

GEOCHEMICAL DISTRIBUTION AND POLLUTION ASSESSMENT OF METALS IN CORE SEDIMENTS OF TWO PERENNIAL PONDS, KANYAKUMARI DISTRICT, TAMILNADU, INDIA

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Abstract: The bottom core sediment samples of two perennial ponds were collected and to determine the heavy metal concentrations and pollution status of metals such as Fe, Mn, Cr, Cu, Pb, Zn, Al, Ni, Cd, Na, K, Ca and Mg. To assess the metal contamination in pond sediments, sediment quality guidelines of metals (WSR) were applied. The metal contamination in the study pond sediments were also evaluated by applying enrichment ratio (ER), contamination factor (CF), geo-accumulation index (Igeo) and pollution load index (PLI). Based on enrichment ratio (ER), the core sediment samples of Pond I (Manavalakurichy) and pond II (Thiruthuvapuram) indicating deficiency to minimal enrichment for Cu, Ni, Cd, Al, Cr, Zn and Mn. According to contamination factor (CF), K and Mg were responsible for moderate contamination; Na shows considerable contamination and the metals such as Fe, Mn, Cr, Cu, Zn, Al, Ni and Cd indicating low contamination in pond I and II. According to Igeo, pond I sediments were unpolluted to moderately polluted by Pb. Based on PLI all sampling stations in both study ponds suggest no overall pollution of site quality.

Keywords: Perennial ponds, core sediments, metal contamination

1. INTRODUCTION

Geochemistry characterizes the study of complex processes of pools and fluxes of chemical elements within ecosystems and is considered as an essential fraction of contemporary environmental sciences. The level variability of elements and its various forms in sediments are reflections of various factors, which govern quality of the environment. The distribution of metals in aquatic environment is important in studying environmental pollution as such elements can be toxic even in traces and cause harmful effects. Heavy metals generally exist in low levels in water and attain considerable concentration in sediments and biota (Namminga and Wilhm, 1976). Metals also occur in small amounts naturally and may enter into aquatic system through leaching of rocks, airborne dust, forest fires and vegetation. As heavy metals cannot be degraded, they are continuously being deposited and incorporated in water, sediment and aquatic organisms (Linnik and Zubenko, 2000), thus causing heavy metal pollution in water bodies.

Metal pollution in the aquatic environment is usually caused by land runoff, mining activities, dredging activities and anthropogenic inputs. Sediments in such affected domains not only record its history, but also indicate the degree of pollution (Sahu and Bhosale, 1991). The degree of contamination of aquatic sediments was quantified earlier by comparing the elemental concentration with uncontaminated background levels (Forstner and Muller, 1973; Nikoforova and Smirnova, 1975 and Tomilson *et al.*, 1980).

Many authors prefer to express the metal contamination with respect to average shale to represent the degree of quantification of pollution (Muller, 1979 and Forstner and Wittmann, 1983). Some authors (Baruah *et al.*, 1998) have considered the background value of their area of study to be the geometric mean of concentration at the different sample sites, which is the antilog of the arithmetic average of \log_{10} of the concentration values. As such, this methodology of determining background value has not been considered in the present study. Instead, the world surface rock average (Martin and Meybeck, 1979) of individual metal has been taken to be the background value (Rath *et al.*, 2005).

Soils are usually regarded as the ultimate sink for heavy metals discharged into the environment (Banat *et al.*, 2005), and sediments can be sensitive indicator for monitoring contaminants in aquatic environments. Many calculation methods have been presented to assess the environmental quality, such as enrichment factor, contamination factor, pollution load index and Geo accumulation factor. Pollution index is a powerful tool for processing, analyzing, and conveying raw environmental information to decision makers, managers, technicians, and public (Caeiro *et al.*, 2005). The degree of contamination in the sediments is determined with the help of three parameters like Enrichment Ratio (ER), Pollution Load Index (PLI) and Geo-accumulation Index (Igeo).

2. MATERIALS AND METHODS

2.1 Study area

The pollution status of sediment samples were analyzed in two perennial ponds located in Kanyakumari district (latitude 8°05'30" to 8°34'30" and longitude 77°06'30" to 77°34'00" viz. Manavalakurichy pond (Pond I) and Thiruthuvapuram pond (Pond II), these ponds were selected from two taluks viz Kalkulam and Vilavancode for the analysis of heavy and trace metals of core sediments. The selected study ponds are very large perennial water bodies in those taluks which retain water throughout the year and extensively used for irrigation and domestic use. The location (region) of sample collection sites are

Taluk	Site (Location)
Kalkulam	- Manavalakurichy
Vilavancode	- Thiruthuvapuram

2.1.1 Manavalakurichy Pond

The pond is located in Manavalakurichy in Kanyakumari District (8°13'17" latitude and 77°18'31" longitude) and this pond is a large perennial panchayat water body. This is the largest pond in Kanyakumari. This pond has the higher public utility. Though it is a permanent location for cleaning of vehicles by private vehicle owners, and the water in this pond is mainly used by the local populace for bathing and washing clothes. Animal faeces also pollute the pond. This pond is situated nearby the road.

2.1.2 Thiruthuvapuram Pond

The pond is located in Thiruthuvapuram in Kanyakumari District (8.31497 latitude and 77.1991 longitude). The water in this pond is mainly used by the local populace for bathing, washing clothes and cattle washing. It is also affected by discharge of sewage from the neighbouring areas, and surface runoff from agriculture field during rainy season. Cattle and duck wade into this pond quite often.

2.2. Collection of core sediment samples

The core sediment samples were collected during the period of premonsoon and postmonsoon in 2016. The depth of sampling from bottom sediments depends upon the purpose of investigation. The core sediment samples were collected from the bottom of the pond by using PVC coring tube and they were stored in deep freeze until analysis was performed. The sediment samples were designated as C1(4cm), C2 (8cm), C3 (12cm), C4 (16cm), C5 (20cm), C6 (24cm), C7 (28cm), C8 (32cm), C9 (36cm), C10 (40cm), C11 (44cm), C12 (48cm), C13 (52cm), C14 (56cm), C15 (60cm), C16 (64cm), C17 (68cm), C18 (72cm), C19 (76cm) and C20 (80cm) at various depths. The metals from the core samples like Fe, Mn, Cu, Cr, Pb, Zn, Al, Ni, Cd, Na, K, Ca, Mg were analysed by AAS and flame photometer.

2.3. Sediment pollution assessment

2.3.1 Enrichment ratio (ER)

Enrichment ratios (ER) were used to differentiate between natural and anthropogenic contributions of pollution by determining potential sources of metals to ponds, riverine, estuarine and coastal environments (Feng, 2004). To identify the concentrations of metals, the geochemical normalization of concentrations of metals to concentrations of a conservative element, such as aluminum (Al), iron (Fe), or silicon (Si), was conducted.

According to Zhang and Liu (2002), EF values smaller than 1.5 suggest that heavy metals derived from mainly natural source such as weather processes, while EF values greater than 1.5 suggest that the sources are more likely to be anthropogenic. Enrichment factor analysis, a method proposed by Simex and Helz (1981) to assess trace element concentration, is mathematically expressed as:

$$\text{Enrichment ratio (ER)} = \frac{(\text{C}_x/\text{Fe}) \text{ sample}}{(\text{C}_x/\text{Fe}) \text{ background}}$$

Where, C stands for concentration of metal 'x'. The background value is that of the world surface rock average (Martin and Meybeck, 1979). Fe is taken as a normalization element while determining enrichment ratio (ER). Enrichment factor (EF) can be used to differentiate between the metals originating from anthropogenic activities and those from natural procedure, and to assess the degree of anthropogenic influence. Five contamination categories are recognized on the basis of the enrichment factor as follows: (Sutherland, 2000)

- EF < 2 is deficiency to minimal enrichment
- EF 2-5 is moderate enrichment
- EF 5-20 is significant enrichment
- EF 20-40 is very high enrichment
- EF > 40 is extremely high

As the EF values increase, the contributions of the anthropogenic origins also increase.

2.3.2 Contamination factor (CF)

The contamination factor is used to determine the contamination status of sediment in the present study. The contamination factor was calculated by using the equation,

$CF = \text{Metal concentration in polluted sediment} / \text{Background value of the metal}$ Where, Background value of the metal = World surface rock average given by Martin and Meybeck (1979).

Hakanson (1980) has distinguished four categories of contamination factor.

- $C_f^i < 1$ means low contamination
- $1 \leq C_f^i < 3$ means moderate contamination
- $3 \leq C_f^i < 6$ means considerable contamination
- $6 \leq C_f^i$ very high contamination

2.3.3 Pollution Load Index (PLI)

Pollution Load Index, for a particular site, has been evaluated following the method proposed by Tomilson *et al.* (1980). This parameter is expressed as

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

Where, n is the number of metals (eight in the present study) and CF is the contamination factor. The contamination factor can be calculated from the following relation:

CF (Contamination Factor) = Metal concentration in the sediments/Background value of the metal.

2.3.4 Index of geoaccumulation (Igeo)

Index of Geo accumulation (Igeo) has been used widely to evaluate the degree of metal contamination or pollution in terrestrial, aquatic and marine environment (Tijani *et al.*, 2009). The geo-accumulation index, introduced by Muller (1979) for determining the extent of metal accumulation in sediments, has been used by various workers in their studies (Glasby *et al.*, 1988; Singh, 1999 and Rath *et al.*, 2005).

Igeo is mathematically expressed as: $I_{geo} = \log_2(C_n/1.5 \times B_n)$

Where, C_n is the concentration of element 'n' and B_n is the geochemical background value. The world surface rock average is given by Martin and Meybeck (1979). The factor 1.5 is introduced to minimize the effect of the possible variations in the background or control values which may be attributed to lithogenic variations in the sediment (Mediolla *et al.*, 2008). The geo-accumulation index (Igeo) scale consists of seven grades (0-6) ranging from unpolluted to highly pollute. The degree of metal pollution is assessed in terms of seven contamination classes based on the increasing numerical value of the index as follows: (Huu *et al.*, 2010)

- $I_{geo} < 0$ = means unpolluted
- $0 \leq I_{geo} < 1$ means unpolluted to moderately polluted
- $1 \leq I_{geo} < 2$ means moderately polluted
- $2 \leq I_{geo} < 3$ means moderately to strongly polluted
- $3 \leq I_{geo} < 4$ means strongly polluted
- $4 \leq I_{geo} < 5$ means strongly to very strongly polluted
- $I_{geo} \geq 5$ means very strongly polluted.

3. RESULTS

3.1 Down core profiles

The concentrations of metals in core sediment samples of two ponds are depicted in Fig:1. The maximum concentrations of Fe, Mn, Cr, Cu, Pb, Zn, Al, Ni, Cd, Na, K, Ca and Mg in pond I and II like $5246 \mu\text{gg}^{-1}$ & $3758 \mu\text{gg}^{-1}$, $358.2 \mu\text{gg}^{-1}$ & $284.5 \mu\text{gg}^{-1}$, $97.54 \mu\text{gg}^{-1}$ & $106.8 \mu\text{gg}^{-1}$, $68.8 \mu\text{gg}^{-1}$ & $57.36 \mu\text{gg}^{-1}$, $112.4 \mu\text{gg}^{-1}$ & $95.28 \mu\text{gg}^{-1}$, $129.8 \mu\text{gg}^{-1}$ & $131.5 \mu\text{gg}^{-1}$, $6451 \mu\text{gg}^{-1}$ & $5342 \mu\text{gg}^{-1}$, $56.48 \mu\text{gg}^{-1}$ & $38.22 \mu\text{gg}^{-1}$, $0.491 \mu\text{gg}^{-1}$ & $0.385 \mu\text{gg}^{-1}$, $10700 \mu\text{gg}^{-1}$ & $12300 \mu\text{gg}^{-1}$, $6742 \mu\text{gg}^{-1}$ & $5236 \mu\text{gg}^{-1}$, $348 \mu\text{gg}^{-1}$ & $4540 \mu\text{gg}^{-1}$ and $4125 \mu\text{gg}^{-1}$ & $3470 \mu\text{gg}^{-1}$ respectively.

3.2 Assessment of Metal Contamination

3.2.1 Enrichment factor (EF)

The background value is that of the world surface rock average are given in Table: 1. The average values of enrichment factor obtained in the core sediments of pond I and II are summarized in the Table: 2 and the graphical representation of enrichment factor for two ponds are shown in Fig.2. The results obtained were compared with the five contamination categories as recognized on the basis of the enrichment factor (Sutherland, 2000). Enrichment factors were calculated from the mean concentrations of the heavy metals in the stations of all the four study ponds. The normalizing element used in the study was Fe due to low occurrence variability.

Results of the study showed that the average enrichment values of the metals like Mn, Cr, Cu, Zn, Al, Ni, Cd, K, Ca and Mg

were less than 2 (EF<2) and rest of the metals like Pb and Na were ranged in between EF (2 to 5) in the core sediments of pond I (Kalkulam) and pond II (Vilavancode).

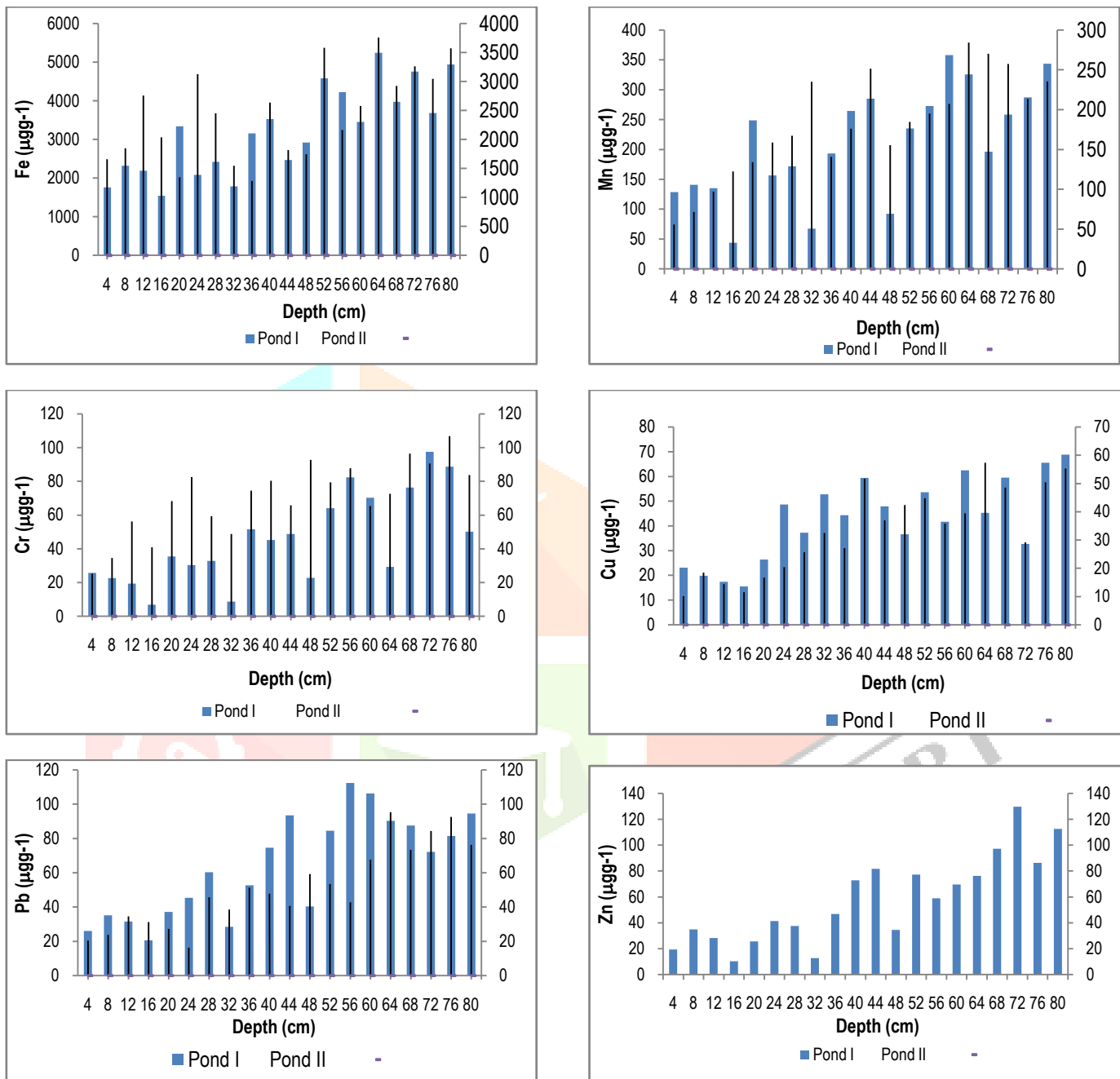


Fig: 1 Geochemical distribution of metals in the core sediments of ponds

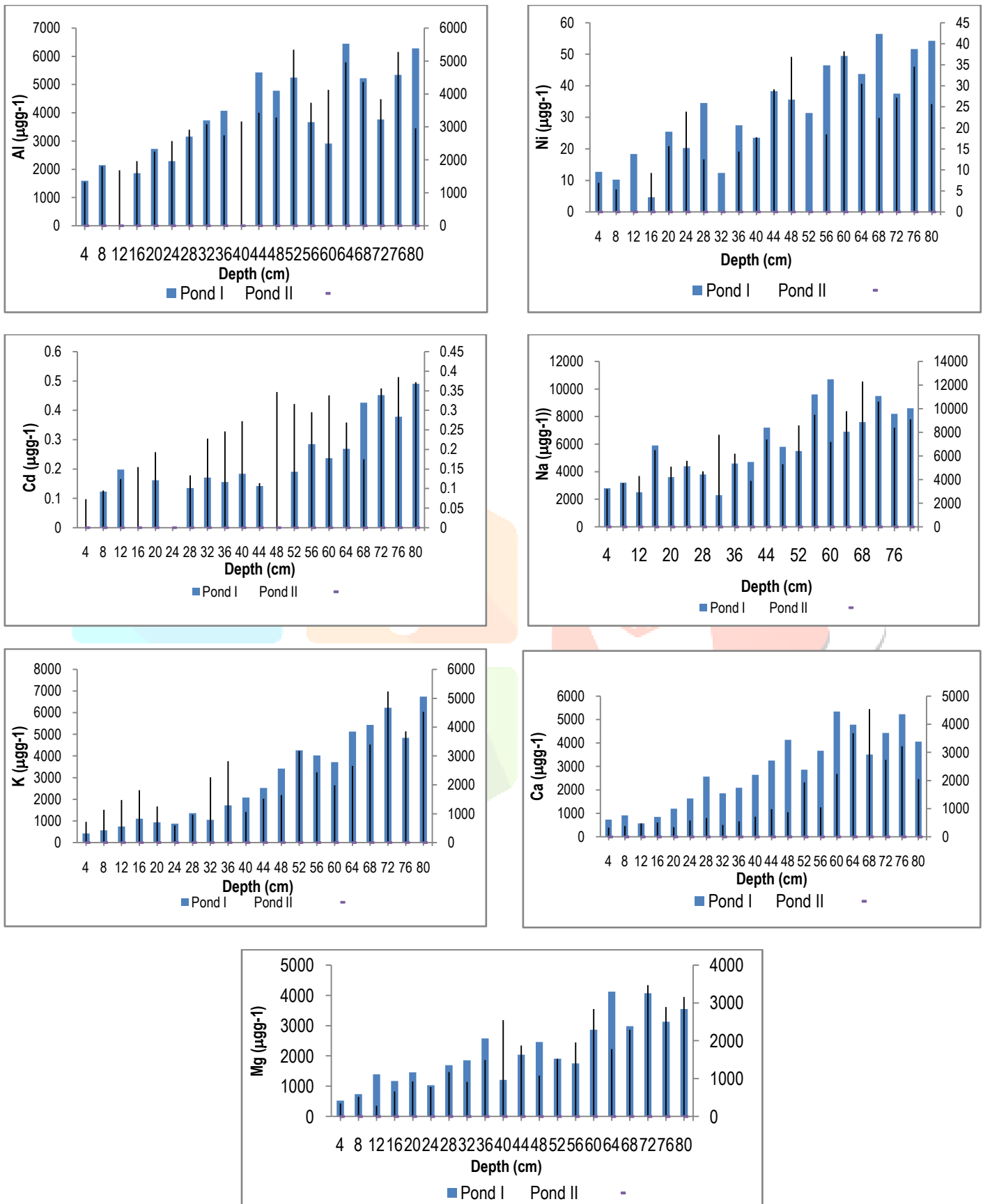


Figure: 1 Geochemical distribution of metals in the core sediments of ponds

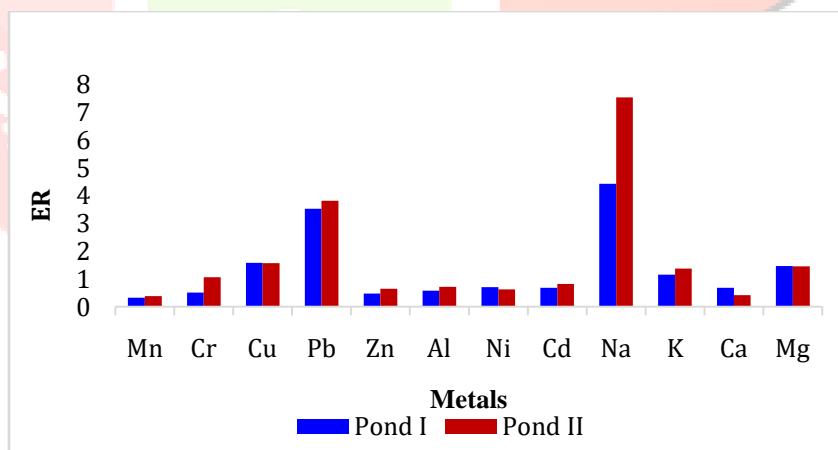
Table: 1 Background values of metals

Metals	WSR
Fe (%)	3.59
Al (%)	6.93
Na (%)	1.42
K (%)	2.44
Ca (%)	4.5
Mg (%)	1.64
Mn (μgg^{-1})	720
Cr (μgg^{-1})	97
Cu (μgg^{-1})	32
Pb (μgg^{-1})	20
Zn (μgg^{-1})	129
Ni (μgg^{-1})	49
Cd (μgg^{-1})	0.3

WSR – World Surface Rock Average

Table: 2 Enrichment ratio (ER) of metals in core sediments of ponds

Ponds	Mn	Cr	Cu	Pb	Zn	Al	Ni	Cd	Na	K	Ca	Mg
Pond I	0.32	0.502	1.575	3.527	0.47	0.58	0.71	0.68	4.43	1.15	0.681	1.465
Pond II	0.39	1.066	1.57	3.82	0.65	0.71	0.62	0.82	7.53	1.37	0.418	1.456

**Figure:2** Enrichment ratio of metals in core sediments of ponds

3.2.2 Contamination factor (CF) and Pollution load index (PLI)

The mean values of contamination factor and pollution load index obtained in the core sediments of pond I and II are summarized in Table: 3 and the graphical representation of contamination factor and pollution load index of four ponds are shown in Fig. 3 and 4. Results of the study showed that the CF values of the metals such as Fe, Mn, Cr, Zn, Al, Ni, Cd and Ca shows low CF < 1 and the CF values for metals like Cu, Pb, Na, K and Mg shows high CF > 1 in pond I. The CF values of pond II, the metals such as Fe, Mn, Cr, Zn, Al, Ni, Cd, K, Ca and Mg shows low CF < 1 and for metals like Cu, Pb and Na shows high CF > 1.

The Pollution Load Index (PLI) does not show much fluctuation. The PLI values in the core sediments were ranged from 0.33 to 1.48 in pond I; from 0.26 to 1.23 in pond II; The mean values of PLI were found to be low (PLI < 1) in pond I and II.

Table: 3 Contamination Factor (CF) and Pollution Load Index (PLI) of metals in the core sediments of ponds

Ponds	Fe	Mn	Cr	Cu	Pb	Zn	Al	Ni	Cd	Na	K	Ca	Mg	PLI
Pond I	0.9	0.294	0.445	1.342	3.19	0.45	0.51	0.65	0.67	4.13	1.221	0.626	1.3	0.8725
Pond II	0.68	0.253	0.694	1.045	2.59	0.45	0.47	0.4	0.75	4.9	0.912	0.315	0.99	1.044

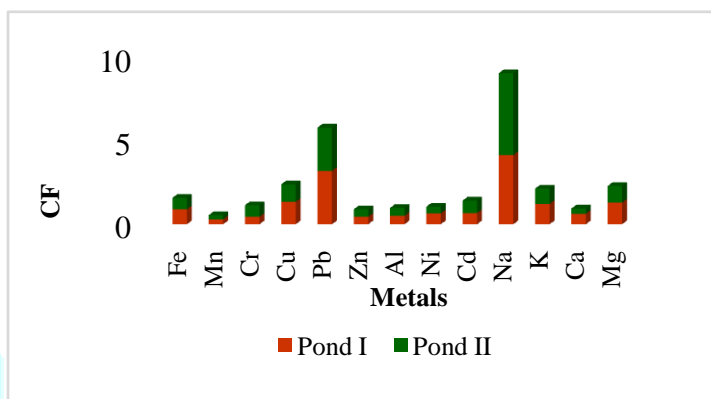


Figure: 3 Contamination Factor of metals in the core sediments of ponds

3.2.3 Index of geoaccumulation (Igeo)

The results of the mean values of Geo accumulation index (Igeo) values in the core sediments of four perennial ponds based on world surface rock abundance are shown in Table: 4 and the variations are shown graphically (Fig. 4). In pond I, the mean of negative Igeo values of Fe, Mn, Cr, Cu, Zn, Al, Ni, Cd, K, Ca, Mg were fall in the class of Igeo< 0 and the rest of metals Pb and Na were fall in the classes of Igeo<1 and Igeo<2. The Geo accumulation index (Igeo) of pond II, the mean of negative Igeo values of Fe, Mn, Cr, Cu, Pb, Zn, Al, Ni, Cd, K, Ca and Mg were fall in the class of Igeo< 0 and Na was fall in the class of Igeo< 2.

Table: 4 Geo - accumulation indices of metals in the core sediments of ponds

Ponds	Fe	Mn	Cr	Cu	Pb	Zn	Al	Ni	Cd	Na	K	Ca	Mg
Pond I	-0.84	-2.54	-1.98	-0.29	0.92	-2.04	-1.37	-1.45	-0.48	1.32	-0.81	-0.66	-0.98
Pond II	-1.21	-2.69	-1.07	-0.69	-0.07	-2.02	-1.78	-1.76	-1.03	1.61	-1.05	-2.77	-0.91

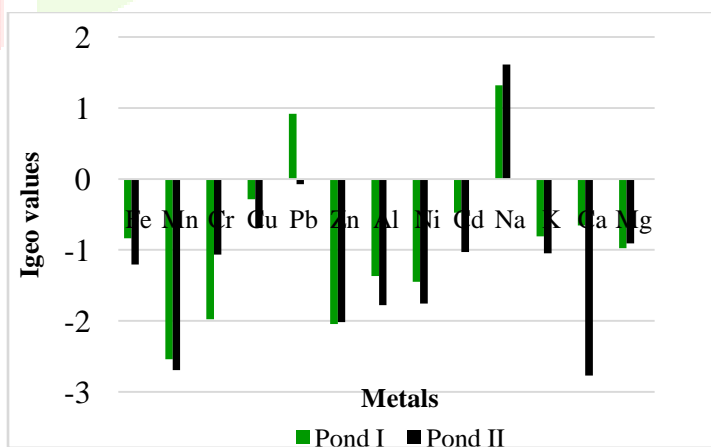


Figure: 4 Geo - accumulation indices of metals in the core sediments of ponds

4. DISCUSSION

The maximum concentrations of Fe, Al and Ni were found in pond I. From the average values between the twenty stations of core samples) the pond wise elemental concentrations and Fe normalized metal concentrations are listed below.

Pond I- Na> Al> Fe > K> Ca> Mg and Pond II- Na> Al> Fe > K> Mg> Ca. Pond I -Mn> Pb> Zn> Cr> Cu> Ni> Cd and Pond II- Mn> Cr> Zn> Pb> Cu> Ni> Cd. The presence of heavy metals in aquatic ecosystems is the result of two main sources of contamination; natural processes and natural occurring deposits and anthropogenic activities. In the fresh water environment, toxic metals are potentially accumulated in sediments and subsequently transferred to man through the food chain. Metals cannot be degraded; they are continuously being deposited and incorporated in water, sediment and aquatic organisms, thus causing heavy metal pollution in water bodies.

4.1 Metal Enrichment

4.1.1 Enrichment ratio (ER)

The enrichment ratio was based on the standardization of the tested element against Fe, which was taken as the reference metal. It was observed that the average enrichment values of Na and Pb were ranged in between EF (2 to 5), suggesting moderate enrichment and the average EF values of Cu, Mg, K, Ni, Ca, Cd, Al, Cr, Zn and Mn were less than 2 (EF<2), suggesting deficiency to minimal enrichment in pond I and II.

From the results of the enrichment factor in both the study ponds confirms that the highest EF values were observed due to the wastewater out fall from the surrounding areas and also the anthropogenic activities. The mean EF values of heavy metals from pond I, and II follows the following sequence:

Pond I - Na (4.43) > Pb (3.53) > Cu (1.58) > Mg (1.47) > K (1.15) > Ni (0.71) > Ca (0.68) > Cd (0.68) > Al (0.58) > Cr (0.50) > Zn (0.47) > Mn (0.32).

Pond II - Na (7.53) > Pb (3.82) > Cu (1.57) > Mg (1.46) > K (1.37) > Cr (1.07) > Cd (0.82) > Al (0.71) > Ni (0.62) > Zn (0.65) > Ca (0.42) > Mn (0.39).

4.1.2 Contamination factor (CF)

Contamination factor was calculated for the two ponds core samples, pond I and pond II based on Hakanson (1980). The values were compared with four categories of C_f^i . It was observed that the CF values of the majority of the metals such as Fe, Mn, Cr, Zn, Al, Ni, Cd and Ca shows low CF< 1 indicating low contamination, the CF values for metals like K and Mg shows high CF>1 indicating moderate contamination and Na indicating considerable contamination in the sediments of both studied ponds. The higher values of all the ponds may be due to the influence of agricultural runoff and other anthropogenic inputs.

4.1.3 Pollution Load Index (PLI)

The Pollution Load Index (PLI) represents the number of times by which the metal content in the sediment exceeds the background concentration and gives a summative indication of the overall level of heavy metal toxicity in a particular sample. The mean values of Pollution Load Index (PLI) in pond I and II were found to be low (PLI<1). Lower values of PLI imply no appreciable input from anthropogenic sources.

4.1.4 Index of geoaccumulation (Igeo)

Igeo values of Fe, Mn, Cr, Cu, Zn, Al, Ni, Cd, K, Ca, Mg fall in the class of Igeo< 0 that is the negative Igeo values showed that sediments were unpolluted with these metals in all the ponds. The sodium (Na) metal was fall in the class of Igeo< 2 indicating that the sediments were moderately polluted by sodium in two ponds (pond I and pond II). But in the case of lead, it was fall in the class of Igeo< 1 in pond I. The above findings show no contamination from Fe, Mn, Cr, Zn, Al, Ni, Cd, K, Ca and Mg. The Igeo values of Na fall in the range of 1-2, while those in case of lead are almost in the range of 0-1. The Igeo values of sodium seem to be influenced by the anthropogenic contribution. But in the case of lead, the stagnant condition prevailing at the bottom of the pond, the dissolved oxygen is completely removed. As a result, free metallic complexes are formed which influence the solubility of metal 'lead' by forming insoluble complexes. These complexes tend to strip the water of its metal content and enrich the bottom sediments with the metal (Merhotra *et al.*, 1991).

5. Conclusions

To investigate the status of metal contamination in two perennial pond sediments, Fe, Mn, Cr Cu, Pb, Zn, Ni, Cd, Na, K, Ca and Mg concentrations were estimated in twenty stations of core samples (C1- C20). The order of the pond wise metal concentrations of tested heavy metals: Fe > Mn > Pb> Zn> Cr> Cu> Ni> Cd (Pond1) and Fe> Mn> Cr> Zn> Pb> Cu> Ni> Cd (Pond2). International sediment quality guidelines (World surface rock average), enrichment ratio (EF), contamination factor (CF), geo-accumulation index (Igeo) and pollution load index (PLI) were applied for assessment of contamination. The ER of the majority of metals Cu, Mg, K, Ni, Ca, Cd, Al, Cr, Zn and Mn were less than 2 (EF<2) in both ponds suggesting deficiency to minimal enrichment. The CF values the metals such as Fe, Mn, Cr, Cu, Zn, Al, Ni, Cd and Ca shows low CF< 1 indicating low contamination, the CF values for elements like K and Mg shows high CF>1 indicating moderate contamination and Na shows considerable contamination in pond I and II. The mean values of Pollution Load Index (PLI) in both ponds (Pond I and II) were found to be low (<1). Igeo values of Fe, Mn, Cr, Cu, Zn, Al, Ni, Cd, K, Ca, Mg fall in the class of Igeo< 0 that is the negative Igeo values showed that sediments were unpolluted with these metals in Pond I and II. The sodium fall in the class of Igeo< 2 indicating that the sediments were moderately polluted by sodium in the study ponds. In pond I, the lead fall in the class of Igeo< 1 indicating that the

sediments were unpolluted to moderately pollute by lead.

6. References

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