Full Length Research Paper

Grain-Size Analysis and Heavy Metals Distribution in Sediment Fractions of Lake Markermeer in the Netherlands

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Abstract

Lake Markermeer is situated in the central part of the Netherlands and before 1976 it had an open connection with River Rhine that was believed to have compromised its sediment quality with the fine sediment having the highest concentration of the heavy metals. This study therefore sought to assess the distribution of the sediment grain size particles and the corresponding distribution of six heavy metals (Mn, Cd, Zn, Ni, Cu, Pb and Cr) in three sediment fractions (> 0.5 mm, 45 µm - 0.5 mm and < 45 µm) of Lake Markermeer in the Netherlands. This was done by taking sediment samples from vertical cores using Beeker Core Borer. Grain-size analysis was done through sieving; digestion and analysis of heavy metal content using Inductively Coupled Plasma Atomic Emission Spectroscopy were carried out. The results showed low and uneven grain-size distribution throughout the sediment cores probably due to disturbances from wave action. The highest concentrations of the heavy metals were found in the finest grain-size (< 45 µm) due to larger surface area and higher adsorption capacity.

Keywords: Grain-size; Heavy metals; Sediment core; Lake Markermeer; River Rhine; Beeker Core Borer.

INTRODUCTION

Lake Markermeer is a freshwater lake located in the central part of the Netherlands and covers a total area of 700 km^2. It is a shallow lake with an average depth of 3.6 m (Van Duin, 1992). 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 (Figure 1). The Lake was created from the larger Lake IJssel, which receives discharges from river IJssel. River IJssel is a tributary to River Rhine which was reported in the early 1970s to have high levels of heavy metals (Beurskens et al.,1994). In view of this, River Rhine is suspected to have contributed to its sediment quality which has been reported to have declined over the

decades as a result of pollution from diffuse and point sources (Vijverberg, 2008).

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 (Hares 2000; Almeida et al., 2002; Xu and Liu, 2004). Therefore, their levels in freshwater bodies may predict the quality of the water body. Heavy metals get into water bodies through industrial effluents, municipal discharges as well as agricultural run-off (Sugirtha and Patterson, 2009). 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 (Mohapatra, 1988; Douben and Koeman, 1989). According to Kelderrman et al. (2012), the Lake sediment is disturbed by wave actions. This implies that

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the Lake may have variable particle sizes and heavy metal distribution. The heavy metals may be bound to organic matter in the sediment and during re-suspension they may be remobilized from the top layers through oxidation. This study sought to assess how heavy metals are distributed in the sediment particle sizes of Lake Markermeer in the Netherlands. Generally fine grain-sized materials have larger surface area for adsorption and that chemical properties such as adsorption capacities are generally dependent on the sediment grain size (Golterman, 2004). In view of the sediment disturbance of Lake Markermeer through wave action (Kelderman et al., 2012) one may expect irregular distribution of grain size with the majority being fine particles.

MATERIALS AND METHODS

Study Area

The study was carried out in Lake Markermeer (Figure 1) located in the central part of the Netherlands. It is a shallow lake with an average depth of 3.6 m (Van Duin 1992). The eastern part of the lake is deeper with an average depth > 4 m and reaching maxima > 10 m while the north eastern as well as the western parts are shallow ranging between 0 - 4 m (Van Duin, 1992).

Sediment Sampling

This research was part of large scale sediment characteristics and dynamics study carried out in Lake Markermeer by Kelderman et al. (2012). Kelderman et al. (2012) found that sediment characteristics such as median grain size and organic matter content showed a spatial pattern to imply wind-induced sediment transport and resuspension. In this particular study, thirteen (13) sediment samples were taken between 21st and 27th November, 2007. Of these, five stations, (8, 51, 49 and 14) had water depths greater than 4.0 m, four stations, (29, 39, 38 and 32) had water depths less than 2.0 m, whereas five other stations, (1, 6, 12, 13 and 21) had intermediate water depths. Sampling was done by hammering a Beeker Corer (Eijekelkamp, Delft) into undisturbed sediment of the lake and collecting them manually. The Beeker Corer which was about 100 cm long with an internal diameter of could not be used to sample loose sediments but there had 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, Delft, The Netherlands, at room temperature. This study which involved assessment of the levels of the seven heavy metals (Ni, Cu, Pb, Zn, Cd, Mn, and Cr) in the original sediment samples as well as for three sieved sediment fractions took place between November 2010 and April 2011.

Sieving of samples and grain size analysis

Sections of the sediment samples 0-5 cm, 5-10 cm, 10-15 cm 15-20 cm and ≥ 20 cm were prepared for sieving. The section 0-5 cm was obtained by mixing about 5 g each of 0-1, 1-2 etc sections. Thus, each of the segments was homogenized by stirring for 24 hours using an IKA-WERK top stirrer machine. The homogenized sediment samples were wet sieved using two Fritsch stainless steel containers with mesh size 0.5 mm on top of the one with mesh size 45 μm. The three fractions (> 0.5 mm, 45 μm - 0.5 mm and 45 μm) were then dried in an oven at 70°C until a constant weight was obtained.

The grain size distribution in the vertical sediment cores was also assessed from the sieved fractions by assigning a phi (φ) value. The grain size expressed in phi units is given as (ϕ = - ^{2}log (d), where d = diameter in mm). Thus, a phi value of 1 was given to the fraction 0.5 mm, while the 45 μm grain size was assigned a phi value of 4.5. This was followed by the computation of the cumulative percentages for the fractions. A graph of cumulative percentage was then plotted against the phi values on a probability paper (Håkanson and Jansson, 1983). The median grain size value was then determined by extrapolating from 50% of the cumulative percentage to the phi unit axis.

Assessment of heavy metals (Ni, Cu, Pb, Zn, Cd, Mn, and Cr)

Digestion of sediment for heavy metals analysis using a closed vessel microwave-assisted digestion method has now become common since it is very fast and also reduces the risk of external contamination (Nadkarni, 1984; Frank and Arsenault, 1996). Each of the dried sediment samples (either the sieved fractions or the original samples) was ground into powder using pestle and a mortar.

Analysis of the seven heavy metals was done in both the original sediment core samples as well as sieved fractions and mass balanced established for each. Each of the dried sediment core samples (either the sieved fractions or the original samples) was ground into powder using pestle and mortar. 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
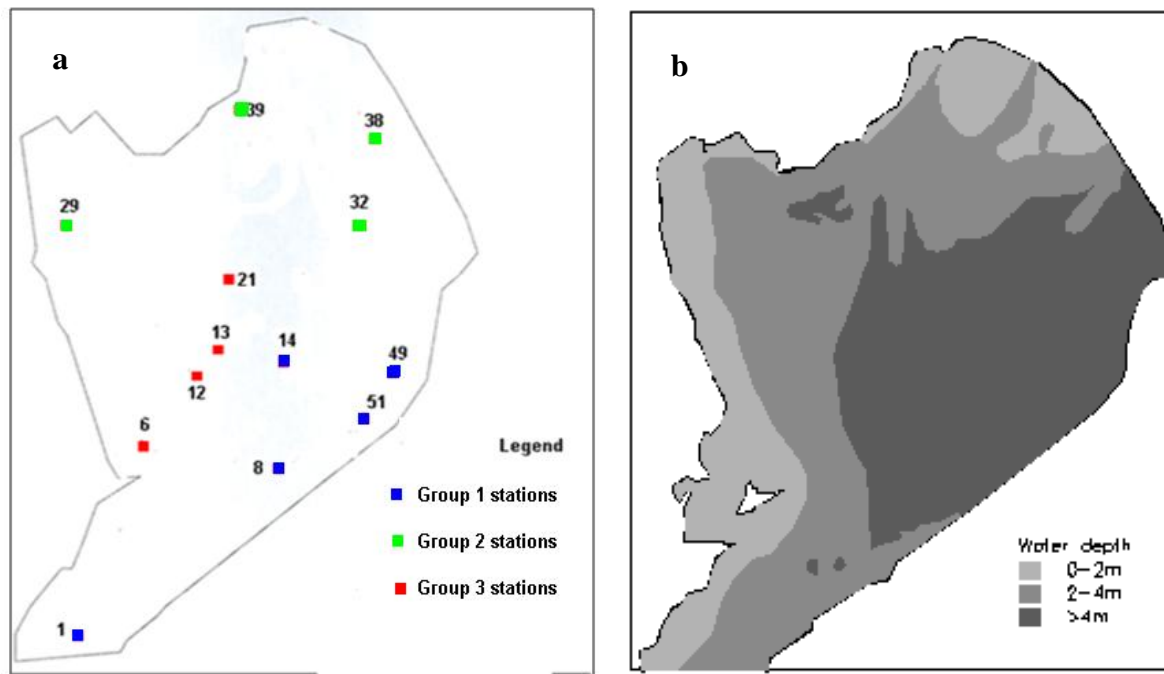
Figure 1. A map of Lake of Markermeer showing the sampling sites (a) and the depth of the study area (b)
Source: (Van Duin,

CRM143R) were also digested. Each of the destructed sediment samples were 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 APHA/AWWA/WEF (2005).

Mass balance

A mass budget or balance was established by comparing the heavy metal concentrations in the original sediments with the sum of the products of heavy metal concentration in each fraction and their respective fractional abundance. Thus, the sum of the product of heavy metal concentration in each of the fractions and their respective abundances were approximately equal to the corresponding concentration in the original sample. The concentrations from the sieved fractions were then compared with the corresponding ones in the original samples and the percentage difference for each of them was determined. The percentage difference was found by dividing the sum of the heavy metals concentrations in the original samples and the sieved fraction and the final result was then multiplied by

hundred percent.

$$\% Difference = \frac{\left|(HM)_{or} - (HM)_{fr}\right|}{\left|(HM)_{or} + (HM)_{fr}\right|} \times 100$$

Where, $[HM]_{or}$ is the heavy metal concentration measured in mg kg^{-1} in the original sediment sample and $[HM]_{fr}$ is the heavy metal concentration measured in mg kg^{-1} in the sieved sediment sample.

The results indicated that the percentage difference between the heavy metals in the original samples and the sieved fractions were < 2% in most of the cases.

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. In addition to this, mass budgets were established by comparing the heavy metal

concentrations in the original sediments with the sum of the products of heavy metal concentration in each fraction and their respective fraction abundance. The percentage of difference was < 2% in most of the cases. Lastly, digestion of sediment and analysis of heavy metals were repeated for some stations. The results gave percentage difference < 0.4 % in most of the cases.

Statistical tools

All analytical results were entered and processed in EXCEL Spreadsheet and R software (Singer and Karwautz, 2010). 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 and the median grain size. 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 (Adiyiah et al., 2013).

RESULTS

Median grain size

The results for the median grain size analysis are shown in Table 1 and Figure 2. The results did not show much variation in the geographical and vertical distribution of the median grain size. Generally high median grain size were found in the surface cores of the sediment samples taken from the eastern part (deeper part of the lake with water depth > 4 m) and low median grain size found in the bottom cores. The north-eastern part of the lake with water depth ranging between 0 - 4 m showed no distinct variation of grain size in sediment cores. Contrary to our expectation, the western and the central parts of the lake showed mixed median grain size distribution. In station 13 for instance, the highest median grain size are found in the bottom sediment core while the lowest in found in the middle layer.

The bolded numbers represent the sampling sites/stations: N/A means the sediment layer was not available for analysis. All median grain sizes are in phi (φ) unit which is - ^{2}log (grain size in mm). A single factor ANOVA could not find any significant difference between the grain median grain size distributions among the vertical sediment cores of the stations (P > 0.05)

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, Cd, Mn and

Cr) and the median grain size are shown in Table 2. The results show that all the heavy metals exhibit some level of positive correlation with Pb being the most strongly correlated while Cd is the weak correlated heavy metal. All the heavy metals showed weak positive correlations with the median grains except Cd (Table 2).

Heavy metals distribution in sieved sediment fractions

The levels of heavy metals in the three sediment fractions > 0.5 mm, 45 µm - 0.5 mm, and < 45 µm are shown in Fig. 3 to 5 and . The results show that the concentration of heavy metals in the fractions differed considerably among the fractions. The highest concentrations of the heavy metals were found in the finest grain-sized fractions (< 45 µm). This was followed by the fraction (45 µm - 0.5 mm) with the least in > 0.5 mm fraction. Thus, apart from Zn where the ratio of Zn concentration in the fraction < 45 µm to those in 45 µm - 0.5 mm was found to be three times (3x) higher, all the rest showed their respective concentrations being twice (2x) in the < 45 µm fraction compared to 45 µm - 0.5 mm fraction. In all the measurements, the levels of Cd were below the detection limit of < 5.00 mg/kg for the ICP-AES.

DISCUSSIONS

Generally, understanding total sediment dynamics is necessary to assess the effects of mitigation measures to improve the water quality (Vijverberg, 2008). In shallow lakes, hydrodynamics and sediment transport are driven by wind. Local wind waves induce erosion of the bed ("wave stirring") and a turbulent boundary layer near the bed (Vijverberg, 2010). Wave action will lead to the redistribution of grain size. The fine and coarse fractions in Lake Markermeer are found to re-suspend rapidly for wind speeds above 5 m/s, to form a uniform concentration profile if these wind conditions persists (Vijverberg et al., 2010). This sediment movement may explain the non uniform distribution of the median grain size. The non uniforms distribution of median grain size supports the hypothesis put across by Vijverberg et al. (2010) and Kelderman et al. (2012) in their study on the sediment characteristics of Lake Markermeer. This may be due to the overall shallowness (average depth 3.6 m) of the lake which made it possible for the sediment to be disturbed by lake current and wave actions leading to their resuspension and transport (Van Duin, 1992).

Additionally, similar grain size distributions were found in the vertical sediment cores of stations 1, 8, 51, 49 and 21 (Figure 1 and 2). In these stations, high median grain size values were found on the surface layers and low median grain size in the bottom layers (Figure 2). This trend is comparable to the grain size

Table 1. Median grain size distribution in the vertical sediment cores of the 13 sampling sites

Layers (cm)	Median grain size (Mdφ) in the various stations												
	1	**6**	**8**	**12**	**13**	**14**	**21**	**29**	**32**	**38**	**39**	**49**	**51**
0 -5	4.5	3.4	3.3	3.2	N/A	2.9	3.3	3.6	2.5	2.4	2.8	3.1	3.3
5 -10	2.4	3.2	2.8	3.5	2.2	3.0	2.4	1.7	2.7	2.7	3.0	2.8	2.4
10 -15	2.6	3.4	2.4	3.6	1.2	2.5	2.5	3.0	2.6	2.3	3.0	2.5	2.5
15 -20	2.6	2.8	1.7	3.5	3.5	2.5	2.5	3.3	2.3	2.3	3.0	2.5	2.5
≥20	N/A	N/A	2.0	3.0	6.8	3.2	2.2	2.5	2.4	N/A	2.9	2.3	2.2
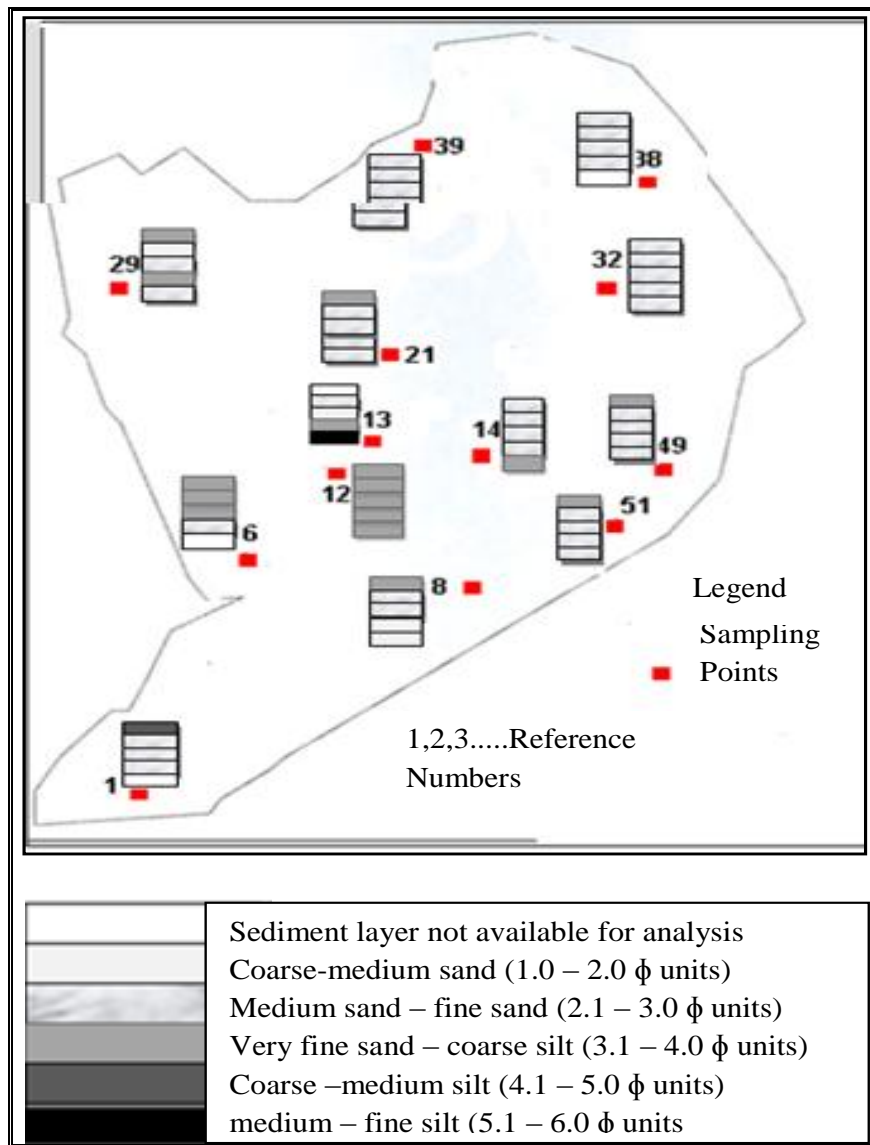
Figure. 2 Median grain size distribution in Lake Markermeer

Table 2. Pearson's product-moment correlation between, the heavy metals the median grain size (Mdφ)

Heavy Metals	Ni	Cu	Zn	Pb	Cd	Mn	Cr
r^2	0.23[*]	0.35[*]	0.20[*]	0.29[*]	0.07[*]	0.39[*]	0.11[*]

Significance level (p > 0.05), * not significant, r^2 is the coefficient of correlation.
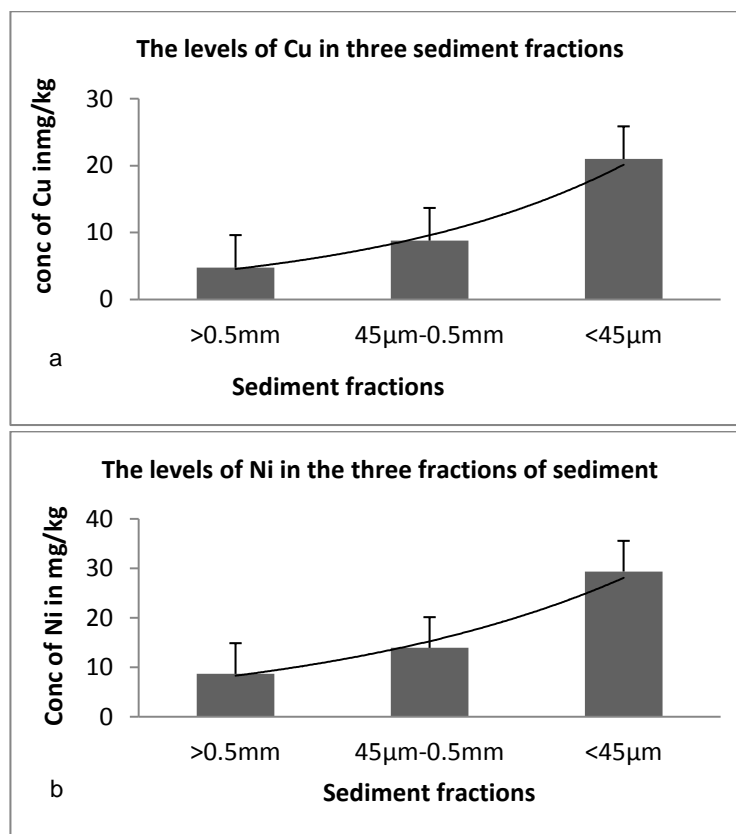The number of observations (n = 14)

Figure. 3 The levels of Ni (a) and Cu (b) measures in mg/kg in three sediment fractions. The difference between the three fractions is statistically significant (p < 0.05). The bars represent averages of 13 measurements for each of the heavy metals. The errors bars represent the standard errors for 13 observations

distribution found by Liu et al. (2010) in the sediment cores of Pearl River Estuary in China. This may be due to the fact that these stations are located in the deeper parts of the lake where there is high deposition with little or no disturbance through wave action or current in the recent times. The observed trend in stations 38, 32 and 39 (Figure 1 and 2) may be due to the fact that the stations are located in the shallow part of the lake. This makes the area susceptible to disturbances such as wave action and current leading to the mixing of the median grain size in the sediment cores of these stations.

High concentrations of heavy metal are generally associated with fine grain-sized sediments (Daskalakis and O'Connor, 1985). In view of this, higher concentrations are expected in the top layers of stations located in the eastern part of the lake (Figure 1 and 2) while those in the north-eastern part of the lake especially stations 32 and 38 (Figure 1 and 2) are expected to have low concentrations in the vertical cores of the sediment. This is because whereas the stations at the eastern part have finer sediment on the surface than the bottom layers, the group stations 2 (especially 32 and 38) have coarse grains which do not exhibit any

clear vertical changes throughout the core (Figure 2 and Table 1). This hypothesis is supported by the observations made in the heavy metal concentrations in the vertical cores of samples taken from the eastern part of the lake. Samples taken from the western part of the lake on the contrary, showed low concentrations on the surface in spite of the fine sediment grains on the surface. Again, higher concentrations of heavy metal are found in the bottom in spite of the coarse grains present (Figure 2). This suggests that factors other than grain-size (input from river Rhine) are responsible for the high concentrations of heavy metals in the bottom lake sediment. This is because according to Golterman (2004), chemical properties such as adsorption capacities are generally dependent on the sediment grain-size. Fine grain-sized materials generally have larger surface area for adsorption. In this study, heavy metal concentrations in three sediment fractions (> 0.5 mm, 45 µm - 0.5 mm and < 45 µm) were compared in 13 sampling sites (Figure 2). The highest heavy metal concentrations were recorded in fractions < 45 µm in all the sampling sites (Figure 3 to 5) .This observation is similar to the observations made in studies on river Rhine/Main (WHO 1980), Zonta et al. (1994) in the
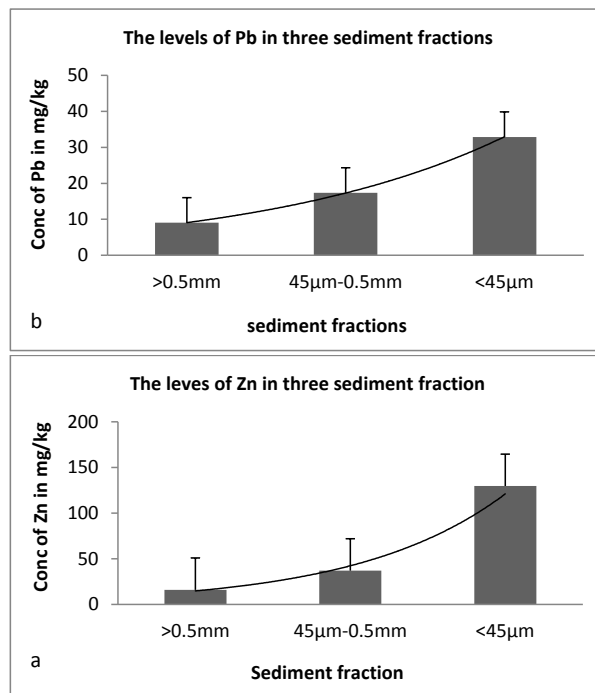
Figure 4. The levels of Zn (a) and Pb (b) measures in mg/kg in three sediment fractions. The difference between the three fractions is statistically significant ($p < 0.05$). The bars represent averages of 13 measurements for each of the heavy metals. The errors bars represent the standard errors for 13 observations
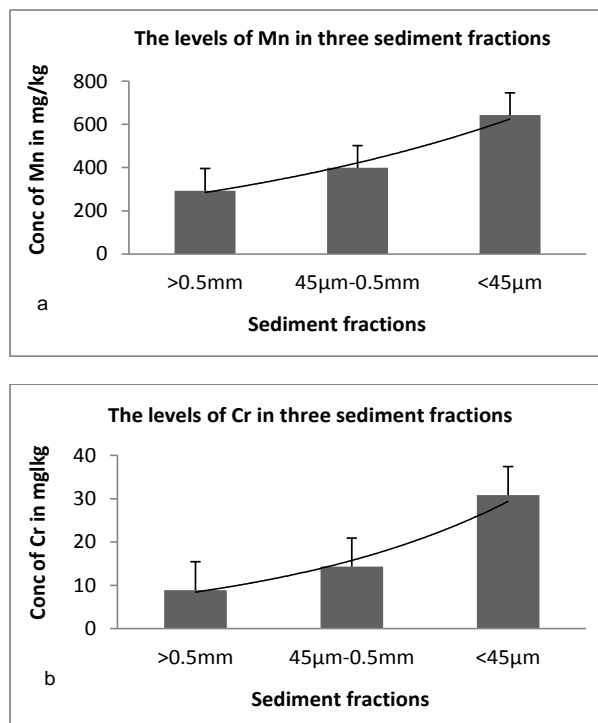

Figure 5. The levels of Mn (a) and Cr (b) measured in mg/kg in three sediment fractions. The difference between the three fractions is statistically significant ($p < 0.05$). The bars represent averages of 13 measurements for each of the heavy metals. The errors bars represent the standard errors for 13 observations.

Venice Lagoon, Italy, Villaescusa-Celaya et al. (2000) in Baja California, Middelkoop (2000), in river Rhine and Meuse floodsplains in the Netherlands, and Daskalakis and O'Connor (1995), in the United States.

CONCLUSIONS

Lake Markermeer is a shallow lake with variable particle sizes which are not uniformly distributed. Owing to a mean water depth of 3.6 m, waves in Lake Markermeer can easily penetrate down to the bed. The median grain-size is very low which gives the sediment high surface area for adsorption of heavy metals. The highest concentrations of the heavy metals were found in the fine grain size range (<45 µm). In view of the low median grain-size and the heavy metals mostly found in the fine grain size range, it recommended that further studies be carried out on the binding forms of the heavy metals in the lake. Again further research is also recommended to better understand the erosion processes around the shore as this could be a potential source of heavy metals and other pollutants to the lake.

ACKNOWLEDGEMENTS

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