Spatial, Temporal and Depth Profiles of Trace Metals in an Urban Wetland System: A Case Study with Respect to the Deepor Beel, Ramsar Site 1207, India

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Abstract

The Deepor Beel is a permanent, freshwater wetland at the southwest corner of Guwahati (India) and it is a major stormwater storage basin for the city. Beel was designated as a Ramsar site (No. 1207) in 2002 and recognized as an important habitat for a large number of migratory aquatic birds. Orchids of commercial value are also found in the forests on the bank. The Deepor Beel is presently under stress due to excessive fishing activities, hunting of water fowl, input of contaminants from the agricultural fields and industries in the surroundings and infestation by water hyacinth. This study reports on monitoring of pH and 10 trace metals (As, Cd, Cr, Co, Cu, Ni, Mn, Pb, Hg, Zn) in the Deepor Beel water at 13 sites for three different depths consisting of surface layer, middle layer or euphotic zone, and bottom layer or euphotic zone x 1.5. The assessment was done bimonthly for a year.

Keywords: spatiotemporal profile, depth profile, wetland, pH, trace metals, Ramsar site, euphotic zone, Deepor Beel

1. Introduction

With an increased understanding of the importance of drinking water quality to public health and raw water quality to aquatic life, assessment of surface water quality has become very important. Trace metals in surface water comes from both point and non-point sources. Point source pollution has been successfully controlled in most watershed management cases. However, water quality deterioration due to frequent discharges of pollutants from non-point sources has remained a major problem. Non-point source pollution does not originate from an identified point. Such spatially-dispersed loads are carried to receiving water by surface and subsurface runoff due to rain events, and by irrigation return flows. Being more diffuse and harder to identify, isolate, and control, this has continued to trouble water quality planners (Maciej, 2000; Ouyang et al., 2009; Lai et al., 2011). The pollutants such as suspended solids, nutrients, pesticides, fertilizers and other inorganic and organic substances contribute substantially to the pollution loads of water bodies and cause the deterioration of water quality. The degradation of water quality due to these contaminants has resulted in altered species composition, impacts on the overall health of aquatic communities in wetland systems and an overall loss of biodiversity (Campbell et al., 1993; Durell et al., 2001; Ouyang et al., 2002; Ouyang, 2005).

Industrialization and urbanization have led to a huge demand on ecology by releasing wastes and effluents to the environment. Water is particularly vulnerable to contamination from discharge of wastewaters by various industries. The tremendous increase in the use of trace metals over the past few decades has inevitably resulted in an increase of metallic substances into the aquatic environment. Trace metals can retard growth and damage kidney. Trace metals are also linked to rheumatoid arthritis, circulatory or central nervous system diseases, various types of cancers, etc. The metals of major concern are arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni) and zinc (Zn). Urban stormwater runoff can be toxic to aquatic organisms due to the presence of toxic trace metals (Marsalek et al., 1999; Schiff et al., 2002; Greenstein et al., 2004). The trace metals are contributed by various non-point sources within and adjacent to urban centers (Sansalone & Buchberger, 1997; Smullen et al., 1999; Buffleben et al., 2002).

Wetlands are a vital line of defense between the nonpoint source pollutants and water quality of streams, rivers and lakes. Because of their position between dry land and water, wetlands protect the most biologically productive ecosystems in the world. Their strategic position within the landscape, wetlands can provide a wide variety of ecosystem services such as (i) improving water quality by filtering sediment, nutrients, and pollutants, (ii) reducing flood damage, (iii) preventing bank and shoreline erosion, (iv) recharging ground and surface water supplies, (v) providing vital fish and wildlife habitat, (vi) offering opportunities for recreation, education, and research, (vii) producing food, forest, and fuel products, etc. and also functioning as important nutrient cycling mechanism for maintaining water quality (Huiping, et al., 2011). Assessing wetland health through monitoring is therefore vital to its protection. Because wetland resources support healthy environments, communities, and economies, effective watershed management should include conservation and restoration of wetlands and their functions. Monitoring water quality helps in taking effective measures for protecting and restoring wetlands and aquatic resources.

The Deepor Beel (26°05'-26°11' N, 91°35'-91°43' E, area 4000 ha, elevation 53 m above MSL) is a permanent, freshwater lake existing in a former channel of the Brahmaputra River in its south bank and in the southwest corner of Guwahati city (Assam, India). It is a large natural wetland having great biological and environmental importance besides being the only major stormwater storage basin for the city. Deepor Beel is endowed with rich floral and faunal diversity. In addition to the huge congregation of residential water birds, Deepor Beel ecosystem harbours large number of migratory waterfowl each year. Deepor Beel has been designated as a Ramsar Site (No. 1207) on November, 2002. Although the original area of Deepor Beel was 4000 ha, due to large scale encroachment and other activities, the area has shrunk considerably and the present area of the actual wetland has been estimated at around 700 ha.

As a component of water quality study in an urban wetland system, the overall objectives of this study are to provide definitive information on concentrations of ten trace metals (As, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, and Zn) and to describe their seasonal and spatial trends. This is based on the hypothesis that Deepor Beel ecosystem is under considerable stress due to the rapid urbanization of the surrounding areas including the construction of a railway track on one side of the wetland.

2. Methods

2.1 Selection of Sampling Sites

There was no previous data on water quality of Deepor Beel wetland and in particular, on the concentration of trace metals. The wetland receives stormwater from the city through a large number of channels and there are also a number of outlets, the major one being a small tributary (the Khana) in the southwest corner, which connects the wetland to the River Brahmaputra. In selecting the sampling stations, all these aspects are taken into consideration. The wetland and its surrounding areas were thoroughly surveyed on boats and finally 13 different sites were selected for collection of water samples. The GPS coordinates of these sampling sites are given in Table 1. Samples were collected bimonthly from June to April (June, August, October, December, February, and April) from each selected site. An outline of the Deepor Beel is given in Figure 1(a). Sampling locations for bimonthly collection of both surface water and depth profiling are given in Figure 1(b).

Table 1. Locations of the sampling sites

S/N	Latitude (N)	Longitude(E)
1	26:06:57.38	91:39:18.61
2	26:07:06.89	91:39:50.62
3	26:06:54.11	91:40:15.02
4	26:07:41.23	91:39:41.00
5	26:07:19.09	91:39:21.46
6	26:07:03.11	91:39:18.79
7	26:07:23.74	91:38:37.28
8	26:07:25.79	91:38:15.43
9	26:07:33.49	91:37:55.56
10	26:06:34.45	91:37:36.30
11	26:06:39.60	91:38:04.16
12	26:06:43.52	91:38:23.21
13	26:06:25.60	91:41:35.41

Figure 1(a). The Deepor Beel wetland system (shaded area) and its surroundings

2.2 Sample Collection and Pre-treatment

Water samples were collected in 1 L polyethylene containers pre-cleaned with 10% reagent grade HNO_3, followed by rinsing three times with deionized water and thoroughly dried in a fume hood.

Water samples were collected at three different depths defined by (a) Surface layer, (b) Euphotic zone, (c) Euphotic Zone x 1.5. Euphotic zone was found with the help of Secchi disk and since light normally penetrates to a depth of 1.5 to 1.7 times the Secchi disk depth, the maximum depth used for sample collection was taken as 1.5 times the Euphotic zone. In some of the sampling stations, however, the water is very shallow and it was not possible to estimate the euphotic zone. In such cases, water samples are collected from surface and bottom layers only. A special water sampler with a trace bottom was used to collect sample from different depths such that the top cover can be opened and closed from the surface. Collection, storage and analysis of the water samples were done following the methods of American Public Health Association (APHA, 2005).

Table 2 shows the euphotic zone depths along with the total depths of the wetland at all the sites for the six batches of sampling. Both wetland depth and euphotic zone depth are not uniform and this can be seen clearly from the values of the mean, the minimum and the maximum transparencies for each sampling. In February and April, the wetland becomes very shallow and the bottom is visible to naked eye in most places and the water can be described as totally transparent. At the high flood time of August, the wetland has the maximum depth as water fills up to the banks, but the euphotic zone and hence the transparency of the water body were maximum only during June when the runoff volume (carrying mud and various debris) did not reach the maximum, which usually happened during August.

In a shallow lake like Deepor Beel, the increased values of the euphotic zone and hence, the depth of the transparent layer during the wet months of June and August were mainly due to several fold increase in water volume and might also be due to the fact that aquatic vegetation had just started to grow as more and more nutrients began to reach the wetland in the form of runoff from the nearby agricultural fields. This, however, had an offsetting influence from the increase in sediment load brought into the water column by runoff and also by

local turbulence created by boats of fishermen, etc. Since the wetland was mostly shallow, thermal stratification could be ruled out and the Secchi disk readings were hardly having any influence due to this. On the other hand, a sharp decrease in water volume during the winter (February) results in excessive vegetation growth (both submerged and emerged types) and the depth of the transparent layer decreased. Figure 2 is in agreement with these observations. The transparency had a decreasing trend from the summer to the winter (decrease in water volume was the main factor). The light penetrates more deeply in clear water wetland allowing photosynthesis to occur and oxygen to be produced in deeper layers. Excessive growth of algae, presence of suspended soil particles, and other materials on the other hand, reduce transparency and photosynthesis in the deeper layers of the water column. Thus, the secchi disk depth is not only related to artificial turbidity created by suspended particles, it is also an effective tool for estimating the wetland's productivity. For most part of the year, the transparency of Deepor Beel water is much less compared to the total depth (Table 2), which therefore indicates the highly productive nature of the wetland. Unplanned development in the surroundings and poor land use practices of the cultivators are responsible for large erosion rate of soil, discharge of natural organic matter and nutrients from the paddy fields to the wetland increasing suspended particulate load and algal growth. This has also been the cause of accumulation of debris at the bottom and the resultant non-uniform depth of the wetland (Table 2).

Figure 1(b). Sampling locations for bimonthly collection of both surface water and depth profiling

Figure 2. Variation of the depth of the Euphotic Zone with sampling months

Table 2. Transparency data for Deepor Beel wetland (TD total depth in cm, EZ euphotic zone depth in cm, T fully transparent, ND not determined)

Batch	June		August		October		December		February		April	
Site	TD	EZ	TD	EZ	TD	EZ	TD	EZ	TD	EZ	TD	EZ
1	230.0	68.5	475.0	77.0	232.0	49.0	82.0	43.5	65.0	31.2	100.0	T
2	210.0	160.0	183.0	73.0	181.0	54.5	51.0	32.5	27.0	15.0	71.0	T
3	137.0	95.0	390.0	51.0	195.0	58.5	52.0	19.5	16.0	8.0	32.0	T
4	90.0	T	240.0	84.0	41.0	NA	30.0	ND	24.0	ND	25.0	ND
5	207.0	T	170.0	77.5	165.0	59.0	67.0	50.1	18.0	T	41.0	T
6	210.0	66.0	475.0	67.0	240.0	58.0	96.0	40.5	66.5	T	96.0	T
7	50.0	21.5	478.0	65.5	137.0	49.0	36.0	19.0	52.0	33.2	32.0	T
8	102.0	52.5	415.0	89.0	239.0	73.5	72.0	45.0	30.0	T	55.0	T
9	205.0	124.0	280.0	90.0	120.0	T	48.0	T	21.0	T	30.0	T
10	130.0	49.0	460.0	72.0	100.0	80.0	42.0	20.0	35.0	T	25.0	T
11	110.0	29.5	500.0	79.0	205.0	97.0	55.0	ND	43.0	T	91.0	48.0
12	95.0	7.0	120.0	109.0	150.0	95.5	49.0	29.5	25.0	T	21.0	T
13	90.0	ND	315.0	41.5	120.0	ND	99.0	ND	91.0	34.0	ND	ND
Mean	143.5	67.3	346.2	75.0	163.5	67.4	59.9	33.3	39.5	24.3	51.6	--
Min	50.0	7.0	120.0	41.5	41.0	49.0	30.0	19.0	16.0	8.0	21.0	--
Max	230.0	160.0	500.0	109.0	240.0	97.0	99.0	50.1	91.0	34.0	100.0	--
SD	60.6	47.5	135.2	17.2	59.8	18.1	21.8	12.1	22.9	12.0	30.1	--

2.3 Analytical Methods

As pH is an important parameter governing the dissolution of the metals in water and vice-versa, the values of this parameter for all the water samples were also reported along with the concentrations of the trace metals. pH was determined immediately at the time of collection of water samples.

The water samples immediately after collection were acidified to a pH < 2.0 by adding 1.5 mL concentrated HNO_3/L or an appropriate volume required to achieve the desired pH. After acidification, the samples were stored in a refrigerator at ~ 4^oC till analysis for the metals is undertaken. Since the water samples were mostly turbid with appreciable load of suspended particulates, the water samples had to be digested to find the concentration of both dissolved metals and that associated with the particles. In this work, nitric acid digestion technique (APHA, 2005) was used. For this, a volume of 100 mL of each acid-preserved, well-mixed water sample was taken in a beaker, 5 mL of conc. HNO_3 was added and the mixture was slowly evaporated on a hot plate in a fume-hood to a volume of 10-20 mL of clear solution. The beaker walls were washed with double-distilled water and the volume was remade to 100 mL in a volumetric flask. This was then used for analysis of the metals with AAS.

The trace metals, As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, and Zn were measured in each water sample with atomic absorption spectrophotometry (Varian SpectrAA-220 AAS). Three point calibrations were done for each metal with certified AAS standards of 1000 mg/L (Merck, Germany). The optimum experimental conditions for AAS measurement are given in Table 3.

Arsenic was estimated by hydride generation atomic absorption spectrophotometry (Varian SpectrAA 220) using Varian VGA77 vapour generation assembly with ETC60 temperature controller as a heat source to atomize the hydride generated with the reducing agent $NaBH_4$ (Merck) and 8M HCl acid. Mercury was estimated with the flameless cold vapor technique using the same combination of reducing agent. All the other metals were estimated in the air-acetylene flame. The data quality was checked by careful standardization, procedural blank measurements, and using spiked and duplicate samples.

Table 3. Optimum conditions for AAS measurements of the trace metals

Metal	Wavelength (nm)	Lamp current (mA)	Slit width (nm)	Optimum working range (μg/mL)
As	193.7	10	0.5	3.0-150.0
Cd	228.8	4	0.5	0.02-3.0
Cr	429.1	5	0.5	0.1- 3.0
Co	240.7	7	0.2	0.05-15.0
Cu	324.8	4	0.5	0.02-3.0
Hg	253.7	4	0.5	2.0-400.0
Mn	279.5	5	0.2	0.02-50.0.
Ni	232.0	4	0.5	0.02-3.0
Pb	217.0	5	1.0	0.1- 30.0
Zn	213.9	5	1.0	0.01-2.0

2.4 Data Analysis

The generated data were subjected to basic statistical analysis and pair-wise linear regression. Analysis of variance (ANOVA) of trace metal concentrations in the surface and the bottom layers for the 13 sampling sites was carried out using one way ANOVA model which relies on an additive decomposition of the data into grand mean, main effects, possible interactions, and an error term (Gelman, 2005). This analysis tests the validity of the 'null' hypothesis that pH and the trace metal concentrations did not differ with (i) depth, (ii) location and (iii) time (Cooper & Gillespie, 2001). The differences are considered significant if F-ratio >> 1.0 and the p-value << 1.0, when the null hypothesis is invalid and the measured values within a group have valid correlation. F-ratio is approximately 1.0 if the corresponding effects are zero; otherwise F-ratio > 1.0. If F-ratio is <1, there is negative correlation within a group. If F-ratio is < 1.0 and p-value is ≈ 1.0, the measured values have a 'chance' element that cannot be neglected.

3. Results and Discussion

Surface water quality helps in evaluating the impacts of natural or anthropogenic point and non-point sources of pollution on ecosystem health (Ouyang, 2005). The basic statistics for the measurements in this work are given in Table 4.

Table 4. Basic statistics of the water quality of Deepor Beel (all metals are in mg/L except As and Hg, which are in μg/L)

S/N	Parameter	Top layer				Bottom layer			
		Min	Max	Mean	SD	Min	Max	Mean	SD
1	pH	2.90	8.30	1.60	2.73	2.40	8.10	1.70	2.79
2	As	0.00	10.95	2.76	1.87	0.00	8.20	2.35	0.82
3	Cd	0.00	0.13	0.05	0.01	0.00	0.20	0.05	0.02
4	Cr	0.00	0.57	0.11	0.04	0.00	0.54	0.13	0.06
5	Co	0.00	11.11	0.47	1.95	0.00	0.61	0.11	0.07
6	Cu	0.00	0.14	0.03	0.02	0.00	0.25	0.05	0.03
7	Pb	0.00	3.19	0.83	0.18	0.00	4.12	0.81	0.34
8	Hg	0.60	34.50	8.10	3.50	0.00	23.70	6.33	1.60
9	Mn	0.01	1.46	0.34	0.17	0.00	1.82	0.44	0.18
10	Ni	0.00	1.38	0.26	0.13	0.00	1.00	0.23	0.17
11	Zn	0.01	0.57	0.21	0.07	0.04	3.39	0.36	0.42

3.1 pH of Water

Small variations in pH of water are observed from one station to another. Similar variations also exist with depth of water columns and time of year. The minimum, maximum and mean values of pH for all sampling stations are shown in Figure 3.

Figure 3. Minimum, maximum and mean values of pH of the Deepor Beel water for surface, middle and the bottom layers

Values remain within a narrow range particularly for the middle layer (or euphotic zone), but for the surface and the bottom (or euphotic zone x 1.5) layers of water, but the range is very wide for the fifth (February) batch of sampling when the water is strongly acidic at sites 1 and 13 for the surface layer, and 4 and 7 for the bottom layer.

These low values might be due to local accumulation of H^+ ions due to low volume of water during this time of the year, stagnancy and decaying aquatic plants, tree leaves, etc. The mean pH of the water column shows an increasing trend from April to October, then as the dry season sets in, the values decrease reaching the lowest value in February. The wetland might have been receiving acidic inflows, either from the municipal wastes dumped into it or from the adjacent soil structure, the impact becoming more pronounced during February. When the pH variations with respect to each sampling site covering all the six batches of samples are taken into consideration, the minimum, maximum and mean values show a pattern as in Figure 4. It is seen that Deepor Beel water has very wide fluctuation of pH at the sites 1, 4, 7 and 13 where the pH spread from almost 3.0 to 8.0 over the different batches. The low values, turning the water strongly acidic at these four sites, appear at the dry period of February in each case.

Figure 4. Minimum, maximum and mean values of pH of the Deepor Beel water for each sampling site taking the surface, middle and the bottom layers together

Water pH related to water column depth is presented in Figure 5 for two batches of samples collected in August and December. In several of the sites, the surface layer has higher pH than that of the bottom layer while the reverse is also true in case of some other sites. The differences between the two layers disappear in some sites (e.g. locations 4 and 12). The variations are most likely to be due to local factors arising from chemical, microbiological and other types of interactions including the effects of small differences in temperature vertically down the water column and also due to variations in turbulence level.

The pH of water determines the solubility and biological availability of nutrients (PO_4^{2-}, N^+, and C) and trace metals (Pb, Cu, Cd, etc.). It also determines the speciation of the constituents and defines the conditions in which they will be available to aquatic life. Photosynthesis uses up hydrogen from water molecules causing the concentration of hydrogen ions to decrease and therefore, the pH tends to increase. The pH may be higher during daylight hours and during the growing season, when photosynthesis is at a maximum. Respiration and decomposition processes lower pH. The pH may change with depth in a lake, due to changes in photosynthesis rates and other chemical reactions (Michaud, 1991). Lake or Beel water is full of chemical "shock absorbers" that prevent major changes in pH. Small or localized changes in pH are quickly modified by various chemical reactions, and therefore, the change may not be measured under some circumstances. All waters possess some amount of buffering capacity and because of this, the pH of natural water hovers between 6.5 and 8.5. A pH of 5.6 or lower has been found to be directly toxic to fish, according to USEPA (Michaud, 1991). Generally, during the summer months in the upper portion of a productive or eutrophic lake, pH remains between 7.5 and 8.5, while in the bottom of the lake or in less productive lakes, pH is lower, 6.5 to 7.5 (Michaud, 1991). Such observations are also valid in the present case.

Figure 5. Mean pH of the surface, middle and bottom layers of the Deepor Beel water for the month of August (top) and December (bottom) (discontinuation in the values for the middle layer (euphotic zone) is due to non-availability of this layer at a few of the sampling sites)

3.2 Trace Metals

Trace metals are found in very low concentration in natural water bodies and are widely distributed in the environment contributed mainly by the weathering of rock minerals and soils (Merian, 1991; O'Neil, 1993).

Their concentrations have however reached alarming proportion in many water bodies during the last few decades principally due to anthropogenic inputs (Preuss & Kollman, 1974; Prater, 1975; Merian, 1991). The results of monitoring of 10 of the most important trace metals in Deepor Beel wetland system have also shown influence of inputs from human activities.

3.2.1 Arsenic

Arsenic is a common element in nature that may be found in earth's crust, ground and marine water and organic world. Incidents of arsenic contamination of groundwater are quite common and have been reported from all over the world. Arsenic is not only toxic but also known to be carcinogenic and in the environment has both natural and anthropogenic origin. It is found in minerals and ores, such as tin-ore, and could be released into the aquatic environment by dissolution and erosion. The levels of dissolved arsenic in unpolluted rivers are of the same magnitude as in seawater with a global average concentration of between 1 and 2 µg dm^{-3} (Maher & Butler, 1988; Yusof et al., 2001). Some arsenic must have come from natural or geogenic origins, but anthropogenic inputs also cannot be ruled out. Highest permissible level for total As (As^{3+}, As^{5+}) in drinking water has been fixed at 7 µg/L (NHRMC, 1996) and 10 µg/L (WHO, 2001; USEPA, 2002). Inorganic As normally appears in water as oxyanionic species of As(III) and As(V), which again may exist in several chemical forms depending upon the prevalent redox conditions (Maity et al., 2005). Inorganic As has been recognized as a human poison since ancient times and large oral doses (above 60 ppm in food or water) is fatal. Even with lower levels of inorganic arsenic (ranging from ~ 0.3 to 30 ppm in food or water), irritation in stomach and intestines, with symptoms such as stomachache, nausea, vomiting, and diarrhea (ATSDR, 2000) are common. As with many metals, As toxicity varies with its state of valency.

Speciation of As was not done in this study and the total As only was estimated. Total As varied from below detection level to 12.92 µg/L (euphotic zone, Sample 13, August). Out of 202 measurements throughout the year, As content was below detection level in 45% of the measurements and only in 13% of the measurements, As content was more than 5 µg/L. The presence of As in the water of Deepor Beel cannot be considered as of much significance but it still may be of concern due to the possibility of accumulation and biomagnifications in the various life forms as well as aquatic plants including microflora. It is to be noted that the wetland continues to produce some amount of fish for the local population and at least some people living on the banks depend on the fish for their livelihood. It is therefore very likely that whatever As present in the wetland finds its way into the people. Relatively high As content was recorded for sampling point 13 (10.95 µg/L, surface layer, June), point 2 (10.10 µg/L, surface layer, October), and point 5 (9.13 µg/L, surface layer, April; 8.20 µg/L, bottom layer, October; 7.43 µg/L, bottom layer, April). As content increased towards the dry season because of reduction in water volume, it also accumulated in the bottom layer. Thus, all the sampling points recorded appreciable arsenic content in the bottom layer during October, December, February and April (in this batch, the surface layer had also considerable As). The bottom layer As contents for these three batches are shown with a bar diagram in Figure 6.

Arsenic chemicals were used extensively in agriculture (Moore & Ramamoorthy, 1984) in the form of arsenical insecticide, Paris Green, as a control agent for the potato beetle (*Leptinotarsa decemlineata*). Two other arsenicals, lead arsenate and calcium arsenate, were in common use by the early 1900s and were quite effective on a variety of insects including the gypsy moth (*Lymantria dispar*), cotton boll weevil (*Anthonomus grandis*), and orchard pests (Baudo et al., 1990). Although the use of As-based insecticides has declined or stopped, its occurrence in the receiving waters continues even after a very long time. The use of As compounds as desiccants, fungicides for grapes (*Vitis vinifera*), and active ingredients in selective herbicides, has continued (Cooper & Gillespie, 2001). It is therefore not surprising that the presence of this toxic metal is still detected in Deepor Beel water

3.2.2 Cadmium

Cadmium is recognized as one of the most toxic elements with possible human carcinogenic effects (Goering et al., 1994; Awofolu et al., 2005). It accumulates in the kidney and liver leading to chronic kidney dysfunction. It induces cell injury and death by interfering with Ca regulation in biological systems (Woodworth & Pascoe, 1982). It has been found to be toxic to fish and other aquatic organisms. It has also been implicated in endocrine disrupting activities, which could pose serious health problems. Sources of Cd include wastes from Cd-based batteries, incinerators and runoff from agricultural soils where phosphate fertilizers are used since Cd is a common impurity in phosphate fertilizers (Awofolu et al., 2005). The United States Environmental Protection Agency (USEPA) has set a limit of only 0.005 mg/L of Cd (II) for drinking water whereas the WHO guideline value is 0.01 mg/L. In this study, Deepor Beel water has Cd-content much above the permissible value in a large

number of measurements. The values spread from below detection limit to 0.20 mg/L (the highest value is observed for the bottom layer, location 2, second batch). The average Cd values are higher in the second batch of August (0.11, 0.14, 0.17 mg/L for surface, middle and bottom layers respectively). Out of 202 measurements throughout the year, Cd content was below detection level in 30.2% of the time while it is above the maximum permissible limit in 61.8 % of the time.

Figure 6. Mean arsenic content (µg/L) of the bottom layer for three batches of sampling

Since a large volume of runoff comes into the wetland during the monsoon season and Cd-content is high during this season, it is likely that Cd originates in the surrounding environment and is carried to the wetland by the runoff. The variations in Cd-content between the surface and bottom layers are shown in Figure 7 which indicates that excepting at sampling sites 5 and 7, the bottom layer has slightly more Cd than the surface layer indicating a tendency of the metal to accumulate towards the bottom.

3.2.3 Cobalt

Cobalt content is below detection limit in the initial stages of measurement and could be found only in December onward as the water volume gets reduced. During this lean season of the winter, the contents were from below detection limit to 0.61 mg/L. However, two large Co contents of 1.14 and 11.11 mg/L were measured during December in the surface layer of sampling points, 6 and 11, respectively. These are attributed to local enrichment from wastes thrown into the wetland by fishermen, etc.

Co has been classified as an essential element and forms part of Vitamin B12 required for red-blood cell synthesis. It is also required in some metabolic activities in organisms. Elevated levels, however, lead to toxicity (Spear, 1981). Co concentration in unpolluted surface water is approximately 2.0×10^{-4} mg/L (DWAF, 1996). In this work, Co concentration exceeded this value only once. Out of 202 measurements throughout the year, cobalt

was below detection level in 57.4% of the data. Toxicological effects of large amounts of Co include vasodilation, flushing and cardiomyopathy in humans and animals (Teo & Chen, 2001). Other effects include loss of body weight and depressed appetite.

Figure 7. Mean Cadmium content (mg/L) of the surface and bottom layers of the Deepor Beel water for all the sampling sites

3.2.4 Copper

USEPA has determined that drinking water should not contain more than 1.3 mg/L of Cu(II). Cu is mostly absent in Deepor Beel water, but appreciable concentrations are found during August (Second batch, bottom layer only) and February (Fifth batch, all the three layers). The maximum content recorded was 0.25 mg/L (Bottom layer, sample 11, second batch), 0.23 mg/L (Middle layer, sample 2, fifth batch) and 0.21 mg/L (Bottom layer, sample 9, fifth batch). In the 202 measurements, Cu content was below detection level 72.2 % of the time with no value found above the permissible limit. Cu-contents of Deepor Beel water did not exceed the maximum permissible value and approximately 28.0 % of the values were other than BDL. Levels of Cu in irrigation and livestock waters have been set as 0 to 0.2 mg/L and 0 to 5.0 mg/L respectively with adverse chronic effects expected at 1 to 10 mg/L (DWAF, 1996). Thus, no adverse effects are expected due to Cu-content (Awofolu et al., 2005).

3.2.5 Chromium

The USEPA sets a maximum level for Cr in drinking water of 0.1 mg/L (USEPA, 2000). Only the total Cr was estimated in this work and speciation of Cr-species was not done. Cr-contents were from below detection level to 0.57 mg/L (Surface layer, location 8, fourth batch). The average Cr was higher in the fourth batch (December; 0.27, 0.13, and 0.17 mg/L respectively for the surface, middle and bottom layers). No Cr was detected in the first batch (June). A comparison of Cr-contents of the surface and bottom layers for the months of August (wet season) and April (dry season) is presented in Figure 8. Cr content was BDL in 26.2% of 202 measurements and was above permissible limit (0.1 mg/L) in 47.5% of the same. In natural lake water, Cr content of up to 0.005 mg/L was recorded (Abbasi et al., 1998). With respect to this, some of the values found in this study were very high.

Figure 8. Mean values of chromium content (mg/L) of the Deepor Beel water for the months of August (second batch) and April (sixth batch)

3.2.6 Manganese

Manganese is neurotoxic and is believed to be responsible for inducing Parkinson like syndrome. Mn content varied from BDL to 1.82 mg/L (Bottom layer, sample 9, fifth batch). Other high concentrations recorded were 1.71 (Bottom layer, sample 8, fifth batch) 1.52 (Bottom layer, sample 4, sixth batch), 1.46 (Surface layer, sample 13, fifth batch), 1.44 (Surface layer, sample 4, sixth batch). Mn contents were higher in the fifth batch (0.45, 0.61, 1.01 mg/L for surface, middle and bottom layers) and also for the sixth batch (0.93, 1.01 mg/L). Mn content was BDL in 38.6% in 202 measurements and exceeded the maximum permissible limit of 0.5 mg/L (WHO, 2004) in 20.2%.

3.2.7 Mercury

Mercury has been used as a fungicide for seed treatment for nearly a century although its use in many countries has been discontinued due to its toxic properties. Hg is both an enzyme and protein inhibitor, and is strongly associated with suspended solids in natural waters. Hg compounds are highly toxic to plants, and concentrations in plant tissues increase with age (Cooper & Gillespie, 2001). Hg content in Deepor Beel water was from BDL to 34.5 μg/L (Surface layer, sample 11, Fourth batch). Other high concentrations were 25.1 μg/L (Surface layer, sample 13, first batch), 25.7 μg/L (Surface layer, sample 2, fourth batch), 26.8 μg/L (Surface layer, sample 11, first batch), 32.1 μg/L (Middle layer, sample 1, fourth batch). Hg was generally high in the fourth batch (34.5, 32.1, 23.7 μg/L for surface, middle and bottom layers) (Figure 8).

Only 20.7% of the 202 measurements had Hg content at BDL, while it was > 1 μg/L (WHO maximum permissible limit, WHO 2004) in 72.2% of the same. The presence of appreciable amount of Hg in Deepor Beel water needs thorough investigation.

Figure 9. Mean Hg-content (μg/L) of the Deepor Beel for the three layers of water of all the batches

3.2.8 Nickel

Nickel is a naturally occurring element found in a number of mineral ores including nickel sulphides, oxides and silicates. It is present in the enzyme urease and is considered essential to plants and some domestic animals. The essentiality of Ni to man has not been demonstrated. Its properties such as strength, corrosion resistance, high ductility, good thermal and electric conductivity and catalytic properties enhance its commercial importance and applications. It is, however, related to renal, cardiovascular, reproductive, and immunological effects in animals. Toxicity of Ni to rainbow trout has been reported. The toxic effects in man are related to dermal, lung and nasal sinus cancers (Awofolu et al., 2005). USEPA recommends that drinking water levels for Ni should not be more than 0.7 mg/L.

Ni contents of Deepor Beel varied from BDL to 1.38 mg/L (Surface layer, sample 11, third batch). Other high concentrations of nickel were 1.18 mg/L (Surface layer, sample 10, third batch), 1.06 mg/L (Surface layer, sample 4, third batch), 1.00 mg/L (Bottom layer, sample 13, fourth batch). The average Ni content was higher in the second (0.31, 0.56, 0.67 mg/L for surface, middle and bottom layers), third (0.89, 0.29, 0.29 mg/L for surface, middle and bottom layers), and fourth (0.31, 0.30, 0.40 mg/L for surface, middle and bottom layers) batches. Variations in the surface and the bottom layers are shown in Figure 10. The values were uniformly high in all the sites with Ni content accumulating downward. This indicates the major input of nickel to be from the runoff water. As the mud in runoff settles down, it carried Ni downward.

Sources of Ni in surface water include anthropogenic sources, combustion of fossil fuels (Merian, 1984), old battery wastes, components of automobiles, old coins, and many other items containing stainless steel and other Ni alloys. Similar sources can be attributed for Ni in Deepor Beel. In the present study, Ni-content was BDL in

54% of 202 measurements, but 8.4 % of the same had Ni more than the maximum permissible limit. Attention has now been focused on the toxicity of Ni at low concentrations because of its potential to cause allergic reactions and also for the carcinogenicity of Ni-compounds (McKenzie & Smythe, 1998). The typical concentration of Ni in unpolluted surface water is of the order of 5.0×10^{-4} mg/L (DWAF, 1996) and 0.015 to 0.020 mg/L (Salnikow & Denkhaus, 2002). In the present study, a few of the values were very large indicating that Deepor Beel water was contaminated. Since all Ni compounds except for metallic Ni have been classified as carcinogenic to humans (IARC, 1990), its presence in Deepor Beel in appreciable concentration is a cause for concern.

Figure 10. Mean Ni-content (mg/L) of the Deepor Beel water for the surface and bottom layers

3.2.9 Lead

The presence of Pb in Deepor Beel water has implications to the biota and also to man. United States Environmental Protection Agency has classified Pb as being potentially hazardous and toxic to most forms of life (USEPA, 1986). Quite a number of human ailments such as chronic neurological disorders, especially in fetuses and children, are attributed to Pb. It enters the environment from automobile exhaust (vehicles using leaded fuels till a few years back), used dry-cell batteries, sewage effluent, runoff of wastes and atmospheric deposition (Awofolu et al., 2005). USEPA has fixed a limit of 0.015 mg/L for Pb in drinking water is.

Pb contents of Deepor Beel varied from BDL to 4.12 mg/L (this high value is measured for the bottom layer at location 13, fourth batch). High Pb contents of 3.19 mg/L (Surface layer, sample 13, fourth batch), 2.87 mg/L (Surface layer, sample 13, fourth batch), 2.65 mg/L (Surface layer, sample 6, fourth batch), 2.60 mg/L (Surface layer, sample 8, fourth batch), 2.51 mg/L (Surface layer, sample 9, fourth batch), 2.30 mg/L (Middle layer, sample 12, third batch), 2.18 mg/L (Surface layer, sample 7, fourth batch), 2.16 mg/L (Surface layer, sample 12, fourth batch; middle layer, sample 5, fourth batch), 2.03 mg/L (Middle layer, sample 5, third batch), were also found. The average Pb contents were higher in the fourth batch (2.24, 1.53, 12 mg/L for surface, middle and bottom layers). A comparison of the average Pb-contents of the surface and the bottom layers for the months of August (second batch) and April (sixth batch) is shown in Figure 11. Statistically, Pb was BDL in only 20.8% of the measurements and was more than the maximum permissible limit (0.015 mg/L) in 77.2% of the same.

3.2.10 Zinc

Zn has low toxicity to man, but prolonged consumption of large doses can result in health complications such as fatigue, dizziness, and neutropenia. Zn is also toxic to fish and other aquatic organisms (Awofolu et al., 2005). Zn contents of Deepor Beel water were from BDL to 3.39 mg/L (Bottom layer, sample 10, third batch). A few other high values were 2.83 mg/L (Bottom layer, sample 10, third batch), 2.65 mg/L (Bottom layer, sample 10, third batch), 1.51 mg/L (Bottom layer, sample 1, second batch), 1.48 mg/L (Middle layer, sample 3, second batch). Zn was high in second (0.15, 0.34, 0.28 mg/L for surface, middle and bottom layers), third (0.33, 0.55,

1.02 mg/L for surface, middle and bottom layers), fourth (0.37, 0.26, 0.22 mg/L for surface, middle and bottom layers) batches. Average Zn-contents for the surface and the bottom layers of the 13 locations are presented in Figure 12. Zn was BDL in 18.3% of the measurements and none of the other values exceeded the maximum permissible limit.

Figure 11. Average Pb-contents (mg/L) for the surface and bottom layers of water of the Deepor Beel

Figure 12. Mean Zn-content of the surface and bottom layers of the Deepor Beel for all the sites

3.3 Pair-Wise Correlation

Reasonable correlations ($r \geq 0.50$) were found between 7 pairs of trace metals, using their mean contents in surface and bottom layers as shown below:

	Trace metals	r
1.	Cr-Pb	+ 0.66
2.	Cr-Mn	− 0.55
3.	Co-Mn	− 0.58
4.	Cu-Mn	− 0.54
5.	As-Mn	− 0.60
6.	Mn-Zn	+ 0.52
7.	Hg-Zn	− 0.55

Positive correlation between Cr: Pb, and Mn: Zn, indicates that these metals have a tendency to occur together, possibly coming from similar sources. The correlation is negative between Cr : Mn, Co : Mn, Cu : Mn, and Hg : Zn. For these pairs of metals, one of the metals predominates over the other indicating that if one of the pair is found in considerable concentration, the other is likely to be present in lower concentration. The negative correlation shows that if one metal of the pair is released from some source to water, it prevents the release of the other from the same source or a different one.

The correlated pairs of metals are expected to have come from similar point sources (e.g. municipal and industrial effluents) and nonpoint sources (e.g. agricultural runoff, soil leaching, etc.).

3.4 Analysis of Variance

One-way ANOVA analysis is presented in Tables 5, 6, and 7 respectively with (i) time (6 bimonthly batches of water samples), (ii) layer (surface and bottom layers), and (iii) sampling sites as the factors. The mean square for each row is the sum of squares divided by the degrees of freedom.

In the present work, with time as factor, F-ratio is > 1.0 in all the cases. Thus, the variations in trace metal concentrations with time are statistically significant and they are likely to follow a definite pattern. Since water volume changes with season therefore, concentrations also change. Also $p = 0$ for all the metals except Co when $p = 0.18$ and F-ratio = 1.53. Thus, Co in Deepor Beel water is not influenced by time as it is not likely to have come from an external source. This is not true for the other metals which vary from batch to batch. The input of these metals depends on sources other than the wetland such as the runoff. pH of the water has F-ratio > 1.0 and p-value = 0 with time as the factor which indicates that pH does differ significantly with time (or batch) and the variations are statistically significant.

With respect to depth of the water column (surface layer and bottom layer), F-ratio is >1.0 only in case of Cu, Mn, Hg and Zn corresponding to which $p =$ zero or near zero (Table 6). The concentrations of the four metals have a positive correlation with depth and the variations are statistically significant. Combined interpretation of F-ratio and p-value for all the other metals does not support any correlation with depth and therefore, the metals, As, Cd, Co, Cr, Ni and Pb have no tendency either to accumulate or decline in concentration with depth. A similar conclusion may be arrived at for pH of Deepor Beel water for which F-ratio < 1.0 and p-value > 0.0, and pH bears no positive correlation to the depth of the water column.

ANOVA analysis with sampling site as variable yields no strong correlation (Table 7). F-ratio is marginally > 1.0 in the case of As, Co, Cr and Hg, but $p \neq 0$. Thus, the metals do not bear any significant correlation with sampling sites. Therefore, each sampling site could be considered as an independent monitoring site without having any relationship with the other sites. This may be due to differences in (i) turbulence level, (ii) human disturbances, (ii) number and density of aquatic plant species, and (iv) depth of the water column.

4. Conclusions

The Deepor Beel wetland system has intensive cultivation in its surroundings which may be described as a vast floodplain and is therefore a high risk area for contamination by metals. Various chemical formulations containing these toxic metals have been in use for pest management and may be considered as the single most

important contributor to wetland water. In addition, these metals may have increased over time through natural accumulation processes involving sediment transport, soil weathering, and atmospheric deposition. pH of water is seen to have large temporal and spatial variations, and therefore, trace metals shift between water and sediment in a pattern which is dependent on time, depth of the water column and also location.

Table 5. Analysis of Variance (ANOVA) with time as the factor (A between groups, B within groups, C total)

Dependent Parameter	Source	Sum of Squares	Degrees of freedom	Mean Square	F-ratio	p-value
pH	A	32.54	5.00	6.51	11.97	0.00
	B	81.55	150.00	0.54		
	C	114.09	155.00			
As	A	495.08	5.00	99.02	27.37	0.00
	B	542.70	150.00	3.62		
	C	1037.78	155.00			
Cd	A	0.32	5.00	0.06	72.39	0.00
	B	0.13	150.00	0.00		
	C	0.45	155.00			
Co	A	6.02	5.00	1.20	1.53	0.18
	B	118.00	150.00	0.79		
	C	124.02	155.00			
Cu	A	0.21	5.00	0.04	26.81	0.00
	B	0.23	150.00	0.00		
	C	0.44	155.00			
Cr	A	0.57	5.00	0.12	14.08	0.00
	B	1.22	150.00	0.01		
	C	1.79	155.00			
Mn	A	21.20	5.00	4.24	49.17	0.00
	B	12.94	150.00	0.09		
	C	34.14	155.00			
Hg	A	1774.10	5.00	354.82	9.78	0.00
	B	5403.93	149.00	36.27		
	C	7178.04	154.00			
Ni	A	6.70	5.00	1.34	24.10	0.00
	B	8.29	149.00	0.06		
	C	15.00	154.00			
Pb	A	53.77	5.00	10.75	47.42	0.00
	B	34.02	150.00	0.23		
	C	87.78	155.00			
Zn	A	7.27	5.00	1.45	9.75	0.00
	B	22.36	150.00	0.15		
	C	29.64	155.00			

When a wetland is affected by human actions, the changes occur rapidly and the deterioration takes place in a shorter time scale of even one's lifetime that normally takes centuries to occur. The present work shows that the water quality of Deepor Beel has been affected quite appreciably by development activities in the catchment areas through changes in pH and input of trace metals.

Table 6. Analysis of Variance (ANOVA) with the layer as the factor (A between groups, B within groups, C total)

Dependent Parameter	Source	Sum of Squares	Degrees of freedom	Mean Square	F-ratio	p-value
pH	A	0.17	1.00	0.17	0.23	0.64
	B	113.92	154.00	0.74		
	C	114.09	155.00			
As	A	0.11	1.00	0.11	0.02	0.90
	B	1037.67	154.00	6.74		
	C	1037.78	155.00			
Cd	A	0.00	1.00	0.00	0.00	0.99
	B	0.45	154.00	0.00		
	C	0.45	155.00			
Co	A	0.50	1.00	0.50	0.63	0.43
	B	123.52	154.00	0.80		
	C	124.02	155.00			
Cu	A	0.03	1.00	0.03	10.56	0.00
	B	0.41	154.00	0.00		
	C	0.44	155.00			
Cr	A	0.00	1.00	0.00	0.15	0.70
	B	1.79	154.00	0.01		
	C	1.79	155.00			
Mn	A	0.51	1.00	0.51	2.34	0.13
	B	33.63	154.00	0.22		
	C	34.14	155.00			
Hg	A	892.08	1.00	892.08	21.71	0.00
	B	6285.96	153.00	41.09		
	C	7178.04	154.00			
Ni	A	0.02	1.00	0.02	0.16	0.69
	B	14.98	153.00	0.10		
	C	15.00	154.00			
Pb	A	0.01	1.00	0.01	0.01	0.92
	B	87.78	154.00	0.57		
	C	87.78	155.00			
Zn	A	0.72	1.00	0.72	3.84	0.05
	B	28.91	154.00	0.19		
	C	29.64	155.00			

Table 7. Analysis of Variance (ANOVA) with the sampling point as the factor (A between groups, B within groups, C total)

Dependent Parameter	Source	Sum of Squares	Degrees of freedom	Mean Square	F-ratio	p-value
pH	A	8.47	12.00	0.71	0.96	0.49
	B	105.62	143.00	0.74		
	C	114.09	155.00			
As	A	124.24	12.00	10.35	1.62	0.09
	B	913.54	143.00	6.39		
	C	1037.78	155.00			
Cd	A	0.01	12.00	0.00	0.19	1.00
	B	0.44	143.00	0.00		
	C	0.45	155.00			
Co	A	9.92	12.00	0.83	1.04	0.42
	B	114.11	143.00	0.80		
	C	124.02	155.00			
Cu	A	0.00	12.00	0.00	0.11	1.00
	B	0.43	143.00	0.00		
	C	0.44	155.00			
Cr	A	0.18	12.00	0.02	1.31	0.22
	B	1.62	143.00	0.01		
	C	1.79	155.00			
Mn	A	0.85	12.00	0.07	0.31	0.99
	B	33.29	143.00	0.23		
	C	34.14	155.00			
Hg	A	593.26	12.00	49.44	1.07	0.39
	B	6584.77	142.00	46.37		
	C	7178.04	154.00			
Ni	A	0.26	12.00	0.02	0.21	1.00
	B	14.74	142.00	0.10		
	C	15.00	154.00			
Pb	A	3.81	12.00	0.32	0.54	0.89
	B	83.98	143.00	0.59		
	C	87.78	155.00			
Zn	A	0.84	12.00	0.07	0.35	0.98
	B	28.79	143.00	0.20		
	C	29.64	155.00			

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