Assessment of the Levels of Heavy Metals in Vertical Sediment Cores of Lake Markermeer in the Netherlands

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Abstract

The sediment quality of Lake Markermeer was assessed based on the levels of seven heavy metals (Mn, Cr, Zn, Cd, Pb, Ni and Cu) in the sediment. This study which took place between November, 2010 and April, 2011 aimed at classifying the sediment core. The study involved taking sediment core samples with a Beeker core borer and having them sectioned into 9 segments. Each of them was digested and analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy at the UNESCO-IHE laboratory in Delft, the Netherlands. The results revealed that the sediments cores were clean probably due to the successful implementation of "The Rhine Action Plan and a ban on the use of leaded fuel in the 90s as well as the use of cleaner production measures by industries. Setting up monitoring station to monitor discharges into the lake may be necessary

1. Introduction

Lake Markermeer is a freshwater lake located in the central part of the Netherlands. It is a shallow lake with an average depth of 3.6 m [25]**.** The lake has variable water depth. Thus, while the eastern part of the lake is deeper (usually greater than > 4 m) the western part is shallow. The Lake was created from a larger Lake IJssel, which used to receive discharges from river IJssel. River IJssel was a tributary to River Rhine which was reported in the early 70s to have high levels of heavy metals [5]. In view of this, River Rhine was suspected to have contributed to its sediment quality which was reported to have declined over the decades as a result of pollution from diffuse and point sources and had resulted in high turbidity and eutrophication [26]. This studied assessed the sediment quality of Lake Markermeer in terms the levels of seven heavy metals namely: Zinc (Zn), Chromium (Cr), Nickel (Ni), Cadmium (Cd), Copper (Cu), lead (Pb) and Manganese (Mn). A comparison was made with the Netherlands standards for classifying heavy metals polluted sediment.

Heavy metals are one of the widespread micro pollutants to freshwater bodies such as lakes and whose presence may affect the water chemistry and the biological or aquatic ecosystems [11,3, 30]. Therefore, their presence in water bodies should be of great concern to people. Heavy metals get into water bodies through industrial effluents, municipal discharges as well as agricultural run-offs [24]. In water bodies, they generally, enter into the water column and get adsorbed onto the sediments but depending on the environmental conditions, they may be released back into the water column when they are disturbed [10,8]. This means that sediments may be a potential source of pollutants as well as being a receptor of heavy metals in the aquatic system and can be used as "pollution archives" when combined with radioisotope chronologies such as ^{210}Pb dating [6,15]**.** It follows that sediment core analysis can provide a historical record of natural background and man-induced accumulation of metals [2].

2 Materials and methods

In view of the high heavy metals levels recorded in the early 70s, in the Rhine river [5] which is believed to have contributed to the sediment quality of River Rhine, in addition to the use of Best Available Technologies (BATs) by industries and a ban on the use of leaded-petrol, a gradual decrease in the levels of heavy metals from the bottom layer to the top layer of Lake Markermeer was expected. To investigate this hypothesis, the levels of heavy metals in vertical sediment cores of Lake Markermeer were assessed and the levels were compared with the Dutch standards for sediment quality.

2.1 Study area and sediment sampling

This research was part of large scale sediment characteristics and dynamics study carried out in Lake Markermeer by [12]. They found out that sediment characteristics such as median grain size and organic matter content showed a spatial pattern to imply wind-induced sediment transport and resuspension. The study was carried out in Lake Markermeer located in the central part of the Netherlands. It is a shallow lake with the average depth of 3.6 m [25]. The eastern part of the lake is deeper with an average depth > 4 m and reaching maximum > 10 m while the north eastern as well as the western parts are shallow ranging between 0 - 4 m [25]. (Fig.1).

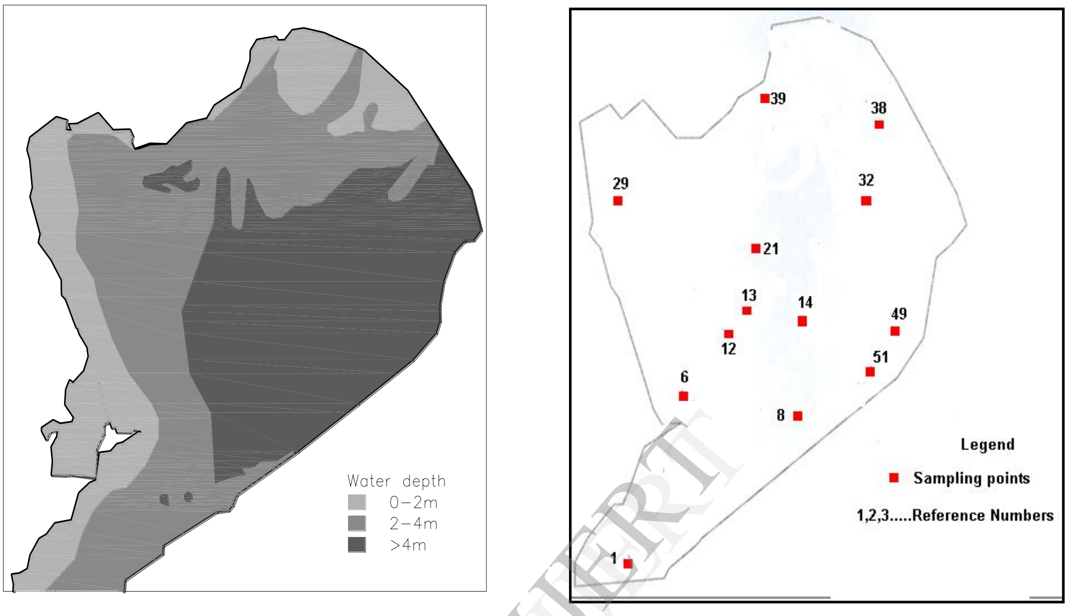

Fig. 1 A map of Lake of Markermeer showing the depth of the study area (a) and the sampling sites (b) Source: [25].

2.2 Sediment sampling

In this particular study, thirteen (13) sediment samples which were taken between 21st and 27th November, 2007 were used. The samples were taken from the sediment cores of Lake Markermeer from thirteen (13) points labelled as 51, 49 and 14 (water depths greater than 4.0 m). Four of these stations, namely 29, 39, 38 and 32 had water depths less than 2.0 m, whereas five other stations, namely, 1, 6, 12, 13 and 21 had intermediate water depths. Each sample was taken by hammering a Beeker Corer (Eijekelkamp, Delft) into undisturbed sediment of the lake and collecting them manually. The Beeker Corer was about 100 cm long and could not be used to sample loose sediments but there was less risk of compaction during sampling. The samples immediately after sampling were sectioned into 9 segments (0-1, 1-2, 2-3, 3-4, 4-5, 5-10, 10-15, 15-20 and ≥20 cm. They were dried and kept in plastic pots in their original strata at the UNESCO-IHE laboratory at room temperature. This study which involved assessment of the levels of the seven heavy metals (Ni, Cu, Pb, Zn, Cd, Mn, and Cr) took place between November 2010 and April 2011.

2.3 Sample preparation and analysis

About 0.5 g of the powdery sediment samples were carefully weighed and transferred into digestion tubes and ten millilitres (10 mL) of 65% HNO_3 was then added to the sediment in each of the digestion tubes. The tubes were then sealed carefully with their respective corks and placed in a Mars 5 duo temperature microwave oven. For quality control, blanks samples (10 mL of 65% HNO_3) and Reference standards (sewage sludge amended soil, BCR CRM143R) were also digested. Each of the digested sediment sample was transferred into a 50 mL volumetric flask and filled with de-mineralized water and kept undisturbed for 2-3 days in order to allow any suspended particles to settle. The supernatant was then decanted into a PPE plastic cup which had also been washed with dilute HNO_3 acid for analysis of heavy metals. Measurements of the heavy metals were done using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on Perkin Elmer optima 3000. Prior to the measurements the ICP-AES was calibrated. All measurements were done according to UNESCO-IHE laboratory procedures which were nearly identical to APHA/AWWA/WEF (2005).

2.4 Quality assurance

In order to ensure that the results produced were scientifically acceptable, the normal laboratory regulations and procedures such as proper cleaning of apparatus, calibration of equipment, analysis of duplicates were strictly adhered to during the research. In addition to these, during digestion of sediment, blanks (65% HNO_3) as well as standards (trace metals in a sewage sludge amended soils) were regularly included in each set of samples digested. The heavy metal concentrations in these were also analyzed. The results revealed that heavy metals in the blanks were all below the detection limit (< 5.00 mg/kg). Again comparison between the heavy metals measured in the amended soils and the actual concentrations indicated that the percentage of difference between them were < 3% in most of the cases.

2.5 Statistical tools

All analytical results were entered and processed in EXCEL Spreadsheet and R software [22]. Additionally, Pearson's product-moment correlation was also used in R to compare the level of correlation between the heavy metal concentrations in the layers. Graphical interpretations were used to outline the variations in core samples. In this study, a probability value $p < 0.05$ was considered as statistically significant [1].

3 Results

3.1 The levels of heavy metals

With the ban on leaded perol and introduction of cleaner production techniques by industries a gradual decrease in the levels of heavy metals from the bottom layer to the top layer of Lake Markermeer was expected in this research. In line with our hypothesis, the results showed a gradual decrease in the levels of all the heavy metals measured (Zn, Cu, Mn, Pb, Cr) from the bottom to the surface layers except Cd which were below the detection limit of 5.0 mg/kg of the ICP-AES used for this analysis (Fig.2 and Table 1). The reduction was initially gradual from the bottom layer (≥ 20 cm) till the layer 0-5cm where very sharp reduction occurred in all the heavy metals studied except Cd that recorded low levels below detection limit. In the case of Pb, Cr and Zn, slightly higher levels were recorded in the layers closer to 5 -10 cm.

Table 1 The levels of heavy metals (HMs) in the various sediment cores of Lake Markermeer

Sediment layers(cm)	**HM Concentration in mg/kg ± S.E**						
	Ni	**Cu**	**Zn**	**Pb**	**Cd**	**Mn**	**Cr**
0-1	8.01 ±2.22	5.08 ±1.41	28.17 ±7.8	7.62 ±2.10	<5.00	194.92 ±53.99	6.93 ±1.92
1-2	8.95 ±2.48	6.48 ±1.80	45.77 ±12.68	14.22 ±3.94	<5.00	254.00 ±70.36	10.45 ±2.89
2-3	10.18 ±3.62	7.35 ±2.12	43.55 ±12.59	12.93 ±3.58	<5.00	254.92 ±73.68	11.93 ±3.30
3-4	13.08 ±3.62	8.59 ±2.38	48.49 ±13.43	17.39 ±4.82	<5.00	326.02 ±90.31	14.80 ±4.10
4-5	15.23 ±4.22	10.44 ±2.89	57.02 ±15.80	23.00 ±6.37	<5.00	366.38 ±101.44	14.19 ±3.93
5-10	15.59 ±4.30	10.11 ±2.80	45.78 ±12.68	21.60 ±5.98	<5.00	413.86 ±114.64	14.89 ±4.12
10-15	15.53 ±4.32	10.35 ±2.87	46.34 ±12.84	20.40 ±5.65	<5.00	489.55 ±135.61	16.90 ±4.68
15-20	15.38 ±4.26	10.50 ±2.91	50.46 ±13.98	17.04 ±4.72	<5.00	467.72 ±129.56	15.90 ±4.40
≥20	18.98 ±6.01	9.44 ±2.99	41.80 ±13.23	17.59 ±5.57	<5.00	463.58 ±146.70	17.67 ±4.89

The heavy metals concentrations represent averages of the various concentrations measured in the respective layers in all the 13 stations. S.E means Standard errors which were obtained from taking averages of 13 observations.

Table 2 Pearson's Product-moment Correlation for the seven heavy metals.

Metal	Ni	Cu	Zn	Pb	Mn	Cr
	1.00					
Cu	0.91***	1.00				
Zn	0.96***	0.84***	1.00			
Pb	0.73**	0.83***	0.63**	1.00		
Mn	0.85***	0.80***	0.90***	0.43*	1.00	
Cr	0.79**	0.73**	0.84***	0.39*	0.92***	1.00

Significance level ***p < 0.001, **p <0 .05 *p > 0.05. (*** means highly significant, **Significant, *not significant): r^2 is the coefficient of correlation. Number of observations, n =78.

3.2 Correlation between the heavy metals and the physico-chemical parameters in the vertical sediment cores

The results from Pearson's Product-moment correlation for the seven heavy metals (Ni, Cu, Zn, Pb, Mn and Cr) are shown in Table 2. The results show that all the heavy metals exhibit some level of positive correlation with Ni being the most strongly correlated. Nickel, Copper and Zinc show very strong and statistically significant positive correlations with all the heavy metals except with Cd (Table 2).

4 Discussions

4.1 Sources heavy metals and classification of sediment cores of Lake Markermeer

According to [24, 16] the sources of heavy metals to sediments are natural processes (geological weathering and biological processes) and human activities (industries, pesticides applications, leaching from garbage and solid waste dumps, fallouts from the atmosphere , or from secondary sources such as from one river to the other. Generally, the sources of these heavy metals to sediments are linked with their use. For instance, if a particular heavy metal has an industrial use, then its source may be from industrial source. Chromium for example is used for making paints, fungicides, chrome plating etc. Therefore the sources of Cr to lake sediments can be attributed to industrial and agricultural sources. Lead is used for making lead acid batteries, as an anti-knocking agent in the petroleum industries so one of the sources can be fallouts from the atmosphere. Inputs of heavy metals to river Rhine are attributed to industrial, agricultural and atmospheric fallouts [23]. Lake Markermeer was created from the larger Lake IJssel, which used to receive discharges from river IJssel. River IJssel is a tributary to River Rhine which was reported in the early 70s to have high levels of heavy metals [5]. In view of the disconnection between Markermeer and River Rhine, in addition to the use of Best Available Technologies (BATs) by industries and a ban on the use of leaded-petrol, a gradual decrease in the levels of heavy metals from the bottom layer to the top layer of Lake Markermeer was expected. The gradual decrease in concentrations of the heavy metals from the bottom to the surface layer for all the heavy metals studied supports our hypothesis put forward. These are comparable to [20] in the Western Ross Sea in Antarctica where a similar trend was observed. Several reasons may account for the low levels of the heavy metals on the surface compared to the deeper cores. According to [12], the Lake sediment is disturbed by wave actions so the heavy metals may be bound to organic matter in the sediment so during re-suspension, they become exposed to oxygen and then they get oxidized and remobilized from the top layers. Another reason is that according to [5, 17], high levels of heavy metals were recorded in the early 70s in River Rhine which necessitated the implementation of some reduction strategies which included the enactment of the Surface Water Act (WVO) in 1970, establishment of Water Purification Boards, polluters were made to pay, industries had to apply for permits for discharge of their waste, Water Boards were made to construct treatment plants to treat industrial and domestic wastes, setting up of the International Rhine Commission and the acceptance of the Rhine Action Plan in 1978 [32]. The Rhine Action Plan which was successfully implemented coupled with other control measures such as a ban on the use of leaded-petrol in 1990 may account for reduction in heavy metals levels in the 90s onwards. The reduction in heavy metal concentrations in river Rhine might have led to a corresponding reduction in the surface cores of Lake Markermeer which had open connection with it.

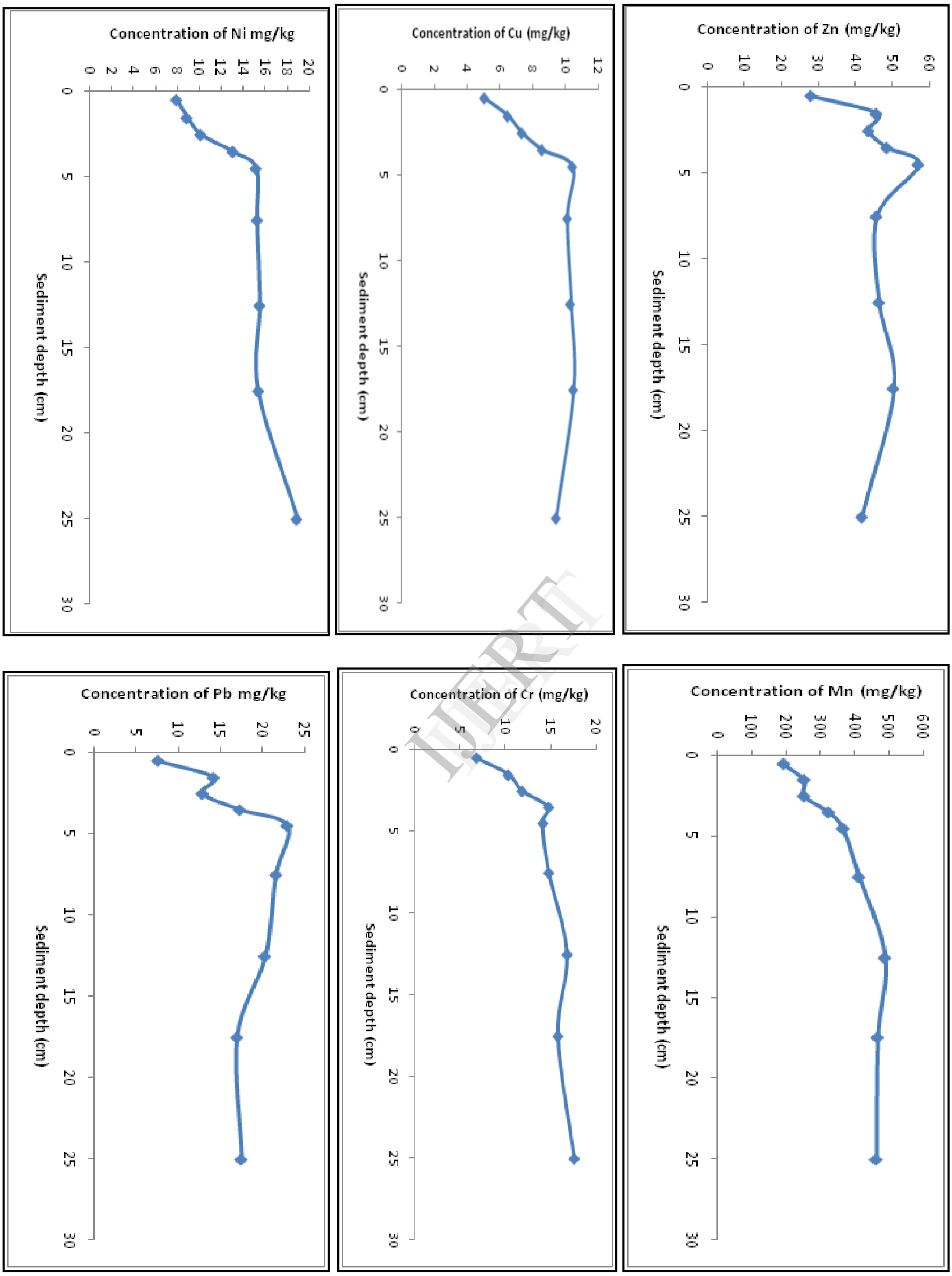

Fig 2 The trends in heavy metals in the sediment cores of Lake Markermeer: The levels of Pb, Cr, Zn, Mn, Ni and Cu measured in mg/kg of sediment samples in the deeper part of the Lake Markermeer: The heavy metals concentrations were plotted using the averages

Positive correlations were observed among the heavy metals. This is comparable to the observation made by [28] in West-four Pearl River Estuary in China. [19,13] in the city of Delft canals, observed similar positive correlations among the heavy metals and attributed it to River Rhine as the source [19, 13]. This means the heavy metals studied may be from a common source which may be river Rhine in this case.

In the Netherlands system of classifying heavy metals polluted sediments, sediments are put into four classes, namely, Class 1, class 2, class3, and class 4 (Table 3). Sediments are said to be in class 1 and 2 if it is not polluted or slightly polluted while class 3 sediments are said to be moderately polluted and class 4 heavily polluted [13]. Generally, sediments in classes 3 and 4 need to be washed or kept under ISM system (Isolate, Store and Monitor). In this study, comparison with the Dutch system of classifying heavy metal polluted sediments showed that all the sediment layers are within class 1 except for Mn which does not have a standard for comparison and Cd which was below the detection limit of 5mg/kg (Table 3). The low concentrations of Cd, Cr, Zn and Ni in the surface layers are comparable to the observation made by [13] in the canal sediment of Delft city [13].

Table 3 Pollution classes with respect to micropollutants contents (mg/kg) for polluted sediments in the Netherlands.

HM	Class 1	Class 2	Class 3	Class 4
Cr	<380			≥380
Ni	<35	35 - 45	45 - <210	≥210
Cu	<35	35 - < 90	90 - 190	≥190
Zn	<480	480 - < 720		≥720
Cd	<2	2 - < 7.5	7.5 - <12	≥20
Pb	<530			≥530

Source: Kelderman et al. *(*2004): HM: represents heavy metals. Sediments are said to be in classes 1 and 2 when they have very low concentrations of the contaminants while class 3 is said to be moderately polluted. Those in class 4 category are said to be heavily polluted an

5 Conclusions and recommendations

The levels of the heavy metals studied generally decrease gradually from bottom layers (≥ 20 cm) to the top (0-5 cm) layers of Lake Markermeer. The levels of Cd were however found to be below the detection limits of 5.0 mg/kg of the ICP-AES used in the analysis. Again all the heavy metals in the Lake sediment studied might be from a common source. Lastly the sediment cores of Lake Markermeer are within the class 1 category which is clean in terms of five (Ni, Cr, Pb, Cu Zn) out of the seven heavy metals studied. The exceptions were seen in Cd which was below detection limit and Mn which was not included in the Netherlands Standards for heavy metals polluted sediments. In view of this, it is recommended that monitoring stations be set up to monitor discharges into Lake Markermeer to ensure that the sediment quality is prevented from deterioration. Also, further studies are recommended for the binding forms of the heavy metals as well as erosion processes around the shore as this could be a potential source of heavy metals and other pollutants to the lake.

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