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Abstract

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Keywords

nsw, hacking, port, bay, gunnamatta, australia, within, particles, pollution, element, trace, spatial, distribution, sediment

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Spatial distribution of sediment particles and trace element pollution within Gunnamatta Bay, Port Hacking, NSW, Australia

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Abstract

A combination of geochemical analysis and hydrodynamic measuring has been established in order to provide an explanation for the spatial distribution of both sediment particles and trace element pollution Gunnamatta Bay, NSW, Australia. Fifty nine samples of surface sediment were collected to determine the spatial concentrations of trace elements in the bay. Moreover, current track pathways and velocities have been measured in the bay. The distribution of trace elements such as chromium, nickel, copper, zinc, arsenic and lead had similar patterns in surface sediments. Trace element pollution is concentrated along the current trajectory in the inner part of the bay, which has deeper sites and higher percentages of mud particles. The highest concentrations of these metals were found to be in sample GU55 from the northeast of the bay, which is close to a surface discharge point and moored boats.

Keywords: Gunnamatta Bay, hydrodynamic measurements, trace element pollution, sediment particles, potential ecological risk assessments.

1. Introduction

Marine sediment pollution caused by trace elements 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 and other activities (Birch et al., 1996; Birch and Mc Cready, 2009; Alyazichi et al., 2015a;b). These activities result in waste containing metal residues. Consequent increased levels of pollution in sediment sinks can have harmful and toxic effects on the marine ecosystem (Hosono et al., 2011; Morelli et al., 2012). Trace elements are dispersed in aquatic habitats and are then deposited in aqueous

environments combined with sediments by mechanisms such as absorption and ion exchange. Muddy particles are considered to be the ultimate sinks for most accumulated trace elements. Thus trace elements in sediments and soils contribute to the contamination of aquatic environments due to their toxicity, persistence, difficult degradation and easy accumulation (Yuan et al., 2004; Dural et al., 2007; Hu et al., 2011). Nonetheless, trace elements can also be released again into the water column as free ions and/or complex compounds from sediments during processes such as physical disturbance, chemical and diagenetic factors (Abrahim and Parker, 2008; Chen et al., 2013).

Although complex and highly technical methodologies have been established in developed countries to assess the spatial distribution of sediment particles and chemical pollution, such as trace elements in bays and estuaries (Bacopoulos et al., 2009; Lapetina and Sheng, 2014), these methods have not really addressed the need to provide methodologies applicable to either remote areas or low-cost technologies especially in countries with a less developed economy or locations.

Complex and costly methods are appropriate where studies are being completed by organisation with adequate technical and financial support. Application of such technology in countries with less developed economies is difficult for both cost and technical reasons. Field data such as tidal levels, current track and wind speed and direction comprise such suitable data (McLean et al., 2002; McLean and Hinwood, 2010). The main objectives of this paper are to investigate the spatial distribution of trace element concentrations for Gunnamatta Bay sediments, to evaluate the influence of current trajectory and track velocity on the concentration and to assess the potential ecological risk of trace elements posed by these marine sediments by comparing them with deleterious biological effect values.

2. Study area

Gunnamatta Bay is located 30 km south of Sydney in New South Wales (Fig.1a), and is one of several bays that form part of the Port Hacking estuary. It has a well-defined catchment area, and is impacted by activities from the Hacking River catchment. Water depths in the bay range between 0.3 cm and 12 m. Gunnamatta Bay is tidal, with maximum tides of approximately 2 m. The tides are semi-diurnal and mix 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 uses 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 (Hayes et al., 1998).





Fig. 1 (a) Geograochical locations map and (b) Fifty nine sediment samples in Gunnamatta Bay, Port Hacking, NSW, Australia.

3. Materials and methods

3.1 Sample collection and preparation

Surface sediment samples were collected using a grab sampler. Only the surface 5 cm of sediment was reserved for analysis. Fifty nine samples were collected during the summer of 2013 (Fig. 1b). Water depth and location were recorded at each site using sonar and Geographical Position System (GPS). Grain size measurements were determined for all sediment samples using a Malvern Mastersizer 2000. This analysis was used to obtain the details of grain size distribution, and to explain the geochemical findings. Percentages of sand, silt and clay contained in each sediment sample were determined.

Trace elements of marine sediments were measured using a XRF SPECTRO-analytical instrument (XEPOS) energy dispersive spectrometer fitted with a Si-docile detector, following an established standard procedure (Norrish and Chappell, 1977). Hierarchical cluster analysis (HCA) was applied to distinguish between the sample groups (Zhang et al., 2013). This was achieved using JMP software to present all variables. Wind data (speed and direction) for the duration of the study was provided monthly by the Bureau of Meteorology (BoM) from the Botany Bay station.

The potential ecological risk index (RI) was used to evaluate the effects of the trace element pollution in the study areas. The RI was originally established by (Hakanson, 1980), and was calculated by using following formula:

$$CF^{i} = C_{\text{sample}} / C^{*}_{\text{background}} \dots \dots 1 \quad (\text{Reboredo, 1993}).$$
$$E_{r}^{i} = T_{r}^{i} \times CF^{i} \dots \dots \dots 2$$
$$RI = \sum_{i}^{n} E_{r}^{i} \dots \dots \dots \dots 3$$

Where C is the measured concentration of each trace element.*Used background (2.5m) for trace elements from previous study (Pease, 2007), CF^i is contamination factor, E_r^i is the monomial potential ecological risk factor, T_r^i is the response coefficient for the toxicity of single trace element, which was adopted to be evaluation criterion, (i.e. Cr=2, Ni=Cu= Pb= 5, Zn = 1 and As=10 Hakanson, 1980; Mei et al., 2011), and RI is the sum of all risk factors for trace elements in sediments. According to Hakanson, (1980) the following terminology is designed to be applied for the RI values Table 1.

 Table 1 Indices and potential ecological risk of trace elements pollution.

RI value	Potential ecological risk
RI< 30	Low risk
$30 \leq RI \leq 60$	Moderate risk
60 ≤RI< 120	Considerable risk
$RI \ge 120$	Very high risk

Arc GIS desktop software was used to plot the sample sites within the study areas, and advanced geostatistical analysis was applied to create maps. Geostatistical analysis using the Kriging method 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).

3.2 Experiments of hydrodynamic activities

A new and practical method of measuring hydrodynamic and geochemical operation was established during this study. This was achieved by building a simple and cost-effective methodology to track current and tide velocities and by mapping and explaining the distribution and pattern of trace metal pollution and sediments within this bay system.

As a result, hydrodynamic conditions including currents and tides in the study area, were measured by drogues (Fig. 2). The drogues were modified from a previous design to permit deployment in water. These were constructed in the workshop at the University of Wollongong. The height of each drogue was 70 cm, and each one consisted of a buoy (ball) with waterproof enclosure to hold a small GPS and a flashing light. A software program was used to plot the movement directions of the drogues, and data from each site measured was uploaded onto Google earth maps and kmz files. Data from the GPS was smoothed to filter out GPS variations and to gain an estimate of average velocities over the drogue track.



Fig. 2 Modified design of the drogue to measure tides and currents.

4. Results and discussion

4.1 Hydrodanmic measuments and spatial distribution of sediment particles and trace elements

Estuaries are typically regarded as mixed systems controlled by the combined influences of tides and catchment flows. Nonetheless, many aspects of their dynamics are influenced by wind forcing. Because wind is inherently variable, determining conventions that apply commonly is a challenge for estuarine physicists (O'Callaghan and Stevens, 2011). Overall, the wind direction trends west or east-northeast at 9 am, changing to west or north-northeast with increased wind speed at 3pm (Fig. 3). Generally, in the summer period, when current tracks were measured, the wind directions were trending west southwest or northeast.



Three drogues were deployed in Gunnamatta Bay; the first and second drogues were at the head of the bay. Number three was in the middle of the bay. As observed in Fig. 4 a, velocities 1, 2 and 3 have peaks in velocity; this is because of the effects of boats moving past during measurement. The fast movement of these drogues may be attributed to the narrow channel at the mouth of Gunnamatta Bay that causes the tidal currents to become more concentrated. Furthermore, drogue number three moved fasterthan the other two since it was influenced by a greater tidal volume (Fig. 4 b,c and d). The current track velocities in deeper sites had higher speeds, which had a narrow channel at the mouth of the bay, hence current velocities were faster. The currents showed complex circulations, and wind driven currents cause subsequent return flows to be concentrated around the bay margins. The fine sediment particles and trace metals transported by current and tidal activity and are then gradually precipitate at deeper sites in the inner bay during low flow conditions.

Another important factor is wind speed and direction, which can affect the distribution of sediments and trace metals. Winds coming into the bay can deflect tidal current paths and produce set-up, resulting in return flows which in shallow bays trend along the bay margins. Waves in shallow bays also produce circulation which trend towards the bay margins. The main discharge points carry materials from catchment areas that are pushed into the bays. The sediment pathway into the bay is in the form of a jet since water velocity decreases gradually when entering the bay, causing deposition of coarse materials close to discharge points and then fine particles farther into the bay. Moreover, local waves are also active in the shallow waters close to the discharge points, leading to re-suspension and transport of fine particles into deeper sites, where the current and waves are less active and cannot disturb the bottom sediments. This hydrodynamic method using drogues can be applied in developed countries but is very applicable in remote locations or low-cost technology countries.



Fig.4 (a, b, c and d) Current track velocities for three drogues in Gunnamatta Bay.

As can be seen in Fig. 5, sediment grain size and water depth varied within the bay. Fig. 5a shows that the highest percentages of sand were in shallow water (<1.0 m; Fig. 5b) near the shoreline and over the sand barrier at the mouth of the bay. These areas had high tidal and current activity, which disturbs and transports the fine and very fine particles into deeper areas. The mud (silt and clay) percentages were concentrated within the inner

bay (Fig. 5c) where water depths were higher (5.8-12 m; Fig. 5b) and the waves had less effect on bottom sediments. Therefore, the fine and very fine particles can gradually settle within the inner bay (Alyazichi et al., 2014).



Fig. 5 (a) Sand percentages, (b) water depth (m), and (c) muddy percentages in Gunnamatta Bay.

As shown in Table 1, trace element concentrations were compared with the deleterious biological effect values in marine sediments. Effects were measured based on guidelines suggested by the U.S. National Oceanic and Atmospheric Administration (Long et al., 1995; Connor et al., 1998; Ligero et al., 2002; Word and O'Connor, 2005) and ranged from effect range low (ERL) to effect range median (ERM).

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

Trace elements (ppm)	Cr	Ni	Cu	Zn	As	Pb
Range	4-107	0.4-20	3-398	6-413	1-12	2-203
ERL	81 <mark>(4)</mark>	20.9 <mark>(-)</mark>	34 (23)	150 <mark>(8)</mark>	8.2 <mark>(9)</mark>	46.7 <mark>(16)</mark>
ERM	270 (-)	51.6 <mark>(-)</mark>	270 <mark>(1)</mark>	410 <mark>(1)</mark>	70 <mark>(-)</mark>	218 <mark>(-)</mark>

Values enclosed in parentheses are the number of samples exceeding ERL and ERM.

Overall, the mean concentrations of trace elements were below the ERL and ERMvalues, except copper which was higher than ERL. Samples GU17, GU18, GU21, GU25, GU27, GU30, GU39, GU40, GU45 and GU55 located in the inner bay, exceeded the ERL for copper, zinc, arsenic and lead. In addition, in sample GU55 concentrations of trace elements such as copper and zinc exceeded the ERM, and lead reached the ERM value

(i.e. 398 ppm for copper, 413 ppm for zinc and 203ppm for lead). The wide variations in concentrations of trace elements within the bay were due to sources of pollution (discharge points and stormwater outlets), boatyards, and watercraft as well as sediment types (muddy particles and organic matter).

Prediction maps of chromium, nickel, copper, zinc, arsenic, lead, rubidium and bromine are shown in Fig. 6a-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, indicated by Rb, and organic matter, indicated by Br, that play important roles as a traps for trace elements (Mayer et al., 1981; Fernandes et al., 2011). These metals were also concentrated close to discharge points from the catchment area. In contrast the lowest levels of trace elements were found to be along the shoreline, as well as in the mouth of the bay, areas in areas containing abundant pure coarse sand (Alyazichi et al., 2014).







Fig. 6 Spatial distribution of trace metals in ppm in the bay. (a) Cr, (b) Ni, (c) Cu, (d) Zn, (e) As, (f) Pb, (g) Br and (h) Rb.

4.2 Potential ecological risk (RI)

The potential ecological risk index (RI) is the most popular method used in order to evaluate the hazards of the trace elements for both human and environmental ecosystems, which indicate the concentration of trace elements in biological toxicology, environmental chemistry and ecology (Table 1; Guo et al., 2010; Jiang et al., 2014; Yang et al., 2014)

On the one hand, the results of RI values indicate some sites in the Gunnamatta Bay have considerable to very high risk (exceeding and/or slightly less than 120 RI), This is because these sites are close to discharge points;

watercraft and boatyards as well as sediment types that are dominated by muddy particles. Moreover, the highest RI value at some sites (north-east) in Gunnamatta Bay exceeded 120 (RI about 288), which was caused from boatyards compared with other sites (Fig.7). On the other hand, low risk sites are also indicated in the Gunnamatta Bay, located around the edges and mouths of the bays (Fig.7), where the sediment fractions are dominated by coarse particles (sand and/ or coarse silt) and current and waves are more active in these sites, leading to transportation of fine particles and trace elements toward deeper areas.

4.3 Hierarchical Cluster Analysis

Trace element pollution, once released, enters into current and wave circulation and then settles in marine sediments in areas with anoxic environmental conditions. The statistical analysis in this study was conducted using hierarchical cluster analysis (HCA), that enabled the classification of the samples into three groups (Table 3 and Fig. 8).

The main variables that define the red group were the high percentages of mud, low content of sand and high trace element concentrations. As illustrated in the red group (Table 3), the rubidium level indicates a high percentage of clay, while bromine reflects the existence of common organic matter in this group, both of which act as traps for trace elements (Mayer et al., 1981; Fernandes et al., 2011). The green group contained lower concentrations of clay and organic matter than the red group. The blue group differed completely, with high percentages of sand, low percentages of mud and low concentrations of trace elements. Therefore, the red group was considered to be significantly contaminated, and the green group was considered to be moderately polluted. These samples were located in the middle and inner parts of the bay as well as close to discharge points. In contrast, the blue group represents areas with low or no pollution, and samples were located around the margins and at the mouth of the bay (Fig. 8).



Fig.7 Potential ecological risk index for Gunnamatta Bay.

Table 3 Mean and standard division for each variable o	of the three clusters
computed by HCA.	

Variables	Cluster	Cluster	Cluster
	А	В	С
Depth (m)			
Mean	9.7	6.9	3.6
SD.	2.9	2.6	2.7
Sand%			
Mean	23.2	55.9	91.1
SD.	13.6	11.7	8.9
Silt%			
Mean	66.0	37.2	7.7
SD.	11.7	9.4	7.6
Clay%			
Mean	10.8	6.9	1.2
SD.	2.9	2.5	1.1
Cr			
Mean	70.4	38.0	13.0
SD.	26.8	20.7	9.4
Ni			
Mean	13.9	6.4	3.2
SD.	2.9	2.4	1.8
Cu			
Mean	124.5	51.9	15.4
SD.	94.7	12.2	14.0
Zn			
Mean	196.5	80.5	25.5
SD.	81.5	27.2	23.2
As			
Mean	9.7	5.4	2.5
SD.	1.5	1.3	1.3
Br			
Mean	220.6	153.4	60.7
SD.	42	31.5	24.5
Rb			
Mean	34.9	13.7	8.7
SD.	6.9	5.5	3.6
Pb			
Mean	92.5	40.3	14.3
SD.	41.8	11.2	13.0



Fig.8 Sketch classifying all the variables in the bay.

The current track velocities recorded in Gunnamatta Bay had the capability to transport fine particles and trace element pollution within the bay. As a result, the hydrodynamic measurements were applied in the study area to provide useful information and to help explain the distribution of sedimentary particles and geochemical properties that could lead to knowledge transfer to other bay systems, including those in remote areas, especially in developing countries.

5. Conclusions

Geochemical analysis and track current velocities were applied in Gunnamatta Bay, Port Hacking. It is located in the southern part of Sydney, NSW, Australia. The spatial distribution of trace elements is controlled by discharge points from residential areas, boat moorings, boatyards and sediment fractions. Sediment samples located in the inner and middle of the bay, as well as in the vicinity of stormwater outlets, have a high concentration of trace elements, and they indicated as considerable to very high risk. However, fine sandy samples have the lowest levels of trace elements and low risk, which are located along the shoreline and mouth of the bay. Furthermore, GU55 surface sediment sample exceeded the very high risk, and also effect range low and medium, because it is in the vicinity of boatyards and a major discharge point. Trace element pollution derived from anthropogenic activities including urbanisation, industrialisation and agriculture have rapidly increased over time since European settlement around this area.

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