Migration and Speciation of Lead and Copper in a River System Polluted from a Chloralkali Plant

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The analytical scheme proposed in this paper can be applied for speciating chloralkali plant effluents and the receiving river water body.

INTRODUCTION

While all forms of ecological systems are affected to varying extent by heavy metals, aquatic environment pollution by heavy metals has assumed a global significance in recent years. The heavy metals are most insidious pollutants because of their non-biodegradable nature[1]. Though atomic absorption spectrophotometry (AAS) is the most common analytical technique deployed for measurement of total metal concentration, estimation of total metal concentration alone is insufficient to know about its bioavailability or interaction with sediments and suspended particulate matter. An insight into various physico-chemical forms of heavy metals is necessary to understand their transport, fate, distribution and behaviour in aquatic system. Several analytical and separation methods such as solvent extraction, ultrafiltration, ion-exchange, dialysis, ultraviolet irradiation, gel chromatography and electrochemical techniques *viz.* Differential Pulse Polarograph (DPP) & Anodic Stripping voltammetry (ASV) have been attempted to distinguish metal species in natural waters[2,3] Among all analytical techniques, ASV has been found to be the most sensitive and widely applicable electrochemical technique for speciation studies in recent years[4]. This being due to availability of *in-situ* preconcentration step, that enhances its sensitivity and also capability to sense fraction of total metal.

In this report of work a study made to understand the distribution and partitioning of copper and lead in a river receiving effluents from a chlor-alkali plant is described. Monitoring studies for total and fractions of metal species for three different seasons. *viz.* summer, monsoon and winter were carried out for one year.

EXPERIMENTAL

Sampling Sites

Effluent and river water samples were taken from different sampling sites as depicted in Fig. 1. Site 1 represents the reference point upstream

in the river. Site 2 is the effluent discharge point located 1 km down-stream of reference point. Samples were also collected from sites 3, 4 & 5
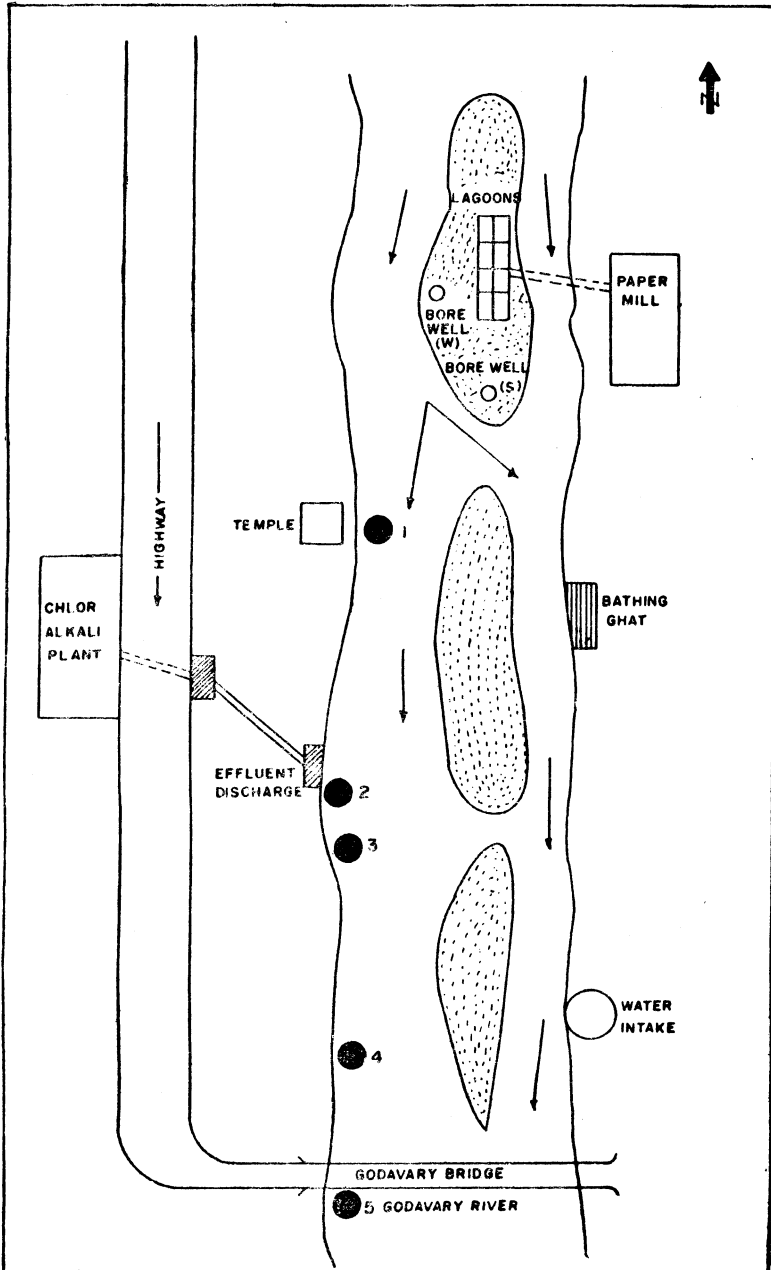

Fig. 1.   Map Showing Sampling Locations for Chlor-Alkali Plant

located 1.1 km, 2.5 km and 3.5 km downstream of reference point respectively. The effluent samples from the discharge point were also collected and characterized.

Reagents

Generaly all chemicals used during experimentation were of Analytical Reagent Grade (Fluka, Puriss). Stock standard solutions (1000 ppm) of Pb and Cu were prepared by dissolving electrolyte grade metal in minimum quantity of conc. HNO_3 and volume made up with double distilled water. Working standards were prepared by diluting stock solutions. Acetate buffer used as supporting electrolyte[7] was prepared from sodium acetate-acetic acid mixture. Nitrogen gas purified by reported method[8] was used for purging analyte solution.

Equipments

Polarographic Analyser (EG & G Princeton Applied Research, Model 384B) with Static Mercury Drop Electrode assembly (PARC Model 303A) interfaced with magnetic stirrer (Model 305) were used. Voltammograms were recorded using plotter (Houston, DMP-40). Photochemical assembly (Model 7840) from M/s. Ace Hanovia, USA was used for ultraviolet (UV) irradiation.

SPECIATION PROCEDURE

Sampling, Filtration and Storage of Water Samples

Each sample was collected in polythene container of 1 litre capacity previously leached with nitric acid. A part of the sample (125 ml), for total metal estimation, was preserved on site by acidifying with 1 ml conc. HNO_3. Remaining portion of sample was returned to the laboratory as soon as possible and 500 ml of sample volume was filtered through 0.45 Um membrane filter using Millipore filtration assembly under vacuum. The filtrate was divided into two aliquots of 250 ml. each, one portion of which was stored unacidified at 4°C for quantifying ASV–labile and organically bound metal fractions and the other portion was acidified with 1 ml of conc. HNO_3 for estimation of total filtrable metal. The above procedure was followed for each of the samples collected.

ASV–Labile Metal

The next step followed after filtration was estimation of ASV–Labile metal. To estimate, 5 ml of filtered sample was run in DPASV mode using 0.04M acetate buffer with instrumental conditions similar to those reported earlier[5]. The "peak height comparison" method was used for calculation of labile metal concentration.

Total Filtrable Metal

50 Ml aliquot of filtrate was subjected to digestion with nitric acid. Concentration of Pb and Cu was estimated in digested aliquot adding 0.1M acetate buffer using DPASV technique with similar instrumental conditions as described earlier[5].

Bound Metal

The unreactive form often referred as bound metal was calculated from the difference in concentrations of total filtrable and ASV–Labile metal. This includes both organically and inorganically bound species.

Organically bound Metal

50 Ml aliquot of filtered sample at its natural pH was taken in a quartz cell having water jacket for cooling sample continuously during UV-irradiation. Irradiation was carried out for 8 hrs adding 0.1% H_2O_2 as oxidant[3]. The aliquot of sample was analyzed after UV-irradiation for increase in ASV-labile fraction in 0.04M acetate buffer using ASV technique[5,6]. The difference in the concentrations of ASV-labile metal estimated prior to and after UV-irradiation was accounted for organically bound metal.

Particulate Bound Metal

Estimation of particulate bound fraction was carried out by digesting membrane filter along with retained particulate matter on it, with 5 ml of 1 : 1 nitric acid and sulphuric acid mixture and 45 ml of double distilled water. The contents were then digested on a water bath and filtered through Gooch crucible (G4 type) and finally volume was made up with double distilled water. Particulate bound fraction was estimated by ASV-technique with appropriate blank corrections.

Total Metal

Total metal analysis was carried out by taking an aliquot of unfiltered sample followed by digestion with nitric acid and estimating Pb and Cu concentrations in 0.1M acetate buffer using DPASV technique.

RESULTS AND DISCUSSION

In order to assess the efficacy of proposed speciation scheme, a case study of typical chlor-alkali plant effluent discharged into river was made. The samples collected at upstream and downstream of effluent outfall were subjected to trace metal speciation. Speciation was carried out for Pb and Cu. The general physico-chemical characteristics of the samples collected during summer, monsoon and winter seasons are represented in Table 1. Concurrently speciation has also been carried out in the effluent

TABLE 1

PHYSICO-CHEMICAL CHARACTERISTICS OF RIVER AT DIFFERENT SAMPLING LOCATIONS

Sampling location	Season*	pH	Temperature (°C)	Turbidity (NTU)	Conductivity (μS/cm)	Total solids	Total dissolved solids	Total suspended solids	Alkalinity	Hardness Total	Ca	Mg	Chlorides	Sulphates	Nitrates	Dissolved organic Carbon
										mg/l						
Reference point	S	7.5	30.0	240	277	326	164	162	57	92	60	32	17	12	1.2	1.5
(1 km upstream of effluent outfall)	M	8.0	29.5	320	226	544	200	344	84	84	44	40	11	9	ND	1.5
	W	8.3	28.0	310	215	144	118	26	108	104	50	54	15	13	ND	1.5
Outfall point (1 km downstream of reference point)	S	8.0	30.5	205	656	542	338	204	109	164	96	98	132	31	1.1	1.5
	M	7.8	30.0	320	239	552	156	396	84	92	48	44	21	19	ND	1.0
	W	8.2	30.0	340	230	138	136	2	114	104	50	54	17	15	ND	2.0
1.1 km downstream of reference point	S	8.1	30.0	245	354	354	208	146	116	104	52	52	33	19	0.5	3.0
	M	7.8	30.0	325	235	510	152	418	82	88	48	40	13	105	ND	1.5
	W	—	—	—	—	—	Data not available —		—	—	—	—	—	—	—	—
2 km downstream of reference point	S	7.8	30.0	240	320	344	184	160	106	100	80	20	19	18	0.8	3.0
	M	8.1	29.5	330	201	552	140	412	80	88	56	32	8	8	ND	2.0
	W	8.3	29.0	320	224	134	116	18	112	100	50	50	13	11	ND	2.0

TABLE 1 (cont.)

3.5 km downstream	S	7.8	29.0	250	285	322	120	202	97	96	36	60	19	14	0.5	4.0
of reference	M	8.1	30.5	310	199	548	140	408	82	76	48	28	11	9	ND	1.5
point	W	8.4	30.0	350	252	152	148	4	112	104	50	54	16	1	ND	1.5
Treated	S	7.9	31.0	20	2070	1914	1902	12	97	516	380	136	683	75	1.0	1.0
Effluent	M	3.2	31.0	10	7280	5792	5732	60	60	1812	1500	312	1979	50	ND	ND
	W	6.1	30.5	20	9680	6412	6288	124	16	3526	1954	1592	2089	29	ND	ND

*S—Summer
M—Monsoon
W—Winter

samples in order to know the concentration of various metal forms in the effluent and its likely impact on the receiving river water. The results obtained are presented in Table 2. The concentrations of various fractions of Pb and Cu at different locations have been summarized in Tables 3 and 4. It is observed that during summer season the ASV-Labile lead, the most toxic form, exists in the range of 20% of the total metal in the effluent while at upstream (site 1) the level observed was only about 5%, further it decreases downstream sites and ultimately reaches negligible concentration. These observations are in agreement with the results obtained by Benes and Stulik[9] which suggest that presence of low concentration of ASV-labile lead in natural waters. Particulate bound lead in the effluent is observed to be low as compared to ambient levels in the river. The bound form was found to be more than 50% at all sampling sites.

Speciation of copper reveals that ASV-labile copper at site 1 is around 4% of total metal. The absence of labile metal in the effluent indicates its tendency to undergo complexation and this is also exhibited by its appearance in organically bound form at different sites. Particulate bound metal decreases downstream with distance, however at site 5 (3·5 km from reference point), it increases due to influx of particulate matter originating from construction of bridge.

The speciation results (Tables 5 and 6) of samples of monsoon season reveal that the concentration of ASV-labile Pb increases during monsoon and this may probably change the fate of metal further downstream. It is also observed that the ASV-labile metal concentration decreases from 8.7% (at site 2) to almost negligible further in the river downstream. In the upstream (site 1) 91% of metal is present in bound form, thus eliminating the possibility of any immediate impact on aquatic life. During monsoon, labile copper is absent and metal is entirely present in non-labile or bound form (60-80%) at all sampling sites except at site 4 where 90% of metal is present in particulate bound form. This is reflected by high levels of suspended solids and turbidity present in the sample as seen in results of Table 1.

Tables 7 and 8 show the concentration of various fractions of Pb and Cu in winter season. It has been observed that at all sampling locations, Pb is present in the dissolved form but absence of ASV-labile metal indicates the presence of metal in bound form which is known to be non-toxic[10-12]. The total metal concentration is also low as compared to other seasons. The concentration of metal in monsoon has been found to be maximum and can be attributed to dispersion of metals from sediments and is also reflected by high suspended solids. Speciation of copper indicates that the concentration of metal in the upstream is

TABLE 2

CONCENTRATION OF VARIOUS FRACTIONS OF LEAD AND COPPER IN TREATED EFFLUENT DURING DIFFERENT SEASONS

Metal	Season*	ASV-labile I		Total filtrable II		Bound (II-I)		Organically bound		Particulate bound		Total metal μg/L
		μg/L	%	μg/L	%	μg/L	%	μg/L	%	μg/L	%	
Lead	S	5.6	21.6	20.1	77.6	14.5	55.9	1.8	6.9	3.9	15.1	25.9
	M	54.9	97.5	100.2	86.7	45.3	39.2	7.8	6.7	6.6	5.7	115.6
	W	Nil	Nil	20.4	80.9	20.4	80.9	Nil	Nil	5.3	21.0	25.2
Copper	S	Nil	Nil	8.2	69.5	8.2	69.5	2.0	16.9	2.2	18.6	11.8
	M	Nil	Nil	53.2	84.7	53.2	84.7	Nil	Nil	0.4	0.6	62.8
	W	Nil	Nil	45.8	64.9	45.8	64.9	Nil	Nil	16.2	23.0	70.6

* S—Summer
M—Monson
W—Winter

TABLE-3

CONCENTRATION OF VARIOUS FRACTIONS OF LEAD AT DIFFERENT SAMPLING LOCATIONS (SUMMER)

Sampling location	ASV-labile I μg/L	%	Total filtrable II μg/L	%	Bound (II-I) μg/L	%	Organically bound μg/L	%	Particulate bound μg/L	%	Total metal μg/L
Reference point (1 km upstream of effluent outfall)	4.8	5.7	60.8	72.8	56.0	67.1	Nil	Nil	19.9	23.8	83.5
Outfall point (1 km downstream of reference point)	6.9	19.1	23.4	64.6	16.5	45.6	5.8	8.7	11.7	32.2	36.2
1.1 km downstream of reference point	Nil	Nil	18.1	61.8	18.1	61.8	Nil	Nil	9.8	33.4	29.3
2 km downstream of reference point	Nil	Nil	50.5	85.6	50.5	85.6	Nil	Nil	6.3	10.7	59.3
3.5 km downstream of reference point	Nil	Nil	15.2	60.8	15.2	60.8	Nil	Nil	9.3	37.2	25.0

TABLE-4

CONCENTRATION OF VARIOUS FRACTIONS OF COPPER AT DIFFERENT SAMPLING LOCATIONS (SUMMER)

Sampling location	ASV-labile I µg/L	%	Total filtrable II µg/L	%	Bound (II-I) µg/L	%	Organically bound µg/L	%	Particulate bound µg/L	%	Total metal µg/L
Reference point (1 km upstream of effluent outfall)	3.1	3.7	62.3	73.9	59.2	70.2	8.9	44.3	20.1	23.8	84.3
Outfall point (1 km downstream reference point)	3.2	8.8	9.11	25.1	5.9	16.3	8.9	24.5	22.0	60.6	36.3
1.1 km downstream of reference point	3.8	8.1	36.0	77.1	32.2	69.2	7.3	15.6	7.3	15.6	46.7
2 km downstream of reference point	2.9	6.2	38.1	81.9	35.2	75.7	7.0	15.1	6.2	13.3	46.5
3.5 km downstream of reference point	3.4	4.7	24.8	34.3	21.4	29.6	5.9	8.2	48.1	66.6	72.2

TABLE-5

CONCENTRATION OF VARIOUS FRACTIONS OF LEAD AT DIFFERENT SAMPLING LOCATIONS (MONSOON)

Sampling location	ASV-labile I µg/L	%	Total filtrable II µg/L	%	Bound (II-I) µg/L	%	Organically bound µg/L	%	Particulate bound µg/L	%	Total metal µg/L
Reference point (1 km upstream of effluent outfall)	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	18.3	91.0	20.1
Outfall point (1 km downstream of reference point)	9.5	8.7	93.8	85.9	84.3	77.3	Nil	Nil	14.8	13.6	109.1
1.1 km downstream of reference point	Nil	Nil	78.3	94.8	78.3	94.8	Nil	Nil	9.4	11.4	82.6
2 km downstream of reference point	2.3	2.3	86.4	87.2	84.1	84.9	Nil	Nil	21.2	21.4	99.1
3.5 km downstream of reference point	Nil	Nil	87.8	81.7	87.8	81.7	Nil	Nil	13.8	12.8	107.5

TABLE-6

CONCENTRATION OF VARIOUS FRACTIONS OF COPPER AT DIFFERENT SAMPLING LOCATIONS (MONSOON)

Sampling location	ASV-labile I		Total filtrable II		Bound (II-I)		Organically bound		Particulate bound		Total metal
	μg/L	%	μg/L	%	μg/L	%	μg/L	%	μg/L	%	μg/L
Reference point (1 km upstream of effluent outfall)	Nil	Nil	97.2	63.8	97.2	63.8	8.0	5.2	36.2	23.8	152.4
Outfall point (1 km downstream of reference point)	Nil	Nil	65.6	79.9	65.6	79.9	10.2	12.4	10.2	12.4	82.1
1.1 km downstream of reference point	Nil	Nil	50.3	60.7	50.3	60.7	15.0	18.1	27.6	33.3	82.9
2 km downstream of reference point	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	70.7	90.6	78.0
3.5 km downstream of reference point	Nil	Nil	24.2	56.0	24.2	56.0	9.8	22.7	11.0	25.5	43.2

TABLE 7

CONCENTRATION OF VARIOUS FRACTIONS OF LEAD AT DIFFERENT SAMPLING LOCATIONS (WINTER)

Sampling location	ASV–labile I		Total filtrable II		Bound (II–I)		Organically bound		Particulate bound		Total metal
	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L	%	µg/L
Reference point (1 km upstream of effluent outfall)	Nil	Nil	19.4	53.7	19.4	53.7	Nil	Nil	12.7	35.2	36.1
Outfall point (1 km downstream of reference point)	Nil	Nil	15.7	48.3	15.7	48.3	Nil	Nil	15.0	46.2	32.5
2 km downstream of reference point	Nil	Nil	32.6	83.2	32.6	83.2	Nil	Nil	3.8	9.7	39.2
3.5 km downstream of reference point	Nil	Nil	18.8	68.6	18.8	68.6	Nil	Nil	5.6	20.4	27.4

TABLE 8

CONCENTRATION OF VARIOUS FRACTIONS OF COPPER AT DIFFERENT SAMPLING LOCATIONS (WINTER)

Sampling location	ASV-labile I		Total filtrable II		Bound (II–I)		Organically bound		Particulate bound		Total metal
	μg/L	%	μg/L	%	μg/L	%	μg/L	%	μg/L	%	μg/L
Reference point (1 km upstream of effluent outfall)	8.0	11.4	53.4	76.2	45.4	64.8	14.0	20.0	10.2	14.6	70.1
Outfall point (1 km downstream of reference point)	8.0	16.6	46.5	96.7	38.5	80.0	12.3	25.6	0.9	1.9	48.1
2 km downstream of reference point	6.6	26.6	16.9	68.1	10.3	41.5	6.4	25.8	3.9	15.7	24.8
3.5 km downstream of reference point	4.1	11.7	27.2	77.7	23.1	66.0	7.2	20.6	5.6	16.0	35.0

more in comparison to the discharge point. Exactly similar trend has been observed for summer and monsoon season. This may be due to domestic effluent discharges as observed at site-1 The concentrations of ASV–labile metal in the river decreases downstream, 60–90% of copper is present in dissolved form, but about 25% of metal is organically bound. Hence, copper is unlikely to cause any immediate threat to the aquatic system.

Thus, it can be inferred from the above discussions that the analytical scheme proposed can be applied for speciating chloralkali plant effluents and the receiving river water body. The results discussed above enlighten and emphasize the need for monitoring total heavy metal concentrations as well as their various physico-chemical forms.

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