Study the Route of Entrance of Toxic Metals in the Arabian Sea

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Summary: Analysis of trace metals Cr, Fe, Pb, Zn and Hg was conducted in the Industrial wastewater at different locations (Korangi Industrial Area stream and SITE stream) using standard methods of analysis. Some physicochemical parameters like pH, Phosphates, Total Dissolved Solids, BOD and COD were also investigated. It was found that the toxic contents are more in the stream flowing along SITE, where as the Korangi Industrial Area stream contains fewer amounts of toxic metals. The maximum level of Pb was observed (0.9 mg/L) in Korangi stream and mercury was found (0.225 mg/L) in SITE. Chromium found under the permissible range (0.960 mg/L) in Korangi and (0.915 mg/L) in SITE. These two streams are found to be bringing a lot of toxic substances along with water. All two streams are also one of the major sources of toxic substances for the Arabian Sea especially for Karachi coastal area.

Introduction

Study and investigation of environmental pollution has gained a lot of attention now a day. Different substances occur naturally in our environment as a consequence of natural events. Many diseases are caused by the inability of environment to support the mineral needs of plants and animals in adequate, safe or non-toxic amount. It has been established that the excess or deficiency of trace elements can terminate life [1]. Water pollution is also a serious problem caused by dissolved inorganic and organic compounds, biological materials (bacteria and viruses) and suspended solids. Industrialization and urbanization have increased marine pollution in Pakistan. The trace metal contents in marine organism are found to reflect localized industrial wastes carried to sea [2].

The overall quality of waste water is not only dependant upon presence of trace metals, but also on physicochemical parameters such as pH, TDS, BOD, COD etc. TDS is a measure of total dissolved solids (salts). Biochemical oxygen demand (BOD) is a measure of quantity of dissolved oxygen in the biological process, the higher the BOD, the more polluted a water sample is considered to be. The more oxygen is consumed by microorganism the less dissolved oxygen is available to support life of aqueous organism. The chemical oxygen demand (COD) measures the quantity of a strong oxidizing agent required to oxidize all oxidizable contents.

A survey report of PCSIR laboratories Karachi and SCOPE Karachi shows that water of Layari River is contaminated with untreated industrial wastes, this cause deterioration in the quality of salt works located along one of the Layari delta. This also causes hazard to marine environment [3]. Naqvi and Coworker have investigated trace metal content (Co, Cu, Fe, Pb and Zn) in Karachi coastal area water [4]. With comparison to other coasts the concentrations of these metals were higher then other (Table-1). A prominent variation in concentration was seen with the distance from one sampling area to other [4].

The present study was carried out to investigate the alarming conditions of industrial wastes in the stream flowing along the industries. This investigation also provides information about the sources of entrance of toxic substances in the Sea. These sources may farther be investigated by expanding the area of study.

Results and Discussion

Trace metal data is shown in Table-2, and physicochemical parameters of the wastewater in Table-3. 'A' samples were taken out from Korangi Industrial Area and 'B' samples were from S.I.T.E stream. The average overall precision for the estimation of trace metals investigated and physicochemical parameters are within 2.0%. The listed values are the average value for at least three independent estimation of each water sample collected per month.

Table-1: A Comparison of our Results with those Obtained from Some Foreign Coasts.

Collocating place	Concentration (PPb)					
	Cd	Co	Cu	Fe	Pb	Za
Newzeland coast	--	--	4.8	--	--	30.0
South California Coast	--	--	3.0 to 1.3	11.0 to 0.6	--	10.0 to 4.0
Medit, Red & Arabian Sea	--	--	--	--	--	1.0
Tokyo Bay	0.06	0.0	1.0	9.4	0.2	4.3
Land sea of Japan	0.04	0.5	1.08	67.0	5.0	67.0
North Pacific ocean	0.02	0.02	0.0	0.2	0.2	0.20
Wajima	0.038	0.30	1.1	--	1.8	--
Sosogi	0.33	0.10	1.4	--	1.7	--
Noroshi	0.031	0.20	1,4	--	0.6	--
Kolji	0.031	--	1.1	--	0.7	--
Anamizu	0.088	0.20	1.0	--	0.7	--
Manzen	0.029	--	1.0	--	0.7	--
Bath Island	5.61 to 0.89	7.66 to 3.19	12.7 to 0.88	11.4 to 5.4	9.46 to 2.05	6.21 to 0.64
Korangi	4.07 to 2.02	5.23 to 2.34	11.7 to 2.92	12.8 to 4.84	8.87 to 1.43	4.08 to 0.89
Keamari	4.43 to 0.90	10.20 to 0.33	6.87 to 3.96	11.73 to 7.21	6.05 to 0.86	8.19 to 3.08

Source: Naqvi I. I., Gul, Z., Habib, S., Zehra, I., and Mehboob, A. A.; *Jour. Chem. Soc. Pak.* **15**, 1 (1993)

Table-2: Trace Metal Contents in Industrial Streams

S.No	Sampling sites	Concentration(mg/L)				
		Cr ± SD	Fe ± SD	Pb ± SD	Hg ± SD	Zn ± SD
1.	S-1A	0.960 ± 0.05	18.7 ± 2.0	0.135 ± 0.01	0.105 ± 0.01	1.85 ± 0.2
2.	S-2A	0.460 ± 0.04	14.4 ± 1.5	0.220 ± 0.02	0.220 ± 0.02	1.80 ± 0.2
3.	S-3A	0.250 ± 0.02	18.8 ± 1.5	0.900 ± 0.05	0.095 ± 0.01	1.85 ± 0.2
4.	S-1B	0.915 ± 0.10	30.6 ± 2.0	0.145 ± 0.01	0.180 ± 0.01	2.00 ± 0.2
5.	S-2B	0.410 ± 0.04	30.0 ± 2.1	0.190 ± 0.02	0.135 ± 0.02	1.90 ± 0.2
6.	S-3B	0.420 ± 0.04	17.1 ± 1.5	0.195 ± 0.02	0.225 ± 0.02	1.95 ± 0.2
7.	S-4B	0.810 ± 0.04	18.0 ± 1.4	0.185 ± 0.02	0.105 ± 0.01	2.00 ± 0.2
8.	Limits[a]	1.000	02.0	0.500	0.010	5.00

a: National Environmental Quality Standard, Pakistan Environmental Protection Agency, Islamabad (1993).

Table-3: Physicochemical Parameters of Industrial Streams

S.No	Sampling Sites	Physicochemical Parameters (mg/L)									
		Temp ^0C	pH	Cl^-	SO_4^{2-}	PO_4^{3-}	TDS*	SiO_3	BOD	COD	Oil & Grees
1.	S-1A	40	6.6	1250	25.0	25.0	5.6	25.0	760	268	--
2.	S-2A	40	6.5	1610	28.3	30.0	7.3	75.0	540	126.5	2125
3.	S-3A	40	7.8	1770	25.2	42.4	8.2	150	595	430	1115
4.	S-1B	38	7.1	1400	103.0	96.0	3.6	15.0	204	573	54
5.	S-2B	37	7.7	1300	45.0	39.0	4.7	25.0	177	621	45
6.	S-3B	39	8.9	1900	16.0	64.0	4.9	13.0	426	1154	48
7.	S-4B	41	7.7	2400	60.0	104	4.85	300	171	515	15
8.	Limits[a]	40	6-10	1000	6.00	---	3.5	---	80	150	10

* Percentage

a: National Environmental Quality Standard, Pakistan Environmental Protection Agency, Islamabad (1993).

These values show that Zinc and Chromium values fall with the permissible range as given by Pakistan Environmental Protection Agency (PEPA) [5]. The permissible range for chromium is < 1.0 mg/L and Zn is 5.0 mg/L and the estimated value was lower comparatively. Whereas the lead content exceeded to the upper allowed limited of PEPA standards [5]. The low level of all metals was observed in the sample S-1A except chromium. Concentration of chromium was found to be in maximum amount for S-1A (0.96 mg/L) and minimum for S-3A (0.25 mg/L). Iron was found to be maximum in S-1B (30.9 mg/L) and minimum at S-2A (14.4 mg/L). Lead was observed maximum in S-3A (0.900 mg/L) and minimum at S-1A (0.135 mg/L). Mercury was found to be maximum in S-3B (0.225 mg/L) and minimum at S-3A (0.095 mg/L). Zinc was found to be maximum (2.0 mg/L) at S-1B

& S-4B and minimum (1.8 mg/L) at S-2A. Therefore, wastewater coming from the industries contains large amount of lead in it. The values of Iron are found higher comparatively with the permissible range due to its presence in the form of chelate in the wastewater.

All physicochemical parameters are high. The level of silica was observed higher at high pH. Values of other physicochemical parameters COD, BOD, TDS have higher value comparatively with the recommended values. SO^{2-}_4 and PO^{3-}_4 are less as compare to the recommended values. The pH of the sample was within the controlling range.

Fig-1A demonstrates the route of Korangi Industrial Area stream and sampling point. At S-1A effluents coming from tanneries and petroleum refinery are mixed. In tanneries chromates are extensively used. That's why chromium is found maximum at this point. Tetra ethyl lead (TEL) is mixed with gasoline to increase the octane number, which cause the presence of lead at this point. At sampling point S-2A, effluents of different industries i.e. Dyeing, Rubber, Chemical and textile industries are mixed. The untreated effluents contain a large amount of heavy metals such as Pb, Cr Hg, and Zn. Therefore, Hg and Pb are in increasing order from S-1A to S-3A. At S-3A, the amount of Pb was nearly double to the recommended values (0.900 mg/L) [5]. At that point a truck-stand and some kind of workshops are in operation. Gasoline is fluently used in these workshops. Petroleum gasoline & diesel spills are also absorbed in the upper crust of that place. The place is in entirely dangerous condition (Pb concentration is maximum at S-3A). Some amount of the metal (Pb) must be absorbed in the banks of stream, which toxifying the crust. The soil of these areas is in dangerous conditions as it may have more insoluble Pb, than the liquid effluent.

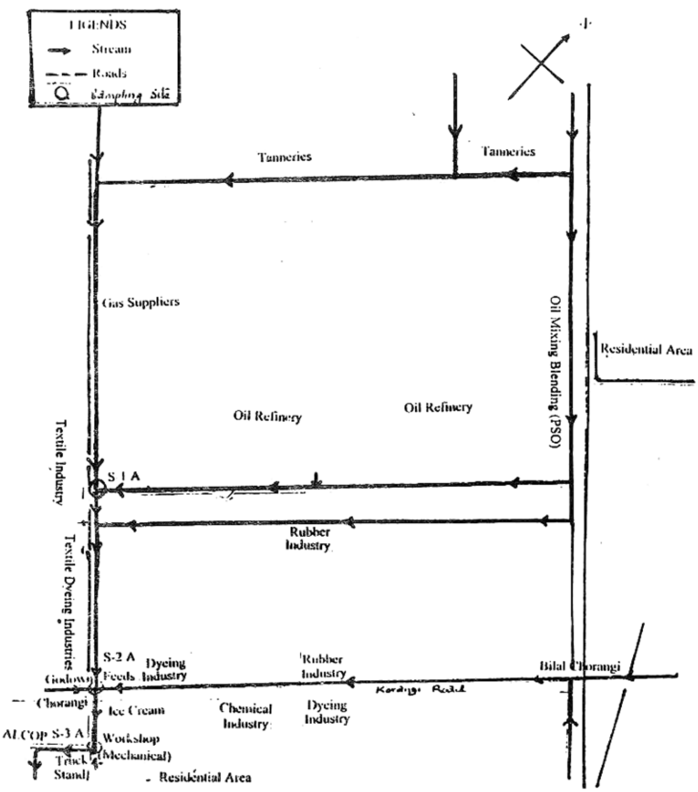

Fig. 1A: Korangi Industrial Area.

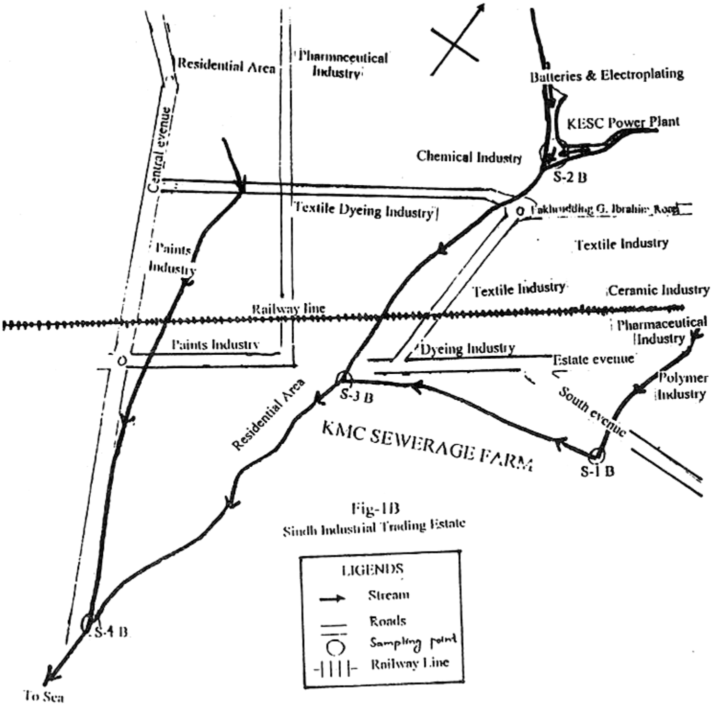

Fig. 1B: Sindh Industrial Trading Estate.

Fig. 1B demonstrates the route of industrial stream along SITE. S-1B is the sampling point at which all metals are at about their maximum value. Textile, tenneries and other industries are responsible for this increase. S-2B is the second point at which batteries, metallic can and textile industries are located. The investigated metals concentration is contributed by these industries. S-3B and S-4B including route of different textile, paints and dyeing industries contribute towards increase in the investigated metals concentration. The major toxification found in this limited study is due to chromium and lead.

These water streams falls in the Arabian Sea. The entire two streams bring these toxic substances to sea and become a major source of toxifying the Arabian Sea. Which contaminate the marine environment and marine organism tends to accumulate all these toxic metals in the edible tissues. In future studies the sources, which are toxifying the stream can be investigated, by expanding the area of study.

Table-4: Instrument and Analytical Parameters

Metals	Cr	Pb	Fe	Zn	Hg
Wave length (nm)	357.9	283.3	248.3	213.9	253.7
Lamp current (mA)	--	15.0	30.0	10.0	15.0
Slith width (nm)	0.7	0.7	0.2	0.7	0.7
Acetylene flow rate (ml/min)	10-14	10-14	10-14	10-14	10-14
Air flow rate (ml/min)	40-45	40-45	40-45	40-45	40-45
Air pressure (psi)	60-80	60-80	60-80	60-80	60-80
Acetylene pressure (psi)	12	12	12	12	12

Experimental

Apparatus

Plastic bottles (1.0 liter) were used for sampling, these bottles were pre washed with Nitric acid and then with deionized water. Bottles were found free from trace metals and were capable for retaining a given sample for a period of 7-9 days without causing a detectable change in trace metal or any anionic or cationic concentration. Atomic Absorption Spectrophotometers Perkin-Elmer model – 2380, equipped with standard burner, the air acetylene flame was used for trace metal analysis. Operational conditions are shown in Table-4. Standard hollow cathode lamps (Cathodeon®) were used for each element.

Reagents and Solution

Merck AR grade reagents were used for digestion. For the analysis of trace metals Cr, Fe, Pb, Hg, Zn, stock solutions (500ml) were prepared from BDH Spectrosole AA standard (1000 ppm). The working standard solutions were obtained after diluting the stock to the required concentration.

Sample Treatment

Samples of industrial effluents were collected from three sample points of Korangi industrial area and four sampling points of SITE as shown in fig-1A and fig. 1B. Samples were collected during Jan to May 1997. A metallic thief with a one-liter bottle was used as sample collector. These samples were collected from top, bottom and center of streams. Samples were filtered with Whattman-41 filter paper and preserved at pH 2.0 by using HNO_3 – HCl (1:1). Residue was digested in 6 ml of HNO_3 - HCl (1:1) [6]. For the analysis of mercury interference of sulphide and free chlorine were inhibited by the addition of $KMnO_4$.

b) Analysis

The experimental procedure for the estimation of physico-chemical parameters and trace metals were adopted from literature [4-9]. The calibration curves of elements (Cr, Fe, Pb, Hg, Zn) were obtained for concentration Vs absorbance data, were statistically analysed using fitting of straight line by least square method (using Microsoft Excel). A back reading was also taken and necessary correction was made during the calculation of percentage concentration of various elements. Determination of Pb was carried out by flameless (ETAAS) and Cr, Fe by flame atomic absorption spectrometry (FAAS). For the estimation of trace metals, APDC- MIBK (Ammonium pyrolidine dithiocarbamate-Methyl isobutyl ketone) method was used. Hg was measured by cold vapor technique [4,8,9].

By AAS technique the detection limits of Cr, Cu, Fe, Pb and Zn were found to be 0.004-2.0, 0.01-2.0, 0.01-3.0, 0.007-1.0, and 0.006-0.8 ppb respectively.

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