text{SO}_4$  1mM, pH adjusted to 3 with  $(\text{NH}_4)_2\text{SO}_4$ ], followed by spectrophotometric determination after reduction of phosphomolybdate to molybdenum blue with ascorbic acid. The % of organic matter was calculated by potassium dichromate oxidation in strongly acidic solution. The % of organic carbon was calculated from % organic matter [20]. The dried sediment sample was homo-genized and was

separated in size fraction with a set of sieves (Endecotts test sieves) (Griffin and George London) of known mesh size (250, 102 and 60  $\mu\text{m}$ ). The fraction 60  $\mu\text{m}$  was used for the determination of metal contents. Na, K, Ca and Mg were extracted from (5 g) air dried sediments by shaking (1 hr) with ammonium acetate (1M, pH 7) (125 ml) and determined by flame atomic absorption spectrophotometer. Bioavailable contents of Fe, Mn, Cu and Zn in sediments (20 g) were extracted by shaking with diethylenetriamine penta acetic acid (DTPA) reagent for 2 hr [21]. Total metal contents of Fe, Cu, Ni, Mn, Co, Pb, Cd and Zn in sediments (1 g) were extracted by digestion with aqua regia [22] and final volume was adjusted to 25 ml.

The spectrophotometric studies were carried out with Hitachi 220 spectrophotometer (Hitachi Ltd. Tokyo, Japan). Conductivity measurements were made with WTW 320 conductivity meter. pH was measured with Orion 420A pH meter. The metal contents were determined with Varian Spectr AA-20 atomic absorption spectrophotometer using air acetylene or nitrous oxide-acetylene flame with the operating conditions recommended by the manufacturer. The analysis was carried out in triplicate with integration time 3 sec. and delay time 3 sec.

## Conclusions

The sediments of Fuleli canal were alkaline in nature. The average conductance of Fuleli canal sediments (affected areas) was about two to four times higher than non-populated sediments (Station 1). The enhancement factors of phosphates, sulphates and calcium ions in comparison with reference point sediment were similar to conductance. The existence of quite high levels of mobile elements iron (above 1900  $\mu\text{g/g}$ ) and manganese (above 300  $\mu\text{g/g}$ ) in sewage unaffected sediments (station 1) reflected the dominance of lithogenic (geochemical) factor for their presence. The concentrations of metals in Fuleli canal sediments from station 2 to 7 were further augmented by secondary impact of sewage water.

## References

1. J.R. Senten, R.H. Chaliar, *Int. J. Environmental Studies*, **37**, 79 (1991).
2. N. Managa, *Jr. J. Environ. Sci.*, **2**, 60 (1983).
3. S. Bamford, E.O. Akoto, I. Aboh, C.A. Biney, L.A. Antwi, *Biol. Trace Elem. Res.* **26-27**, 279 (1990).
4. A.V. Hirner, K. Kirsotakis, H.J. Tebschall, *Appl.*

- Geochem.* **5**, 491 (1990).
5. S.T. Ingle, S. Vishwaranjan, S.A. Suryawanshi, B.G. Kulkarni, *Environ. Ecol.*, **11**, 747 (1993).
  6. Y. Lin, Q.Li, *China Environ. Sci.*, **5**, 110 (1994).
  7. J. Suschka, S. Ryborz, I. Leszczynska, *Wat. Sci. Tech.* **29**, 107 (1994).
  8. C. de, V. Marinela, L. de, M. Hilda, A. Katuska, *Analyst*, **119**, 623 (1994).
  9. J.Tarique, M. Jaffar, M. Ashraf, M. Moazzam, *Toxicol.Environ. Chem.*, **47**, 571 (1995).
  10. Denis "Basic, Soil science Analysis, A Guide to Current Use, John Wiley & Sons Ltd. England (1993).
  11. B.D. Nedwell, C.M. Brown, Sediment Microbiology, Society for General Microbiology, Academic Press A subsidiary of Harcourt Brace Jovano-Vich Publisher, London NW (1992).
  12. P.E. Kepkay, J.A. Novitsky, *Marine Biology* **55**, 261 (1980).
  13. J. Schoer, U. Nagel, H. Eggersgluess, U. Forstner, Metal contents in sediments from Elbe, Weser and Ems estuaries and from the German Bright (Southern North Sea) Grain size effect. In "Transport of Carbon and Minerals in Major world Rivers Part I" (Eds. E. T. Degens), Mitt Geol. Palaont. Inst. Univ. Hamburg SCOPE/UNEP Sonderbd. 52, 687 (1982).
  14. N.K.Baruah, P.Kotoky, G.C.Bhattachayya Boral, *Science Total Environ.* **93**, 1 (1996).
  15. I.A. Ansari, V.K. Dewani and M.Y. Khuhawar, *J. Chem. Soc. Pak.*, **21**, 359 (1999).
  16. W.L. Lindsay, N. Norvell, *Soil Sci. Soc. Am. J.* **42**, 42 1(1978).
  17. R.A. Day, A.L. Underwood, Quantitative Analysis, 4th ed. Prentice Hall, New Jersey (1980).
  18. Standard methods for examination of water and waste water, 15th ed. APHA-AWWA. WPCE, New York (1981).
  19. E.A. Slewart, Chemical Analysis of Ecological materials, 2nd ed. Blackwell scientific publication, Oxford, London (1989).
  20. E.L. Ariel, P. Rio, Organic carbon export by Riverine waters of Spain, in "Transport of carbon and Minerals in major world rivers part-III, (Ed. E.T Dagens, S. Kemp, H. Soliman) Mitt. Geol. Palaont. Inst. Univ. Hamburg, SCOPE/UNEP Sonderband 55, 267 (1983).
  21. W.L. Windsey, M.Yagi, L. Aoyama, Nogaku Kenkyu, (4), 15 (1985).
  22. Standing committee of Analysts, Extractables in soils, sewage sludge, treated soils and related materials. Methods for examination of water and Associated Materials HMSO, London (1982).