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Keywords

Oyster Bay, sediments, trace metals, Hierarchical cluster analysis and pollution

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Spatial and Temporal Distribution and Pollution Assessment of Trace Metals in Marine Sediments in Oyster Bay, NSW, Australia.

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Abstract

The disposal of untreated urban and industrial wastewater has a deleterious effect on both the water and sediment quality of Oyster Bay located in south Sydney, Australia. The present investigation was undertaken to evaluate the potential pollution of marine sediments in Oyster Bay. The results of metals were compared with adverse biological effect values Effect Range Low (ERL) and Effect Range Median (ERM). Spatial distribution of trace metals was estimated by applying geographic information system. The results indicated that the sediments were polluted with Cu, Zn, As and Pb, which exceeded ERL levels. However, these metals were still below ERM values, and other metals Cr and Ni were below ERL. Moreover, the highest concentrations of metals were around discharge points and in the inner bay. Further, trace metals could be attributed to human activities within the bay as they declined in concentrations with increasing sediment depth.

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1. Introduction

Many anthropogenic sources cause trace metal contamination of aquatic environments such as estuaries, bays, rivers, lakes and lagoons. Pollution results from the discharge of waste from urbanization, industrialization, municipal wastewater, atmospheric deposition, agricultural uses and various other sources (Hosono et al., 2011; Morelli et al., 2012). Trace metals are dispensed into aquatic habitats, are then deposited in and soils by various processes such as absorption, ion exchange and metal substitution. Clay minerals are considered to be the ultimate sinks for accumulated metals. Therefore, the levels of trace metals in the sediments play an important role in the contamination of aquatic environments. This is due to their toxicity, persistence and easy accumulation (Hu et al., 2011). However, trace metals can also be released again into the water column as free ions and/or complex compounds from sediments under processes such as physical disturbance, chemical and diagenesis factors (Zoumis et al., 2001). Consequently, increasing levels of metals can be harmful for marine flora and fauna. This increase may lead to reduced growth and impaired reproduction leading to a decline in species diversity. In addition, trace metals may enter into human bodies through the food chain, resulting in serious health problems such as brain damage and various other types of illness (Alves et al., 2013; Huang et al., 2014). The objective of the present research was, firstly, to measure the spatial distribution of trace metals within the sediments using a geographic information system (the Kriging method) as well as temporal distribution, and secondly, to evaluate the ecological risk of trace metals posed by these sediments by comparing them with deleterious biological effect values guidelines (effect range low and effect range mediana) and previous studies.

2. Methods and Materials

Oyster Bay, which is located 15 km south of Sydney (Fig.1), is one of the bays along the coast of Botany Bay. It is affected by activities from the Georges River catchment area 800 km². In Oyster Bay water depths are generally shallow. It has maximum tidal ranges of about 2 m (Kingsford and

Suthers, 1996). The catchment area of Oyster Bay is highly urbanised, with commercial, light industrial and domestic land use areas.

Fig. 1: Sediment samples and core locations in Oyster Bay off Botany Bay area, NSW, Australia.

Surface sediment samples were collected using a grab sampler. The 5cm of surface sediment was reserved for analysis. A total of 55 samples were collected during the summer of 2012 (Fig.1). Water depth and location were recorded at each site using sonar and Geographical Position System (GPS). Subsurface sediment cores were collected later from the sites with the highest heavy metal concentrations using a push core. Grain size measurements were determined for all sediment samples (sand, silt and clay) using a Malvern Mastersizer 2000. Trace metal concentrations were measured using a x-ray fluorescence (RFSPECTRO-XEPOS) energy dispersive spectrometer fitted with a Si-docile detector, and following the established procedure of Norrish and Chappell, (1977). Hierarchical cluster analysis was used to distinguish between the characteristic of samples (Zhang et al., 2013), this analysis was undertaken using JMP software to consider all variables (trace metals and sediment particles).

GIS software was used to plot the sample sites within the study area, and advanced geostatistical analysis (Kriging) were applied to create maps. Kriging is a moderately quick interpolator that can be exact or smoothed depending on the measurement error model. It is a flexible means to evaluate graphs of spatial autocorrelation. The Kriging method uses statistical models that generate a variety of map outputs, predictions, prediction standard errors, and probability. Kriging interpolation can be rigorously evaluated according to several cross-validation indicators as follows: the absolute value of the average mean standardized error (MSE) should be close to 0; there should be a minimal root mean square prediction error (RMSE), which should be close to the mean standard error (AME), and the standard root mean square (RMSS) should be close to 1

(Krivoruchko, 2011; Chen et al., 2013). These parameters are calculated by using the following equations:

$$ME = \frac{1}{n} \sum_{i=1}^n (P_i + M_i) \dots\dots\dots 1$$

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (P_i - M_i)^2} \dots\dots\dots 2$$

$$MSE = \frac{1}{n} \sum_{i=1}^n [(P_i - M_i)/\sigma_i] \dots\dots\dots 3$$

Where: n is the number of the sites; P_i and M_i are the predicted and measured values at sites i respectively; σ_i is the Kriging standard error at sites.

In the interpretation of geochemical data, the choice of background values plays an important role. Several authors have used the average shale values or the average crustal values because they did not have local background values. In this study, the background values obtained from the core were used as a reference baseline for each trace metal.

3. Results and Discussion

As can be seen in Fig.2, sediment grain size and water depth varied within the bay. Fig.2a shows that the highest percentages of sand were at the edges and shoreline of the bay, where the water depth was shallow (< 0.7 m; Fig.2b), and which had high tidal and current activity. The muddy (silt and clay) percentages were concentrated within the inner bay (Fig.2c), where water depths were higher (0.9 m - 1.9 m; Fig. 2b), and the waves had more limited lower effect on the bottom sediments. Therefore, the fine and very fine particles settle within the inner bay.

Fig.2: a- Percentage of sand, b- water depth and c- percentage of mud.

As shown in Table 1, trace metal concentrations were compared with the deleterious biological effect values in marine sediments. Based on guidelines suggested by the U.S. National Oceanic and Atmospheric Administration Ligerio et al. (2002) and ranged from effect range low (ERL) to effect range median (ERM).

Table 1: Basic statistics of trace metals ($\mu\text{g/g}$) within the bay, with ERL and ERM values.

Trace metals	Cr	Ni	Cu	Zn	As	Ba	Sr	Pb
Min.	8.9	7.0	9.8	43.4	1.9	45	29	14.2
Max.	126.9	38.8	62.7	385.9	25.7	217	138	198.2
Mean $\pm$ SD.	51 $\pm$ 32	18 $\pm$ 7	35 $\pm$ 12	204 $\pm$ 84	15 $\pm$ 6	150 $\pm$ 48	100 $\pm$ 31	98 $\pm$ 48
ERL	81(13)	20.9 (20)	34 (24)	150 (40)	8.2 (44)	NA	NA	46.7 (45)
ERM	270	51.6	270	410	70	NA	NA	218

NA: not available.

(N): number of samples exceeded ERL and no sample exceeded ERM.

Overall, the mean concentrations of all metals were below their ERM guidelines. However, the concentrations of copper (Cu), zinc (Zn), arsenic (As) and lead (Pb) were above the ERL in most of the sample locations. These effects represent contamination in most locations. On the other hand, chromium (Cr) and nickel (Ni) were below the ERL levels, representing no significant contamination by these metals. In addition, the concentration of trace metals varied widely within the bay, depending on sources of pollution (discharge and stormwater outlets) and sediment types. Prediction maps of trace metals such as Cr, Ni, Cu, Zn, Pb and As are shown in Fig.3 and the concentration of these metals generally exhibit variable patterns of distribution. The highest concentrations of these trace metals were in the inner and middle parts of the bay, which also contained high percentages of mud particles.

These trace metals were also concentrated in close proximity to discharge points from the catchment area, while the lowest levels of trace metals were found along the edges and shoreline, as well as in the mouth of the bay, areas with abundant clean quartz sand.

Fig.3: Distribution of trace metals (a-Cr, b-Ni, c-Cu, d- Zn, e-Pb and f-As) within Oyster Bay Where: arrow indicates discharge points.

Generally, the concentrations of trace metals increased with decreased sediment depth. Between 45-40cm, concentrations of trace metals remained constant, which indicates a natural background of trace metals. From 40cm to 20cm both Zn and Pb concentrations rose rapidly, and Cr, Cu and Ni increased moderately. From 20cm upward surface sediment metals remained stable at the same concentrations, while As showed a gentle increase (Fig.4). The decline in the level of metals with increasing sediment depth indicates the accumulation of trace metals since the first European settlement, which includes sewage runoff, atmospheric emissions and gas-fumes from both vehicles and boat exhaust (Irvine and Birch, 1998; Birch, 2011).

Fig.4: Variations of trace metals with depths (cm) in a sediment core in Oyster Bay.

Hierarchical cluster analysis (Fig.5, Table 2) enabled the classification of the samples into three groups. The main variables that defined the red group were high percentages of mud, low sand content and high levels of trace metals. As illustrated in Table 2, both strontium and barium were highly concentrated in the sediments, which is related to the abundance of organisms with shells (molluscs, foraminiferal and ostracods), which are more tolerant of pollution, such as *Ammonia teccarii* (For.) and *Cyprideis torosa* (Ost.); (Foster et al., 2012). The green group contained lower concentrations of variables than the red group with high percentages of sand, low percentages of mud and lower levels of trace metals except for chromium, which may be derived from heavy minerals such as hematite, contained in silty sand (Johnston and Chrysochoou, 2014). However, the blue group differed completely, with high percentages of sand, low percentages of mud and low concentrations of trace metals. Therefore, the red and green groups were considered to be moderately to highly polluted with samples located in the inner bay, while the blue group represents areas with low or no pollution and samples located at some of the edges of the bay.

The trace metal concentrations that were measured in Oyster Bay were compared with the levels of trace metals determined in a range of studies (Table3; Birch and Taylor, 1999; Jones et al., 2003). Huon estuary is essentially a non-industrialised zone and consequently should contain a low level of potentially toxic trace metals Jones et al. (2003). In contrast, the Port Jackson estuary has a high concentration of trace metals and would be expected to have toxic metals, due to high amounts of waste water discharged into the estuary (Irvine and Birch, 1998).

Table2: Depth, percentages and concentrations of variables in different classification groups.

Variables	Cluster A	Cluster B	Cluster C
Depth	1.1	0.9	0.5
Sand	6.9	26.1	54.3
Silt	75.7	59.5	36.3
Clay	17.4	14.4	9.4
Cr	47.7	66.3	28.9
Ni	20.1	19.6	8.8
Cu	40.2	33.1	14.0
Zn	242.5	193.3	68.6
As	20.0	11.7	4.5
Sr	124.0	84.7	38.8
Ba	185.3	126.2	57.3
Pb	132.7	67.4	24.4

Fig.5: Classification map for all variables.

As Table3 illustrates, the sediment quality in Oyster Bay is considered to be polluted with trace metals especially for Cu, Zn and Pb compared to the sediments in the Huon estuary, but to have less pollutants than sediments in the Port Jackson estuary. The main anthropogenic pollution

sources of trace metals in the samples of the study area can be attributed to discharge points and stormwater drains from roadways and residential areas, as well as the number of boatyards and the large numbers of moored watercraft. Oyster Bay provides a good instance of the distribution of pollutant concentrations by current and wave activity, which is deemed to be a sheltered environment, protected from high winds and thus having low tides and wave activity. As a consequence, fine and very fine particles are gradually precipitated within the Bay (Mc Lusky, 1989).

Table 3. Comparison of trace metal from Huon estuary and Port Jackson with study area.

Trace metals ($\mu\text{g/g}$)	Cr	Ni	Cu	Zn	As	Pb
Huon / Range	5-80	2-28	7-32	2-66	4-25	2-48
Mean	71	20	17	40	16	25
Port Jackson /Range	BDL	5-24	9-1053	108-7622	BDL	38-3604
Mean		22	188	651		364
This study/ Range	9-127	7-39	10-63	43-386	2-26	14-198
Mean	51	18.5	35	204	15	98

Where: BDL= below detection limit.

4. Conclusions

In order to evaluate the environmental status of the trace metals Cr, Ni, Cu, Zn, Pb and As, these metals were analysed in both surface and subsurface marine sediments from Oyster Bay, NSW, Australia. Statistical analysis such hierarchical cluster analysis was used. In general, the findings show that the bay is highly contaminated with $\text{Pb} > \text{Zn} > \text{Cu}$ respectively and there is also moderate contamination from As. However, there was low or no contamination from Cr and Ni. Three groups were defined. The first and second groups represented moderately to highly polluted environments, while the third group represented unpolluted environments. The trace metals in Oyster Bay have accumulated over time from source such as discharge points and boats, and especially gas fumes from the exhausts of vehicles and boats.

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6. References

- Alves, A. S., Adão, H., Ferrero, T. J., Marques, J. C., Costa, M. J., & Patrício, J., 2013. Benthic meiofauna as indicator of ecological changes in estuarine ecosystems: the use of nematodes in ecological quality assessment. *Ecological Indicators*, 24, 462-475.
- Birch, G., F., 2011. Contaminated soil and sediments in a highly developed catchment-estuary system (Sydney estuary, Australia): an innovative stormwater remediation strategy. *Journal of Soils and Sediments*, 11, 194-208.
- Birch, G., & Taylor, S., 1999. Source of heavy metals in sediments of the Port Jackson estuary, Australia. *Science of the Total Environment*, 227, 123-138.
- Chen, C., Zheng, B., Jiang, X., Zhao, Z., Zhan, Y., Yi, F., & Ren, J., 2013. Spatial distribution and pollution assessment of mercury in sediments of Lake Taihu, China. *Journal of Environmental Sciences*, 25, 316-325.

- Foster, W. J., Armynot du Châtelet, E., & Rogerson, M., 2012. Testing benthic foraminiferal distributions as a contemporary quantitative approach to biomonitoring estuarine heavy metal pollution. *Marine Pollution Bulletin*, 64, 1039-1048.
- Hosono, T., Su, C.-C., Delinom, R., Umezawa, Y., Toyota, T., Kaneko, S., & Taniguchi, M., 2011. Decline in heavy metal contamination in marine sediments in Jakarta Bay, Indonesia due to increasing environmental regulations. *Estuarine, Coastal and Shelf Science*, 92, 297-306.
- Hu, G., Yu, R., Zhao, J., & Chen, L., 2011. Distribution and enrichment of acid-leachable heavy metals in the intertidal sediments from Quanzhou Bay, southeast coast of China. *Environmental Monitoring and Assessment*, 173, 107-116.
- Huang, P., Li, T. G., Li, A. C., Yu, X. K., & Hu, N.-J., 2014. Distribution, enrichment and sources of heavy metals in surface sediments of the north Yellow Sea. *Continental Shelf Research*, 73, 391-405.
- Irvine, I., & Birch, G. F., 1998. Distribution of heavy metals in surficial sediments of Port Jackson, Sydney, New South Wales. *Australian Journal of Earth Sciences*, 45, 297-304.
- Johnston, C. P., & Chrysochoou, M., 2014. Mechanisms of chromate adsorption on hematite. *Geochimica et Cosmochimica Acta*, 138, 146-157.
- Jones, B. G., Chenhall, B. E., Debrezion, F., & Hutton, A. C., 2003. Geochemical comparisons between estuaries with non-industrialised and industrialised catchments: the Huon and Derwent River estuaries, Tasmania. *Australian Journal of Earth Sciences*, 50, 653-667.
- Kingsford, M. J., & Suthers, I. M., 1996. The Influence of tidal phase on patterns of ichthyoplankton abundance in the vicinity of an estuarine front, Botany Bay, Australia. *Estuarine, Coastal and Shelf Science*, 43, 33-54.
- Krivoruchko, K. 2011. Spatial Statistical Data Analysis for GIS Users. United States: Esri Press.
- Ligero, R. A., Barrera, M., Casas-Ruiz, M., Sales, D., & López-Aguayo, F., 2002. Dating of marine sediments and time evolution of heavy metal concentrations in the Bay of Cádiz, Spain. *Environmental Pollution*, 118, 97-108.
- Mc Lusky, D. S., 1989. *The Estuarine ecosystem (2nd edition)*. Blackie Academic Professional, Glasgow, 215 p.
- Morelli, G., Gasparon, M., Fierro, D., Hu, W. P., & Zawadzki, A., 2012. Historical trends in trace metal and sediment accumulation in intertidal sediments of Moreton Bay, southeast Queensland, Australia. *Chemical Geology*, 300-301, 152-164.
- Norrish, K., & Chappell, B., 1977. X-ray Fluorescence Spectrometry. In: Zussman, J. (ed.) *Physical Methods in Determinative Mineralogy*. Academic Press London. 201- 272.
- Zhang, W., Zhao, D., & Wang, X., 2013. Agglomerative clustering via maximum incremental path integral. *Pattern Recognition*, 46, 3056-3065.
- Zoumis, T., Schmidt, A., Grigorova, L., & Calmano, W., 2001. Contaminants in sediments: remobilisation and demobilisation. *Science of the Total Environment*, 266, 195-202.