

# ZINC , COPPER, CADMIUM, LEAD , MANGANESE AND NICKEL POLLUTION IN VATTAKAYAL LAKE, KOLLAM DISTRICT, KERALA.

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## Abstract

some heavy metals are essential trace elements, most of them can be toxic to all forms of life at high concentrations due to formation of complex compounds within the cell. Unlike organic pollutants, heavy metals once introduced into the environment cannot be biodegraded. They persist indefinitely and cause pollution of air, water, and soils. Most of the lakes in tropical region of India face severe effect of heavy metal pollution, as a consequence of industrial revolution and urban agglomeration, all have serious detrimental impact on people and ecosystems those who rely on such bodies of water. Vattakayal lake system was one of the most productive ecosystems of Kerala, now became heavily polluted due to the effluents from KMML Titanium dioxide pigment plant at Sankaramangalam which pose grave environmental problems, affecting the biota directly or indirectly. In this study both surface and bottom water samples were seasonally analyzed for determining the concentration of metals such as zinc, copper, cadmium, lead, manganese and nickel. The result showed that the sites of the lake, near the industrial area was more contaminated with the metals than the sites of non industrial area. An increasing trend of metal concentration was observed in the bottom water than surface water. The physico-chemical parameters such as temperature, pH and salinity were also analyzed to understand the metal accumulation in water body. The prevailing conditions of temperature, pH and salinity in Vattakayal lake waters have indicated the enhanced rate of accumulation of metals. Statistical analysis was performed using statistical package for social science (SPSS) version 16.0. Pearson correlation analysis was performed to identify the relationship of various hydrographical and physico chemical parameter.

## Key words

Vattakayal lake, bio accumulation, metal toxicity, Minamata disease, Itaiitai disease.

## Introduction

Lakes are complex and dynamic ecosystems that are constantly influenced the environment. Both chemical and biological components of the lake system changes continuously, these changes cause re equilibration, creating a new steady state (Reddy et. al., 2004). If the ecology of the lake changes drastically, it will harmfully affect both human beings and resources. Substances such as heavy metals, metalloids, petroleum

hydrocarbons, chlorinated organic and polycyclic aromatic hydrocarbons, which might be released in to the lake system, cause great threat (Panda et.al. 2006). Due to the non bio degradable, persistent and toxic nature of heavy metals, it is of great concern about distribution and behavior of heavy metals in the aquatic environment (Shirlin, et.al. 2014). Tragedies such as Minamata incident and Itaitai disease have occurred due to the heavy metals pollution by the irrational discharge of industrial effluents. Therefore in the modern era, metal toxicity is one of the hottest topic (El- Hassan and Jiries 2001).

Of the six heavy metals studied, metals like zinc, copper and nickel serve as essential micro nutrients, since its availability affect the physiological and biochemical activity of aquatic organism. Metals like manganese is very significant in controlling biogeochemical processes and non essential metals like cadmium and lead have no known biochemical, nutritional and physiological functions in organisms. Since these metals are non bio degradable it became highly toxic at elevated concentrations (Ashraf et. al., 2008). Presences of heavy metals in waters of lake system are of extreme importance due to their impact on ecosystem. (Forstner and Wittmann, 1982).

Extensive studies have been conducted on heavy metal contamination and toxicity in water (Bryan, 1984, Viarengo, 1985, Nriagu and Pacyana., 1988; Mattivertta, 1989; George Thomas and Fernandez 1996, Mohan and Omana 2004, Suneela et. al., 2007, Panday et. al.,2008, Wang et.al., 2011, Ondarza et. al.,2012, Karim et.al.,2015). Only very limited studies are reported about heavy metal pollution of Vattakayal lake system, which is the nursery ground for vast resources of several fishes and molluscs and many people are depending on the lake for their livelihood. Hence the present study was undertaken with an aim of analyzing heavy metal concentration in water and its relation with physico chemical features such as pH, salinity and temperature.

## Materials and Methods

### Study area.

Vattakayal lake, a big brackish water lake about 5km away from KMML (Kerala minerals and Metals limited) company, Chavara, Kollam District, Kerala, India lies between 8°51n and 8°45 N latitude and 76°32'E and 76°34'longitude having a circumference of 90 acres. A part of T S canal the national water way starting from Shornur and ending in Thiruvananthapuram stretching from Vattakayal lake to Ashtamudy lake. Vattakayal lake system was one of the most productive ecosystems of Kerala now became heavily polluted, clay deposition observed as thick layer so the depth of the water body became every much reduced and living organisms were almost absent in some regions of this lake.

### Sample collection and preservation

Water samples were collected from four locations in Vattakayal during premonsoon, monsoon and postmonsoon seasons. Each sample was kept in good quality polyethylene bottles and placed in an ice box. Both surface water samples and bottom water samples were collected by using Von Dorn water sampler. Each sample was a combination of four or five sub samples. After collection each samples were immediately brought to the laboratory for analysis.

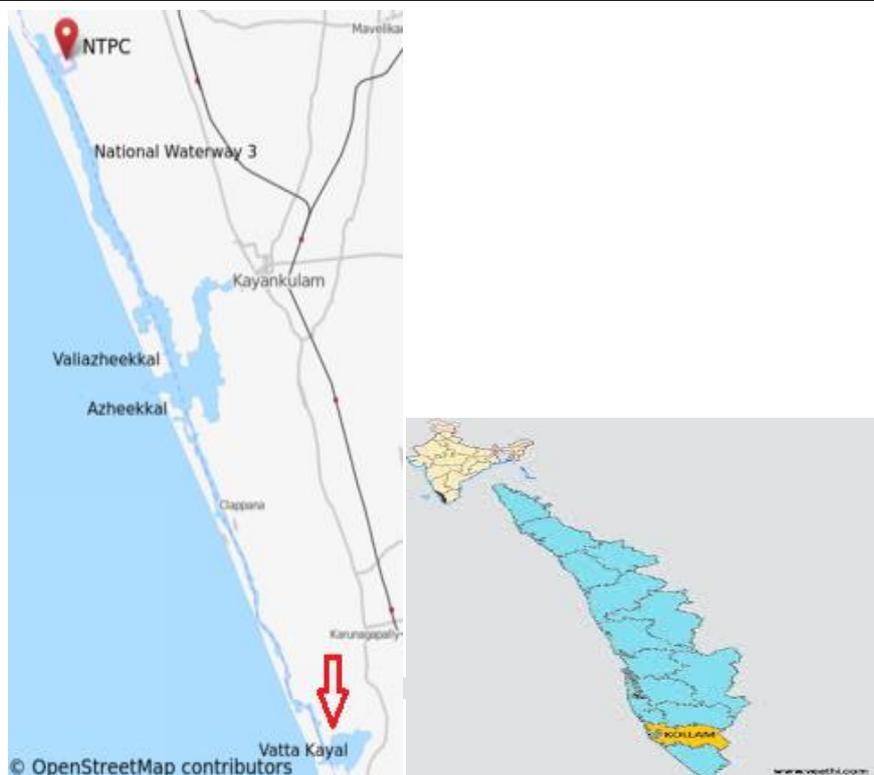


Fig I. Map showing the Vattakayal Lake and sample locations.

### Sample analysis.

#### Physicochemical analysis of water

Water quality parameters such as pH, salinity and temperature for water samples were analyzed as per standard producers of APHA (APHA, 1998).

Hydrogen ion concentration of water samples was measured at the site itself with a portable pH meter of  $\pm 0.1$  accuracy (model, pH Tester 1, 2, Eutech instruments UK). The temperature of water was recorded with the help of a centigrade thermometer. Salinity of the water samples was estimated by Mohr-Knudsen method (Muller, 1999).

#### Heavy metal analysis of water

Filter papers loaded with suspended particulate matter were digested using concentrated  $\text{HClO}_4$  and  $\text{HNO}_3$  in the ratio 1:3, which is then evaporated to dryness. The obtained residue was then dissolved in 0.1 N  $\text{HNO}_3$  and made up to a definite volume (APHA, 1998).

Water samples preserved in acids were pre concentrated using 1% solution (1 ml) of chelating agents APDC (ammonium-1-pyrrolidine dithiocarbamate), DDDC (diethyl ammonium diethyl dithiocarbamate) and 30ml chloroform in several steps (APHA 1998). From the above mixture extraction of solvent was done after adjusting the pH of the acidified sample to 4 to 5 by the addition of ammonium hydroxide. By using sub boiling distilled concentrated  $\text{HNO}_3$ (2ml) the chloroform layer was acidified and metals were brought into the aqueous phase by equilibration with Milli- Q water. This aqueous layer was then transferred to a standard flask, boiled off the excess chloroform and made up to a definite volume. Metal determinations were carried out on the concentrates by graphite furnace atomic absorption spectrometry (Perkin Elmer model 3110, with HGA 600) calibrated using standard solutions prepared by dilution of 1000mg $l^{-1}$  standard solutions (Merck). Analytical blanks were prepared using same procedures and reagents.

## Statistical Analysis

Statistical analysis was performed using statistical package for social science (SPSS) version 16.0. Pearson correlation analysis was performed to identify the relationship of various hydrographical and physico chemical parameter. Spatial and temporal variations of hydrographical and heavy metals (Zn, Cu, Cd, Pb, Mn, and Ni) were assessed by two way analysis of variance (ANOVA) without replication with season and stations as sources of variations.

## Result and discussion

### Physico- chemical parameters

Water quality parameters such as pH, temperature and salinity were analysed and the summary of the result is given in the table 1. Station wise variations of physico chemical variations is graphically represented in the figure.1a. Hydrogen ion concentration in station I and II was acidic, the average pH of station I and station II are  $2.53 \pm 0.57$  and  $2.87 \pm 0.51$  respectively. While in non industrialized areas pH average is  $7.33 \pm 0.37$  (station III) and  $7.47 \pm 0.46$  (station IV). pH value showed minimum in pre monsoon season while maximum in monsoon season. Acidic effluents released from the industry might be the reason for low pH in the water body.

Temperature is an important physical factor of any habitat and temperature plays a vital role in biochemical reactions and self purification of aquatic systems. The water temperature in station I range from  $27.5^{\circ}$  to  $30.8^{\circ}\text{C}$  in surface water and  $27.3^{\circ}$  to  $30.5^{\circ}$  in bottom water. Pre monsoon temperature shows highest values is  $30.8^{\circ}\text{C}$ , monsoon temperature is the minimum which is  $27.3^{\circ}\text{C}$ . In station II temperature ranges between  $27.1^{\circ}\text{C}$  to  $29.9^{\circ}\text{C}$  in the case of surface water and  $27$  to  $29.8^{\circ}\text{C}$  in bottom water, here also highest values observed in pre monsoon and minimum temperature value in monsoon season. In station III  $27.1^{\circ}\text{C}$  to  $28.5^{\circ}\text{C}$  is the temperature range of surface water, while in the case of bottom water, range between  $27^{\circ}$  to  $28.5^{\circ}\text{C}$ . in station IV  $27^{\circ}\text{C}$  to  $29.7^{\circ}\text{C}$  is the range of temperature surface water and  $27.1^{\circ}$  to  $29.6^{\circ}\text{C}$  in the case of bottom water.

Pre monsoon season showed maximum temperature followed by post monsoon and monsoon in the present investigation. This may be due to the reason that heavy solar radiation, low rain fall, stagnant water condition during pre monsoon season. Similar observations were previously done by Joseph et al., 1984 in Periyar estuary, Geetha Bhadrans (1997) from Ashtamudy lake, Meera and Nandan (2010) from Cochin back waters. Usually exothermic reactions take place in waste materials due to the presence of different chemicals and micro organisms in the waste.

Salinity of aquatic environment is a major controlling factor for various physical chemical and biological processes that occurs in the surroundings. The average of salinity in station I is  $26.08 \pm 2.2$ . Highest salinity observed in pre monsoon season while the lowest in monsoon season. In station II salinity range is  $23.35 \pm 1.48$ . In station III average range is between  $11.24 \pm 0.79$ . In station IV salinity range is between  $21.83 \pm 1.42$ . Maximum salinity observed in station I and II which is nearest to the industrial area. Salinity in the industrial area was higher than other stations, the same observation were previously recorded by Ciji and Bijoy Nandan (2014). Elevated salinity observed at pre monsoon season this might be due to high rate of evaporation and might be due to discharge of high chloride content from the industry. Minimum value observed in monsoon season which might be due to heavy influx of rain water (Sankaranarayanan and Qasim 1969, Mani

Kannan et al., 2011) there is a positive correlation observed between salinity and temperature. Station IV also shows elevated salinity, this station is near to the sea, so tidal actions may occurs, (Pillai et al., 1975 and Geetha Bhadaran (1997).

STATI ONS	TEMPERAT URE	pH	SALINI TY
Station I	29.3±0.2	2.53±0 .57	26.08±2 .2
Station II	28.5±0.13	2.87±0 .57	23.35±1 .48
Station III	27.9±0.1	7.33±0 .37	11.24± 70
Station IV	27.5±0.30	7.47±0 .46	21.83±1 .42

**Table I. Means of physico chemical factors at different stations.**

### Distribution of Heavy metals in water

The seasonal and spatial variation of total heavy meal concentrations were analyzed both in surface and bottom waters collected from four different stations during premonsoon, monsoon and post monsoon periods from June 2014 to May 2015.

Zinc is the most abundant essential trace element in the human body and it is a constituent of several enzymes. Zinc deficiency cause impairment of physical growth and development. The mean concentration zinc in surface waters of station I, II, III, and IV were  $7.4 \pm 1.89$ ,  $4.32 \pm 0.65$ ,  $0.02 \pm 0.009$ ,  $1.20 \pm 0.66$  respectively. While in bottom water the concentration mean value were  $8.18 \pm 1.4$ ,  $4.62 \pm 0.9$ ,  $0.05 \pm 0.01$ ,  $1.42 \pm 0.63$ . Zinc concentration varied from a minimum of  $0.01 \text{ mg}^{-1}$  to a maximum of  $10.11 \text{ mg}^{-1}$  in surface water and from  $0.07 \text{ mg}^{-1}$  to  $10.26 \text{ mg}^{-1}$  in bottom waters. Much concentration of heavy metals occurred in bottom water than the upper water layers, similar observation by Shylesh Chandran, 2016 in Vembanad Lake. This might be because zinc can be recycled from the sediment to the water column by the oxidation of labile organic compound at the sediment water interface. (Selvam et. al., 2012). Maximum zinc concentration observed at station I ( $10.26 \text{ mg}^{-1}$ ) may be due to industrial effluents from KMML factory, directly released into this site. Station II also showed a higher concentration because this station is near to the station I. while station III and station IV showed lowest concentration these two stations are interior part of the lake and fresh water supply occurred in this area.

Copper is also an essential element in metabolism and it is very essential for many enzymes in our body. By large concentration of copper become toxic and leads to liver damage. Average values of copper at four stations I, II, III and IV was in the order  $1.24 \pm 0.23$ ,  $0.50 \pm 0.3$ ;  $0.007 \pm 0.002$ ,  $0.196 \pm 0.11$  in surface water and in bottom water  $1.38 \pm 0.18$ ,  $0.58 \pm 0.3$ ,  $0.010 \pm 0.003$ ,  $0.32 \pm 0.14$ . Elevated concentration observed in station I and II in bottom water layers than surface waters. According to USEPA (2011) copper concentration ranges between 18.0-35.3 ppb is tolerable limit. Based on EU standards copper level  $2.0 \text{ mg}^{-1}$  become upper limit. Copper content stations I and II was above the range of USEPA but within the EU standards. Concentration of copper greater than 1ppm considered to be toxic to aquatic life.

Cadmium is very toxic and poisonous traces of it may cause adverse effect on environment and living things. Cadmium enters in to water exclusively through industrial wastes and land leachates (Paulson et. al., 1993). Cadmium content in the surface water of four stations was  $0.016\pm 0.009$ ,  $0.009\pm 0.01$ ,  $0.004\pm 0.003$  and  $0.004\pm 0.002$ . While the bottom water concentration was  $0.018\pm 0.006$ ,  $0.01\pm 0.004$ ,  $0.003\pm 0.001$  and  $0.005\pm 0.002$ . Station I showed higher cadmium content than other stations this may be due to the reason that this station receives directly the effluents from KMML factory. World average concentration of cadmium is  $0.01\text{mgL}^{-1}$ , station I and II showed higher values than the world average. Continued exposure of cadmium may cause renal arterial hypertension. Significant elevated concentration may cause kidney and liver damage or anemia and may even cause death.

Lead is a most abundant toxic contaminant because it is continuously released into air, water and soil in significant amount. (Branica, 1980). As per USEPA the contamination level of lead is  $0.15\text{mgm}^3$ . Above this level, lead causes brain damage, behavioral problems and mental deficiency, continuous exposure of lead causes nephritis. The mean concentration of lead in surface waters of station I, II, III and IV are  $1.6\pm 0.5$ ,  $0.12\pm 0.01$ ,  $0.007\pm 0.001$ ,  $0.01\pm 0.005$  while in bottom waters the concentration ranged as  $1.71\pm 0.8$ ,  $0.11\pm 0.01$ ,  $0.007\pm 0.001$ ,  $0.01\pm 0.005$ . The level of lead had crossed the stipulated limit at station I and station II, which is about  $0.01\text{mgL}^{-1}$ .

Manganese is an essential element needed for normal functioning of the body of the organism but it become toxic when the concentration exceeds in the human body. Manganese poisoning cause bronchitis, lung embolism and Parkinson disease. Average concentration of manganese in surface waters of station I, II, III and IV were in the order  $1.13\pm 0.3$ ,  $1.004\pm 0.1$ ,  $0.06\pm 0.04$ ,  $0.07\pm 0.01$ , and while in bottom water concentrations were in the order  $1.17\pm 0.3$ ,  $1.03\pm 0.02$ ,  $0.046\pm 0.01$ ,  $0.072\pm 0.02$ . Station I and II showed comparatively higher concentration of manganese, which may be due to the discharge of effluents containing manganese from nearby industry. WHO limit of manganese in water is  $0.5\text{mgL}^{-1}$  (WHO 1991), station I and II manganese concentrations crosses this limit.

Nickel is essential in small quantities when the content increases it become a danger to human life, excess amount of nickel is carcinogenic to human beings. The waste water released from smelting and refining industries are the sources of nickel. Nickel concentration in surface water at all the four station were in the order  $0.55\pm 0.19$ ,  $0.41\pm 0.18$ ,  $0.21\pm 0.04$ ,  $0.26\pm 0.13$  while bottom water average  $0.56\pm 0.20$ ,  $0.42\pm 0.18$ ,  $0.00\pm 0.08$ ,  $0.37\pm 0.2$ . Higher concentration of nickel occurs in all stations but the station I and II values were above the world average nickel content, which is about  $0.49\text{mg L}^{-1}$ . (Taylor et al., 1995).

METALS	STATION I	STATION II	STATION III	STATION IV
ZINC	$7.4\pm 1.89$	$4.32\pm 0.65$	$0.02\pm 0.009$	$1.20\pm 0.6$

COPPER	1.24±0.23	0.50±0.3	0.007±0.002	0.196±0.11
CADMIUM	0.016±0.009	0.009±0.01	0.004±0.003	0.004±0.002
LEAD	1.6±0.5	0.12±0.001	0.007±0.001	0.01±0.055
MANGANESE	1.13±0.3	1.004±0.1	0.06±0.04	0.07±0.01
NICKEL	0.55±0.19	0.42±0.18	0.021±0.04	0.026±0.13

Table 1, Average Metal Concentration of Surface waters of different stations.

METALS	STATION I	STATION II	STATION III	STATION IV
ZINC	8.18±1.4	4.62±0.9	0.05±0.01	1.420±0.6
COPPER	1.38±0.18	0.58±0.3	0.010±0.003	0.32±0.14
CADMIUM	0.018±0.006	0.01±0.04	0.004±0.001	0.005±0.002
LEAD	1.71±0.8	0.11±0.001	0.007±0.01	0.01±0.02
MANGANESE	1.17±0.3	1.03±0.62	0.046±0.01	0.072±0.01
NICKEL	0.56±0.2	0.42±0.18	1.00±0.08	0.037±0.13

Table 2. Average Metal Concentration of Bottom waters of different stations

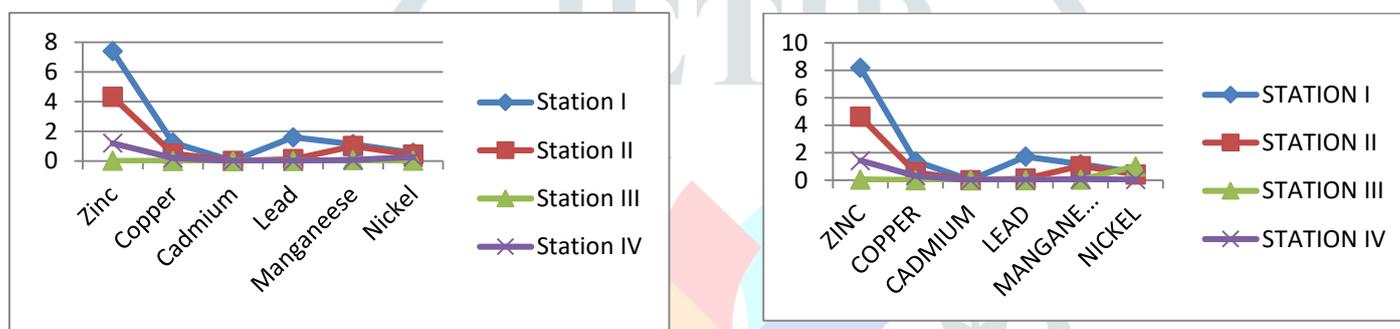


Fig. II Metal concentrations of surface water.

Fig III. Metal concentrations of bottom water.

**Influence of physico chemical factors on Heavy metal distribution in water column**

Using Pearson Correlation, correlation between various water quality parameters such as temperature, pH, and salinity and metals like zinc, copper, cadmium, lead, manganese and nickel were done. pH is negatively correlated with all the studied metal concentration at 0.05 level of significance, while temperature and salinity is positively correlated with concentration of metal. There exist a positive correlation between metals, which indicate the presence of a common source of metal. The metal content present at four stations studied showed a significant variation in Two Way ANOVA.

	pH	Salinity	Temp
pH	1		
Salinity	-.721**	1	
Temp	-.458**	.571**	1
Zinc	-.909**	.820**	.622**
Copper	-.807**	.785**	.687**
Cadmium	-.709**	.672**	.750**
Lead	-.660**	.588**	.544**
Manganese	-.985**	.738**	.445**

Nickel	-.633**	.525**	.842**
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**Table III. Correlation matrix of heavy metals , pH, salinity and temperature of all the samples**

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