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Abstract

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Disciplines

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Environmental Assessment of Benthic Foraminiferal and Pollution in Gunnamatta Bay, NSW, Australia.

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Abstract

We investigated the distribution of trace metals (spatial and temporal) and sedimentary particles in order to identify the relationship between benthic foraminifera and trace metals pollution within Gunnamatta Bay, Port Hacking Estuary, NSW, Australia. Risk assessments of surface sediments were evaluated by using hierarchical cluster analysis (HCA). A total of 59 surface sediment samples and seven subsurface sediment samples were collected, in order to determine the levels of trace metals in spatial and temporal of the bay. Further, six surface sediment samples were examined for existing foraminiferal assemblages in muddy samples, which had high and low concentration of trace metals and sandy samples. The trace metals distribution showed that the trace metals such as chromium, nickel, copper, zinc, arsenic, lead, rubidium and bromine had similar distribution in surface sediments. The results of trace metal concentrations were compared with the deleterious biological effect values in marine sediments. The mean of most trace metals for the Bay were below the Effect Range Low except copper and Effect Range Median. The highest concentrations of these metals were found to be in the north east of the bay sample GU55, which is close to the proximity of discharge points, and craft boats (moored) with concentrations (107, 14, 398, 413, 8, 203, 27 and 182ppm) respectively. Also, this trace metal pollution is concentrated in the inner part of the bay, which is deep, and has organic matter and clay minerals. The benthic foraminiferal assemblages has low species diversity in muddy samples GU25 and GU55 compared to the fine sandy particles in samples GU12 and GU24. Furthermore, the muddy particles that have had high level of trace metals were dominated by species tolerant- pollution such as *Ammonia beccarii*, *Brizalina spathulata* and *Elphidium excavatum*. These have had more opportunity to flourish. In addition, the values of trace metals dramatically decline with increasing depth. This reflects that the potential source of trace metal pollution is from human activity (eg. gasoline fumes and boats), since early European settlement in this area.

Keywords: Gunnamatta Bay, Trace metals, Pollution, Sediment particles, Benthic foraminiferal.

1. Introduction

Sediment pollution by trace metals in estuaries and around coastal areas is an international environmental issue. Contamination results from discharge points, source runoff and human activities related to, industry, agriculture, urban development, mining, shipping and other activities. These activities can provide waste containing metal residues. High levels of pollution can have harmful and toxic effects on the marine ecosystem and biotic resources, and is critical to human health (Hosono et al., 2011; Morelli et al., 2012). Trace metals are dispersed in aquatic habitats, and are then deposited in aqueous environments and combined with sediments and soils by mechanisms such as absorption and ion exchange.

Muddy particles are especially considered to be ultimate sinks for accumulated metals. Therefore, the level of trace metals in sediments and soils contribute to the contamination of aquatic environments due to their toxicity, persistence, hard degradation and easy accumulation (Yuan et al., 2004; Dural et al., 2007; 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 different processes such as physical disturbance, chemical and diagenesis factors. Consequently, increasing levels of trace metals can be harmful for marine flora and fauna such as dwelling micro-organisms such as foraminiferal and ostracods, their growth may be retarded, and because of impaired reproduction and decline of species diversity. Also, trace metals

may enter human bodies via 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., 2013). The main purpose of this paper is: 1- To evaluate the spatial and temporal distribution of trace metals, within sediments. 2-To assess the ecological risk to the sediments. 3- To identify the distribution patterns of benthic foraminiferal assemblages in the bay. 4-To examine the relationship between trace metal pollution and benthic foraminiferal assemblages.

2. Experiments

2.1 Study area

Gunnamatta Bay, which is located 30 km south of Sydney in the State of New South Wales (Fig.1), and is one of several bays that are part of the Port Hacking estuary. It has a well-defined catchment area, and is impacted by activities from the Hacking River catchment area. Water depths in the bay ranged between 0.3-12m. Gunnamatta Bay is tidal, with maximum tides of approximately 2 m. The tides are semi- diurnal, with fresh water discharged from the Georges River (Gray et al., 2001). The catchment area of Gunnamatta Bay is highly urbanised, with the main land use being commercial, light industrial and residential areas. The sources of contamination are mainly from catchment drainage such as stormwater channels that discharge directly into the Bay .

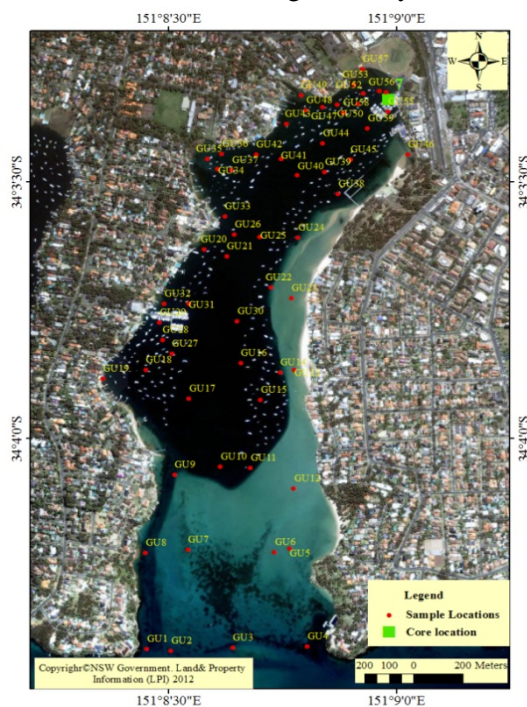


Fig. 1. Sample and core locations in Gunnamatta Bay.

2.2 Sample collections and preparations

Surface sediment samples were collected by a grab sampler. Only the surface 5 cm of sediment was reserved for analysis. A total of 59 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). Moreover, seven samples from subsurface sediment were collected (from the site with the highest concentrations) of trace metals by using push core.

Grain size measurements were determined for all sediment samples using a Malvern Mastersizer 2000. This analysis was used to obtain the details of distribution of grain size, and to explain the geochemical findings. Percentages of sand, silt and clay contained in each sediment sample were determined.

Trace metals were measured using XRF a SPECTRO - analytical instrument (XEPOS) energy dispersive spectrometer fitted with a Si- docile detector, following an established standard procedure (Norrish and Chappell, 1977).

HCA was applied to distinguish between the sample groups (Zhang et al., 2013). This was achieved using JMP software to present all variables.

Arc GIS (v.10) desktop software was used to plot the sample sites within the study areas, and advanced geostatistical analysis was applied to create maps. This geostatistical analysis is known as the Kriging method. This 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 (Li and Heap, 2008). The Kriging method uses statistical models that generate a variety of map outputs, such as predictions, standard errors, and probability. However, Kriging flexibility often requires decision-making. Kriging assumes the data are derived from a stationary stochastic process, while some other methods assume normally distributed data (Chen et al., 2013).

Six sediment surface samples were selected to identify and determine percentages of foraminiferal species. Two samples were selected from three sites with the following characteristics: muddy with high trace metals; muddy with low trace metals; and fine sandy samples. All samples were gently washed through a 63 μ m sieve with tap water to remove muddy particles. The remaining fractions were dried at 60 °C. The total foraminiferal assemblages were counted. The minimum number of specimens used in statistical analysis was approximately 100 for each sample, which was standardised as percentages.

3. Results and Discussion

Sediment grain size and water depth varied within the bay as seen in Table 1. Fig.2a shows that the highest percentages of sand were at the edges, shoreline and mouth of the bay, where the sand barrier and the water depth was shallow at the edges and shoreline (<1.0 m; Fig.2b). These areas had high tidal and current activity, which disturb and transport the fine and very fine particles into deeper areas. The muddy (silt and clay) percentages were concentrated within the inner bay (Fig.2c), where water depths were higher (5.8-12 m; Fig.2b), and the waves slightly less effective on bottom sediments. Therefore, the fine and very fine particles can gradually settle within the inner bay.

Table 1 Range and mean of sediment fractions in Gunnamatta Bay.

Variables	Depth (m)	Sand %	Muddy%
Range (mean)	0.3-12 (5.2)	2.1-100 (72.2)	0-97.8 (27)

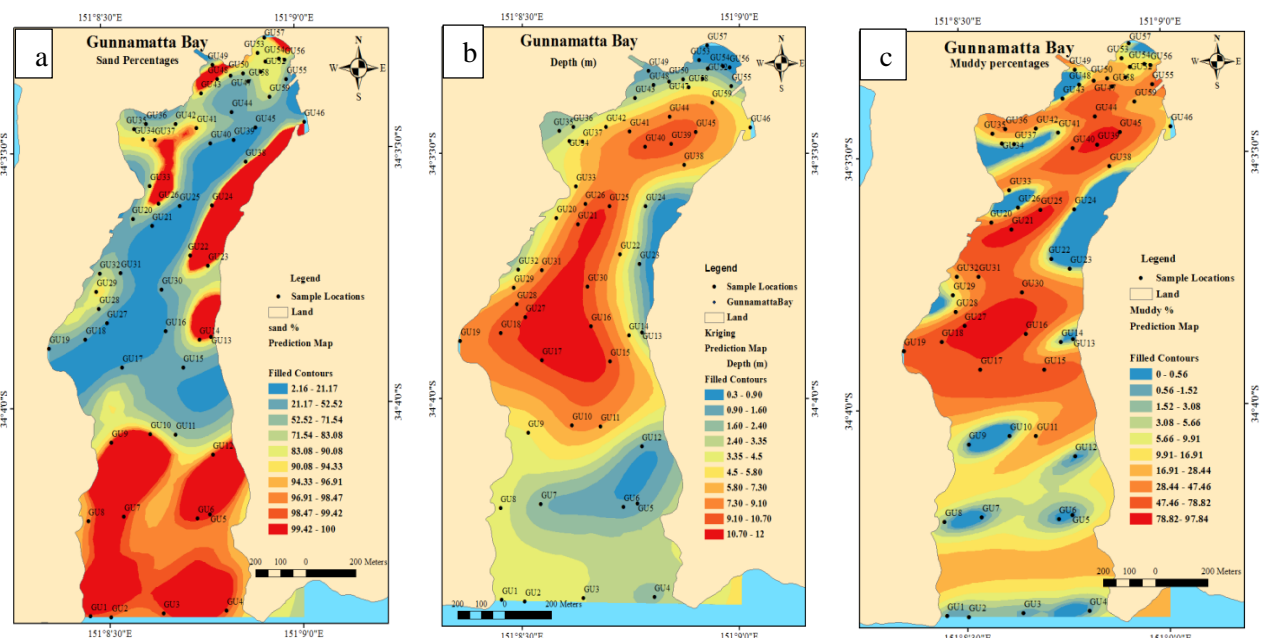


Fig. 2. a - Sand percentages, b- water depth (m) and c- muddy percentages in the Gunnamatta Bay.

As shown in Table 2, trace metal concentrations were compared with the deleterious biological effect values in marine sediments. Effect were measured based on guidelines suggested by the U.S.

National Oceanic and Atmospheric Administration (Long et al., 1995; Ligero et al., 2002) and ranged from effect range low (ERL) to effect range median (ERM).

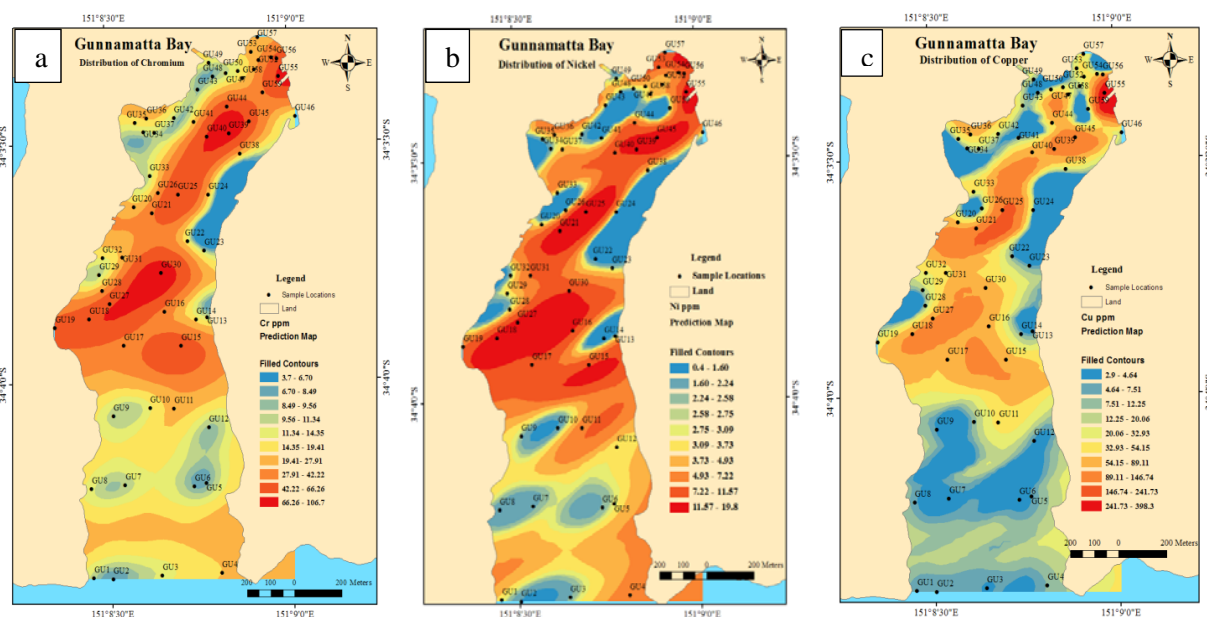
Table 2 Basic statistic range and mean concentrations of trace metals (ppm) in samples of the study area compared with effect range low (ERL) and effect range median (ERM) values.

Trace metals (ppm)	Cr	Ni	Cu	Zn	As	Pb	Rb	Br
Gunnamatta Bay								
Range	4-107	0.4-20	3-398	6-413	1-12	2-203	1.7-48	18-309
Mean \pm SD.	27 \pm 27	6 \pm 5	41 \pm 59	65 \pm 77	4 \pm 3.1	32 \pm 37	14 \pm 11	103 \pm 71
GU25 and GU55								
Mean	102	17	273	330	9	157	37	202
GU44 and GU58								
Mean	44	5	47	79	6	48	15	121
GU12 and GU24								
Mean	7	3	4	11	2	4	10	32
ERL	81	20.9	34	150	8.2	46.7	NA	NA
ERM	270	51.6	270	410	70	218	NA	NA

NA: not available

Overall, the mean concentrations of trace metals were below the ERL and ERM, except copper which was higher than ERL. Samples GU17, GU18, GU21, GU25, GU27, GU30, GU39, GU40, GU45 and GU55), which were located in inner bay, exceeded the ERL for copper, zinc, arsenic and lead. In addition, concentrations of the trace metals such as copper and zinc in sample GU55 exceeded the ERM and lead reach to the ERM value (i.e. 398 ppm for copper, 413 ppm for zinc and 203ppm for lead). The wide variations in concentrations of trace metals within the bay were, due to sources of pollution (discharge points and stormwater outlets), boatyards, watercraft as well as sediment types (muddy particles and organic matter).

Prediction maps of trace metals chromium, nickel, copper, zinc, arsenic, lead, rubidium and bromine are shown in Fig.3 a-h. The concentration of these metals generally exhibit similar patterns of distribution. The highest concentrations of these metals were in the inner and middle parts of the bay, which also contained high percentages of mud particles (clay minerals), and organic matter. Both muddy particles and organic matter can play important role as a trap for trace metals (Mayer et al., 1981; Fernandes et al., 2011). These metals were also concentrated close to discharge points from the catchment area, while the lowest levels of trace metals were found to be along with the edges and shoreline, as well as in the mouth of the bay, areas with abundant pure coarse sand.



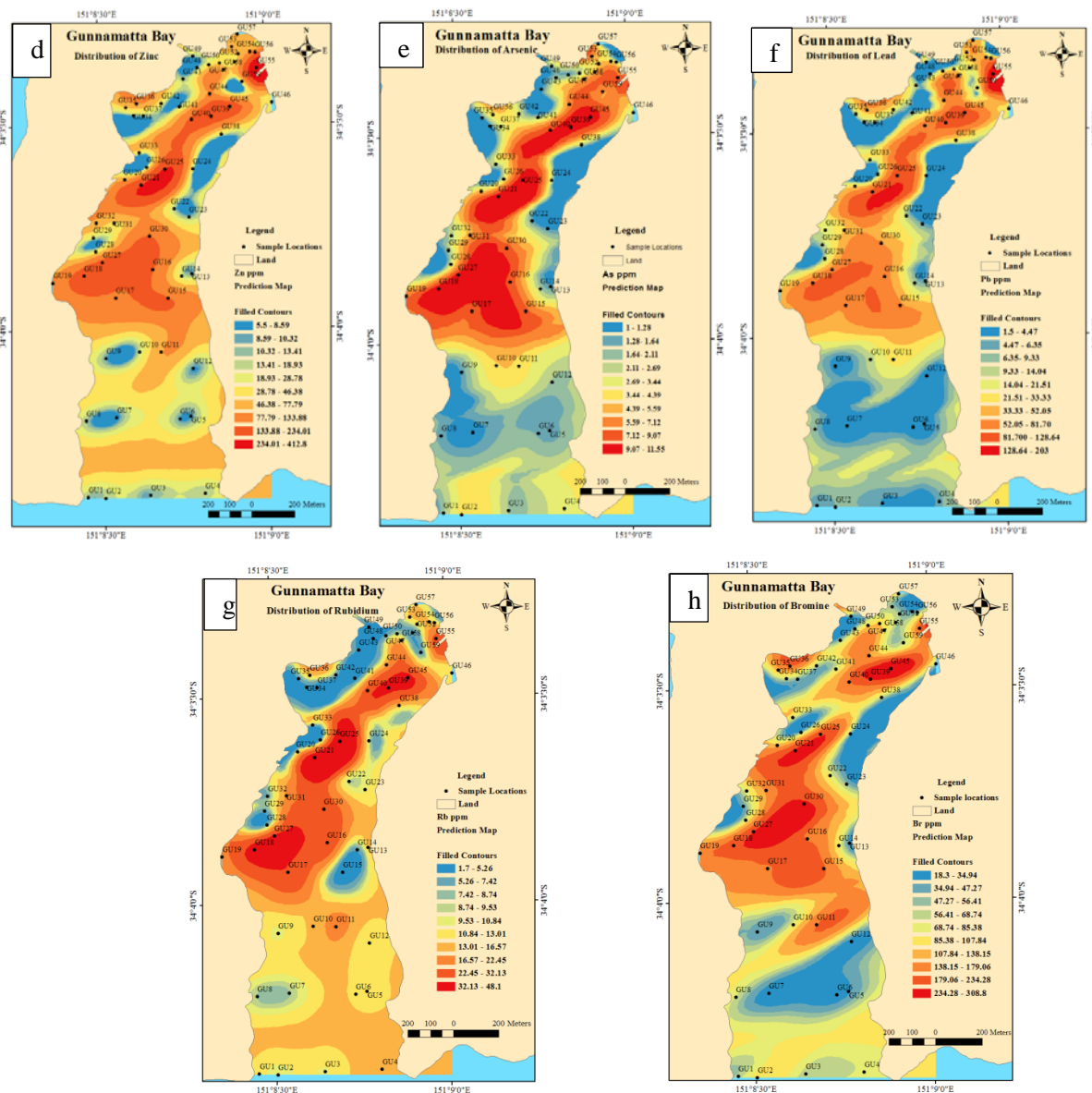


Fig.3. Distribution of metals a- Cr, b- Ni, c- Cu, d-Zn, e- As, f- Pb, g-Rb and h-Br in ppm in the bay.

The concentrations of metals copper and zinc decreased rapidly and lead declined moderately with sediment depth, while chromium remained constant with the increase in sediment depth. The concentrations of copper, zinc and lead in core indicated that the accumulation of these metals started since the first European settlement around these area, whereas chromium does not correlate with pollution, which may be driven from heavy minerals (Johnston and Chrysochoou, 2014; Fig.4).

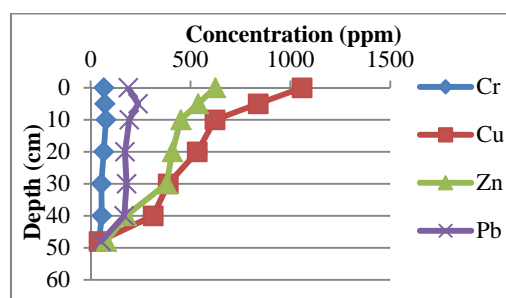


Fig. 4. Variation of trace metals with sediment depth (cm) in Gunnamatta Bay.

The main 38 benthic foraminiferal species were identified in the six samples. Firstly, muddy samples (A) with high concentration of trace metals exceeded ERL for chromium, copper, zinc and lead. Secondly, muddy samples (B) with low concentrations of trace metals and below ERL. Finally, sandy samples (C) Table 3. Species diversity varied between 11-22, was generally higher in the fine sand and muddy with low levels of metals and also below ERL respectively. Species abundance ranged from 1 to 40 individuals per 10g of dry surface sediment. The foraminiferal assemblages in the study area (muddy samples) were composed almost completely of benthic foraminiferal species. This is due to the distance from the open ocean. However, planktonic foraminiferal species are only represented by *Globigerina bulloides* in the sandy samples close to open ocean.

Table 3 Foraminiferal species in surface sediment samples in Gunnamatta Bay.

A- GU55 and GU 25 (Muddy with high level of metals)

Species	Abundances %
<i>Ammonia beccarii</i> (Linne, 1767)	40
<i>Brizalina spathulata</i> (Williamson, 1858)	24
<i>Cellanthus discoidalis multiloculum</i> (Cushman & Ellisor, 1945)	4
<i>Discorbinella bertheloti</i> (d'Orbigny, 1839)	5
<i>Elphidium excavatum</i> (Heron-Allen & Earland, 1913)	11
<i>Elphidium macellum aculeatum</i> (Silvestri, 1901)	2
<i>Parrellina imperatrix</i> (Brady, 1881)	2
<i>Quinqueloculina poeyana</i> (d'Orbigny, 1939)	1
<i>Ramulina globulifera</i> (Brady, 1879)	3
<i>Trichohyalus tropicus</i> (Collins, 1958)	6
<i>Trochammina inflata</i> (Montagu, 1808)	2

B- GU44 and GU58 (Muddy with low level of metals)

Species	Abundances %
<i>Ammonia beccarii</i> (Linne, 1767)	5
<i>Cymbaloperetta bradyi</i> (Cushman, 1915)	4
<i>Dentalina mutsui</i> (Hada, 1931)	2
<i>Elphidium crispum</i> (Linne, 1758)	26
<i>Elphidium jenseni</i> (Cushman, 1924)	3
<i>Guttulina pacifica</i> (Cushman & Ozawa, 1928)	7
<i>Pyrgoella irregularis</i> (d'Orbigny, 1839)	27
<i>Quinqueloculina lamarckiana</i> (d'Orbigny, 1839)	1
<i>Siphogenerina communis</i> (Cushman and Todd, 1944)	5
<i>Spiroloculina canaliculata</i> (d'Orbigny, 1846)	15
<i>Spiroloculina iucida</i> (Cushman & Todd, 1944)	2
<i>Textularia sagittula</i> (Defrance, 1824)	1
<i>Trichohyalus tropicus</i> (Collins, 1958)	2

C- GU12 and GU24 (Sandy)

Species	Abundances %
<i>Bolivina robusta</i> (Brady, 1881)	5
<i>Brizalina spathulata</i> (Williamson, 1858)	3
<i>Cellanthus discoidalis multiloculum</i> (Cushman & Ellisor, 1945)	1
<i>Cribrononion argenteus</i> (Parr, 1945)	3
<i>Discorbinella bertheloti</i> (d'Orbigny, 1839)	2
<i>Elphidium depressulum</i> (Cushman, 1933)	19
<i>Elphidium macellum aculeatum</i> (Silvestri, 1901)	2
<i>Fissurina marginata</i> (Montagu, 1803)	3
<i>Globigerina bulloides</i> (d'Orbigny, 1826)	10
<i>Guttulina pacifica</i> (Cushman & Ozawa, 1928)	2

<i>Loxostomum amygdalaeformis</i> (Brady, 1881)	2
<i>Miliolinella baragwanathi</i> (nov.)	2
<i>Nodosaria perversa</i> (Schwager, 1866)	4
<i>Parrellina verriculata</i> (Brady, 1881)	4
<i>Peneroplis planatus</i> (Fichtel & Moll, 1798)	2
<i>Pyrgoella irregularis</i> (d'Orbigny, 1839)	13
<i>Quinqueloculina anguina arenata</i> (Said, 1949)	3
<i>Quinqueloculina subpolygona</i> (Parr, 1945)	4
<i>Reophax spicalifer</i> (Brady, 1879)	2
<i>Rosalina australis</i> (Parr, 1922)	10
<i>Trochammina ochracea</i> (Williamson, 1858)	2
<i>Vaginulina vertebralis</i> (Parr, 1932)	2

3.1 Distribution patterns of trace metals and sediment fractions

Trace metal pollution once released enter into current and wave circulation and then settle in marine sediments, which have anoxic environmental conditions. The statistical analysis of this study was conducted by hierarchical cluster analysis (Fig. 5, Table 4), and enabled the classification of the samples into three groups.

The main variables that define the red group were the high percentages of mud, low content of sand and high trace metal concentrations. As illustrated in red group (Table 4) rubidium level indicates that the high percentages of mud, and bromine reflects the existence of a high percentage of organic matter in this group, which can play as a trap of trace metals (Mayer et al., 1981; Fernandes et al., 2011). The green group contained less percentage and concentration of variables compared with the red group.

In contrast, the blue group differed completely with high percentages of sand, low percentages of mud and low concentrations of trace metals. Therefore, red was considered to be significant contamination and the green group was considered to be moderately polluted. These samples were located in the middle and inner bay as well as close to discharge points. Nonetheless, the blue group represents areas with low or no pollution and samples were located at the edges and mouth of the bay (Fig. 5).

Table 4: Percentages and concentrations of the variables by HCA.

variables	Cluster A	Cluster B	Cluster C
Depth	9.7	6.9	3.6
Sand	23.2	55.9	91.1
Silt	66.0	37.2	7.7
Clay	10.8	6.9	1.2
Cr	70.4	38.0	13.0
Ni	13.9	6.4	3.2
Cu	124.5	51.9	15.4
Zn	196.5	80.5	25.5
As	9.7	5.4	2.5
Br	220.6	153.4	60.7
Rb	34.9	13.7	8.7
Pb	92.5	40.3	14.3

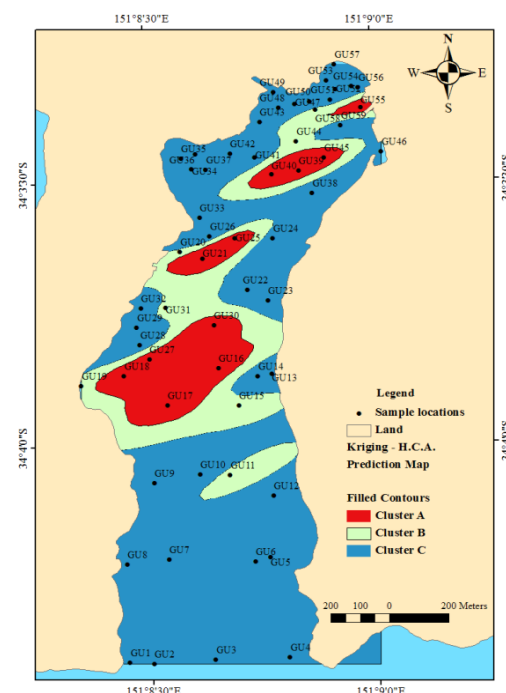


Fig.5. Sketch for classification of all variables in the bay.

3.2 Benthic foraminiferal response to trace metals

Previous research found there was a positive correlation between trace metal pollution and the abundance of benthic foraminiferal species, which made foraminiferal species good bio-indicators of pollution by trace metals (Frontalini and Coccioni, 2008). In addition, foraminiferal species can provide good evidence about any biological change in the past (Alve et al., 2009).

Foraminifera diversity have been deemed indicators of contamination by trace metals and foraminiferal abundance are related to contaminated sites (Bergin et al., 2006). Trace metals can enter into the foraminiferal cell with food and become toxic to benthic species (Yanko et al., 1998). Consequently, a decline tendency in diversity can be indicated as response to trace metals pollution (Debenay and Fernandez, 2009; Alves et al., 2013).

In this research, the lowest foraminiferal diversity was found to be in the muddy samples, having high concentration of trace metals GU25 and GU55 (Table 3), while diversity increases away from discharge points and the middle of the bay toward fine sandy samples GU12 and GU24, which have lowest concentration of trace metals pollution. In other estuaries around the world, foraminiferal diversity has a negative relationship with trace metals (Frontalini and Coccioni, 2008; Li et al., 2013).

Although the availability of community data, the presence or absence of individual foraminiferal species can provide more insight about ecological facts (Debenay and Fernandez, 2009). Previous investigators have found that increasing trace metal pollution can cause an increase in the relative abundance of specific benthic species (Frontalini and Coccioni, 2008; Coccioni et al., 2009), which can be used as a proxy for trace metal pollution. There are several species such as *Ammonia tepida*, *Ammonia parkinsoniana*, *Bolivinelina pseudopunctata*, *Bolivina variabilis*, *Brizalina spathulata*, *Cornuspira involvens*, *Criboelphidium oceanensis*, *Elphidium advena*, *Elphidium excavatum*, *Elphidium magellanicum*, *Haynesina germanica*, *Miliolinella subrotunda*, *Quinqueloculina bicostata* and *Stainforrthia fusiformis* that are known as pollution-resistant and opportunistic species existing in estuary environments contaminated with trace metals (Frontalini and Coccioni, 2008; Romano et al., 2009; Arminot du Châtelet et al., 2011; Foster et al., 2012).

In the present study, *Ammonia tepida*, also reported as *Ammonia beccarii*, *Brizalina spathulata* and *Elphidium excavatum*, are dominant within foraminiferal assemblages in muddy samples. Thus, GU25 and GU55 may reflect the opportunity for this species to withstand contamination by trace metals and tolerant of oxygen deficiency.

As described by (Murray, 2006; Ferraro et al., 2006), some foraminiferal survive and flourish in the most polluted areas, and can exploit chemically and thermally polluted waters, as well as waters with high organic matter. These species were existent in muddy samples GU25 and GU55, which had high concentration of trace metal pollution and organic matter. Consequently, these species can be used as bio-indicators for trace metal pollution in harbours or estuaries.

4. Conclusions

Surface sediments were collected from 59 sites in Gunnamatta Bay, south part of Sydney, Australia, along with subsurface sediments from the identified highest trace metal concentrations. The spatial distribution of trace metals are controlled by discharge points from residential areas, boats and sediment fractions. Sediment samples located in the inner and middle of the bay, as well as vicinity of stormwater outlets have high concentration of trace metals.

Foraminifera species at these sites have low diversity and are recognised by tolerant-pollution *Ammonia beccarii*, *Brizalina spathulata* and *Elphidium excavatum* have more opportunity for survival and thrive in polluted areas, and as such can be used as bio-indicators of trace metal pollution.

Fine sandy samples, have the lowest levels of trace metals, and have the highest foraminiferal diversity including several foraminiferal species.

Trace metal pollution derived from anthropogenic activities including urbanisation, industrialisation and agricultural waste have rapidly increased over time since Europeans settlement around this area.

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