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Risk Assessment of Trace Element Pollution in Gymea Bay, NSW, Australia

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Abstract**—**The main purpose of this study is to assess the sediment quality and potential ecological risk in marine sediments in Gymea Bay located in south Sydney, Australia. A total of 32 surface sediment samples were collected from the bay. Current track trajectories and velocities have also been measured in the bay. The resultant trace elements were compared with the adverse biological effect values Effect Range Low (ERL) and Effect Range Median (ERM) classifications. The results indicate that the average values of chromium, arsenic, copper, zinc, and lead in surface sediments all reveal low pollution levels and are below ERL and ERM values. The highest concentrations of trace elements were found close to discharge points and in the inner bay, and were linked with high percentages of clay minerals, pyrite and organic matter, which can play a significant role in trapping and accumulating these elements. The lowest concentrations of trace elements were found to be on the shoreline of the bay, which contained high percentages of sand fractions. It is postulated that the fine particles and trace elements are disturbed by currents and tides, then transported and deposited in deeper areas. The current track velocities recorded in Gymea Bay had the capability to transport fine particles and trace element pollution within the bay. As a result, hydrodynamic measurements were able to provide useful information and to help explain the distribution of sedimentary particles and geochemical properties. This may lead to knowledge transfer to other bay systems, including those in remote areas. These activities can be conducted at a low cost, and are therefore also transferrable to developing countries. The advent of portable instruments to measure trace elements in the field has also contributed to the development of these lower cost and easily applied methodologies available for use in remote locations and low-cost economies.

Keywords**—**Current track velocities, Gymea Bay, surface sediments, trace elements.

I. Introduction

Marine sediment contamination caused by trace elements in estuaries and bays around coastal areas are considered an international environmental issue because of their toxicity, non-biodegradable and accumulative characteristics. Furthermore, they are not removed from aquatic ecosystems by self-purification [1], [2] and accumulate in sediments and in fine suspended particles. Trace element pollution enters the marine environment from discharge points; source runoff and human activities related to industry, agriculture, urban development, and other activities. These activities result in waste containing element residues. Consequent increased levels of pollution in sediment sinks can have harmful and toxic effects on the marine ecosystem [3], [4]. Trace elements are dispersed in aquatic habitats and are then deposited in aqueous environments, combining with sediments through mechanisms such as absorption and ion exchange. Muddy particles are considered to be the ultimate sinks for most accumulated chemical pollution, such as 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 [5]-[7]. Trace elements can also be released again into the water column as free ions and/or complex compounds from sediments due to such as physical disturbance and chemical and digenetic factors [8], [9]. Although complex and highly technical methodologies have been established in developed countries to assess the spatial distribution of sediment particles and chemical pollution in bays and estuaries [10], [11], these methods have not really addressed the need to provide methodologies applicable to either remote areas or low-cost technologies, especially in countries with less developed economies or remote locations.

Complex and costly methods are appropriate where studies are being completed by organisations 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 [12], [13]. The main objectives of this paper are to investigate the spatial distribution of trace element concentrations in Gymea Bay sediments, to evaluate the influence of current and tide trajectory on these concentrations, and to assess the potential ecological risk of trace elements within these marine sediments by comparing them with deleterious biological effect values.

II. Material and Methods

A. Study Area

Gymea Bay, which is located 30 km south of Sydney Harbour, is one of several bays belonging to the Port Hacking estuary (Fig. 1). Overall, the inner area of the bay has deeper depths (>16 m), and it provides a significant environmental shelter and habitat for flora and fauna, and breeding and nursery habitats for several species, and is of economic and social value (e.g. tourism, business enterprises, fisheries and aquaculture) [14]. The main freshwater discharge points for the catchment areas are shown in Fig. 1, which shows catchment model segments for Yowie Bay and the adjacent Gymea Bay in yellow. These were determined by Sydney

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Water (the statutory authority responsible for water supply and management across Sydney) [15].

The catchment areas of Gymea Bay are urbanized with a population of approximately 40,000 in the local government area. The sources of contamination are mainly from the catchment areas (Fig. 1), and from recreational activities along the coastline, such as watercraft, boatyards and fishing, which can in turn affect the water quality of the bay [15], [16].

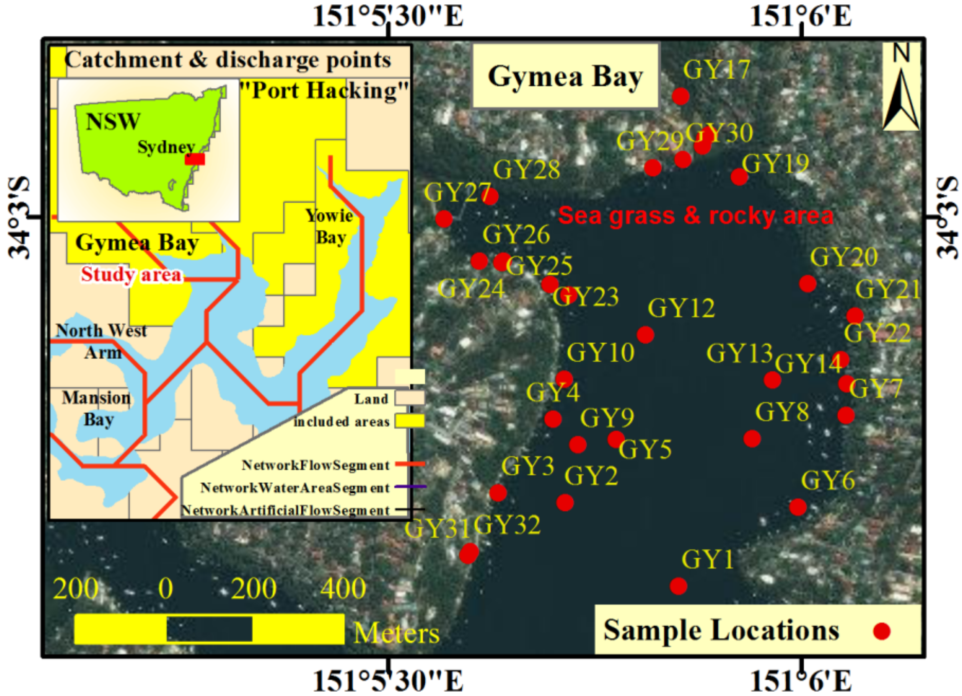


Fig. 1 Geographical locations map showing thirty-two surface sediment samples in Gymea Bay, Port Hacking, NSW, Australia

B. Sample Collection and Preparation

A total of 32 surface sediment samples were collected using a grab sampler during the summer of 2012 (Fig. 1). Only the surface 5 cm of sediment was reserved for analysis. Water depth and location were recorded at each site using sonar and a Geographical Position System (GPS). Sediment grain size measurements and percentages for sand and muddy particles were conducted using a Malvern Mastersizer 2000. Trace elements were measured using an XRF SPECTRO-analytical instrument (XEPOS) energy dispersive spectrometer fitted with a Si-docile detector; following an established standard procedure [17], [18]. ArcGIS desktop software, version 10.2, was applied to create maps for the study area by geostatistical analysis (Kriging method) [19]. 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 inter-active decision-making. Kriging assumes the data are derived from a stationary stochastic process, while some other methods assume normally distributed data [9].

C. Hydrodynamic Activities

Hydrodynamic parameters comprising current speed and direction in the study area were measured by drogues (Fig. 2). Three drogues were modified from a previous design to permit deployment in estuarine water. These were constructed in a workshop at the University of Wollongong. The height of each drogue was 70 cm, and each one consisted of a buoy (ball), with a waterproof enclosure to hold a small GPS and a flashing light. An associated GPS software program was used to plot the speed and trajectory of the drogues and the data was uploaded into Google earth and kmz files. Velocity data from the GPS was not differentially corrected and, therefore, has been smoothed to filter out GPS variations and to gain an estimate of average velocities over the drogue track.

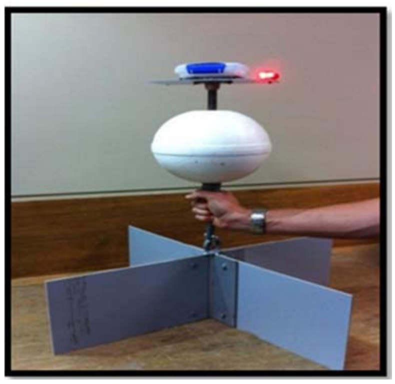


Fig. 2 Modified design of the drogue to measure tides and currents

D. Potential Ecological Risk Index

The potential ecological risk index (RI) was used to assess the effects of the trace element pollution in the study area. The RI was originally defined by [20], and was calculated using [21]:

$$CF^i = C_{sample} / C_{background} \quad (1)$$

$$E_r^i = T_r^i \times CF^i \quad (2)$$

$$RI = \sum_i^n E_r^i \quad (3)$$

where, C is the measured concentration of each trace element; $C_{background}$ concentrations of trace elements in core at 2.5m, which were obtained from [22]; CF^i is the 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 the evaluation criterion i.e. Cr=2, Ni=Cu= Pb= 5, Zn =1 and As=10 [20], [23]; and RI is the sum of all risk factors for trace elements in sediments.

According to [20], the following terminology is designed to be applied for the RI values in Table I.

TABLE I
INDICES AND POTENTIAL ECOLOGICAL RISK OF TRACE ELEMENTS POLLUTION

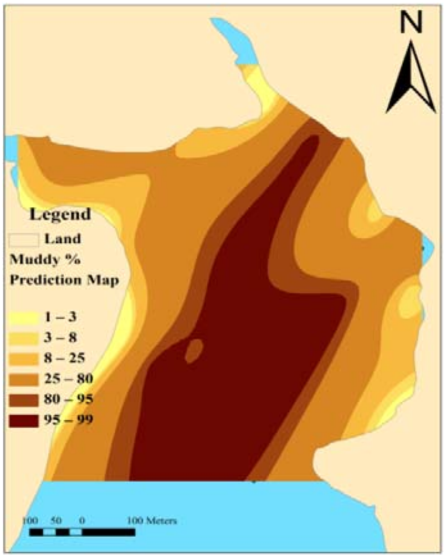
RI value	Potential ecological risk
RI< 30	Low risk
30 ≤RI< 60	Moderate risk
60 ≤RI< 120	Considerable risk
RI ≥ 120	Very high risk

III. RESULT AND DISCUSSION

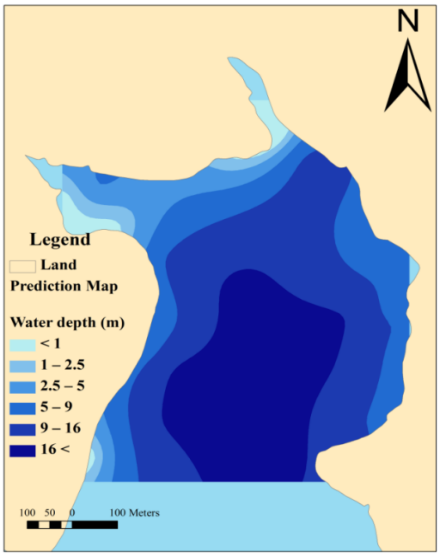
A. Spatial Distribution of Sediment Particles and Trace Elements

Fine sediments (muddy particles) and water depth varied within the bay. Fig. 3 (a) illustrates that the highest percentages of mud (silt and clay) were concentrated within the inner bay where water depths were greater (> 9m; Fig. 3 (b)) and the waves have less effect on bottom sediments. Therefore, the fine and very fine particles can gradually settle within the inner bay [24]. In contrast, the highest percentages of sand were found to be in the shallow water (< 2.0 m; Fig. 3 (b)) near the shoreline and the edges of the bay. These areas have high local wave activity, which disturbs and transports the fine and very fine particles into deeper areas.

Prediction maps of chromium, arsenic, copper, zinc, lead, rubidium and bromine are displayed in Figs. 4 (a)-(g). The spatial distribution of trace element concentrations generally exhibit similar patterns in the bay. The highest concentrations of these elements were found to be in the inner and middle parts of the bay, because these sites have the highest percentages of mud particles and organic matter, which are indicated by rubidium (Rb) and bromine (Br), Figs. 4 (f), (g), respectively. Muddy particles and organic matter can play important roles in absorbing and accumulating the trace elements. Furthermore, trace elements were concentrated around the harbors and marinas where boats are moored, with associated potential contaminant spills. The surface sample sites are close to areas that contain boatyards where boats are painted to prevent fouling. Consequently, these sites are considered to be a sink for trace elements [23], [25], [26]. However, the lowest concentrations of trace elements were found to be along the shoreline and at the edges of the bay, which are dominated by coarse sand percentages [24], and have the lowest percentages of organic matter Fig. 4 (g).



(a)



(b)

Fig. 3 (a) Muddy percentages and (b) Water depth (m) in Gymea Bay

B. Hydrodynamic Measurements

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 force. Because wind is inherently variable, determining conventions that apply commonly is a challenge for estuarine physicists [27].

Information on tides and winds were obtained from Manly Hydraulics Laboratory and the BOM (Bureau of Meteorology) and field efforts concentrated on the collection of velocity and track data for the ebb tidal currents. These ate plotted in Fig. 5.

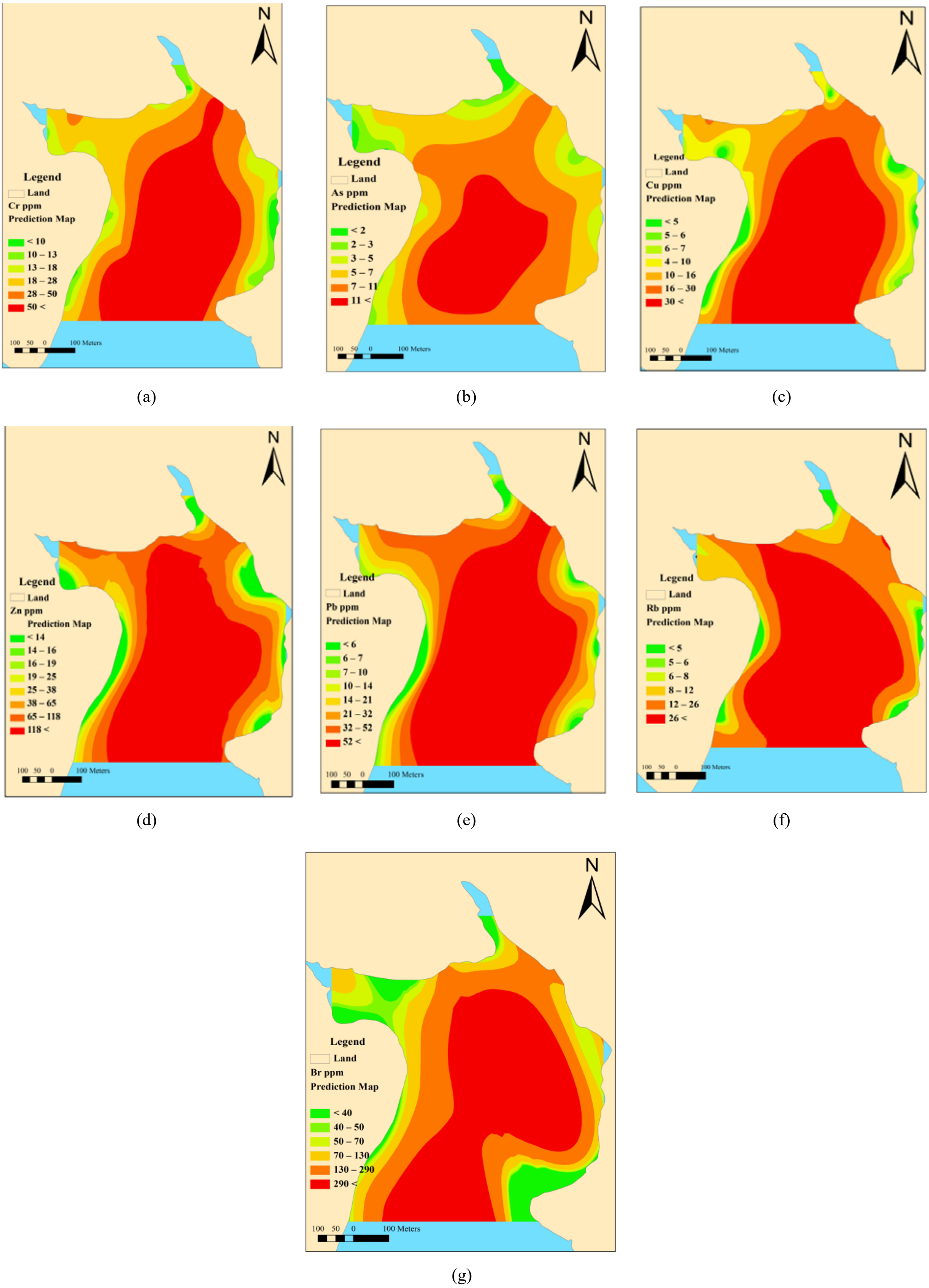


Fig. 4 Spatial distribution of (a) Cr, (b) As, (c) Cu, (d) Zn, (e) Pb, (f) Rb and (g) Br in surface sediments in Gymea Bay

Three drogues were deployed in Gymea Bay; the first and second drogues were at the head of the bay and the third was placed in the inner and middle bay. As observed able in Fig. 5, velocities 1, 2 and 3 have peaks in velocity; this is because of the effects of boats moving past during measurement.

The current tracks showed that drogues 1 and 2 had low velocities (less than 0.005m/sec) compared to 3, which had a faster velocity since it was influenced by a greater tidal volume. This is due to the upstream tidal storage at these locations. In addition, in the third current track, the velocity has the capability to transport fine particles and trace element pollution (Fig. 5 (d)). The currents showed complex circulations, and wind driven currents caused subsequent return flows to be concentrated around the bay margins. The fine sediment particles and trace elements transported by current and tidal activity then gradually precipitate at deeper sites in the middle bay during low flow conditions. In addition, local waves are also active in the shallow waters, 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 could be used in developed countries but is also applicable in remote locations and is cost-effective for developing countries.

Because of the low tidal current speed in the study area, this bay can be considered to be significantly affected by wind, with ebb current tracks being deflected towards the lee shores, depending on wind direction at the time. Thus, movement and subsequent setting of trace elements and suspended sediment particles from catchments will be a result of ebb tidal drainage and dominant wind directions during catchment events.

C. Risk Assessments

The trace element concentrations were compared with the deleterious biological effect values in marine sediments as shown in Table II. The effect range low (ERL) and effect range median (ERM) in estuarine and marine sediments were measured based on guidelines suggested by the U.S. National Oceanic and Atmospheric Administration [27]-[30]. The mean concentrations of trace elements in Gymea Bay sediments were less than both ERL and ERM, which shows no contamination for these elements. However, some sites in the bay exceeded the ERL (Table II), which are considered to be moderately to considerably contaminated, whereas these sites are below ERM. The source of contamination may be gasoline fumes from both car and boat exhausts. In addition, the potential ecological risk index (RI) is also calculated. It is considered the method most frequently used in biological toxicology, environmental chemistry and ecology to evaluate the toxicity of the trace elements for both human and environmental ecosystems, which indicates the concentration of trace elements (Table I) [31]-[33].

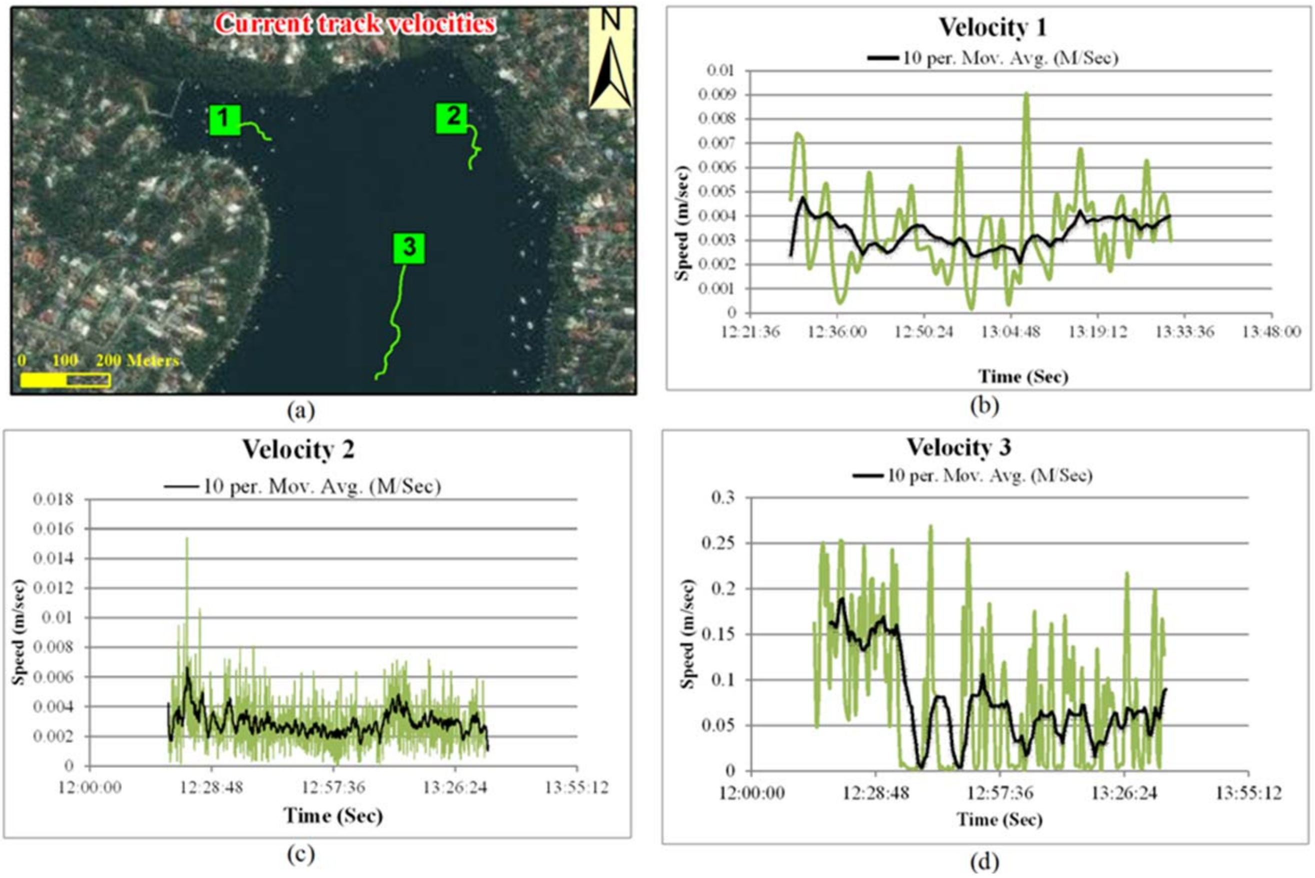


Fig. 5 Current track velocities for three drogues in Gymea Bay

TABLE II
COMPARISON BETWEEN CONCENTRATIONS OF TRACE ELEMENTS (PPM) FROM THE STUDY AREA AND EFFECT RANGE LOW (ERL) AND EFFECT RANGE MEDIAN (ERM) VALUES

Trace elements	Cr	As	Cu	Zn	Pb
Range	6-94	1-14	4-61	11-224	5-113
Mean	6	7	19	65	34
ERL	81 (4)	8.2 (7)	34 (6)	150 (7)	46.7 (8)
ERM	370 (-)	70(-)	270(-)	410 (-)	218 (-)

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

Generally, the results of RI values indicated that surface sediments in Gymea Bay have considerable to low risk (RI about 26). The highest RI value at some sites (inner) in Gymea Bay ranged between 70 and 85. This is because these sites are close to discharge points - watercraft and boatyards - as well as in sediment types which are dominated by muddy particles (Fig. 6). However, the lowest RI value sites are also indicated in Gymea Bay, located around its edges and northwestern areas, (Fig. 6), where the sediment fractions are dominated by coarse particles (sand and/ or silt) and currents and waves are more active, leading to transportation of fine particles and trace elements to deeper areas.

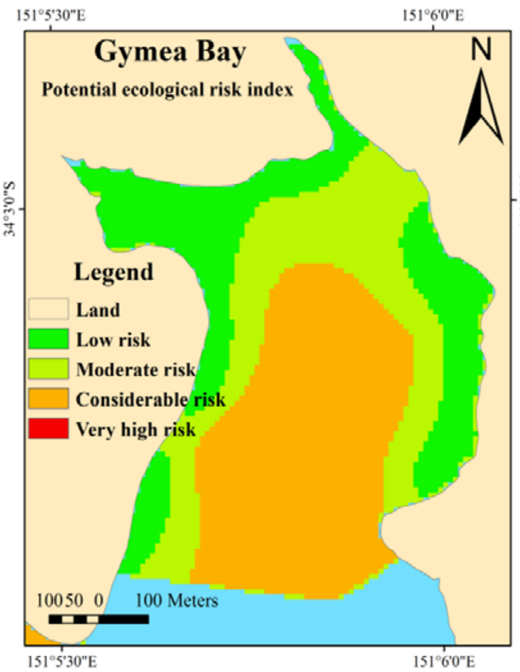


Fig. 6 Potential ecological risk assessment in Gymea Bay, NSW

IV. CONCLUSION

In order to evaluate the environmental status of marine sediments, the trace elements Cr, As, Cu, Zn and Pb, were analysed in surface marine sediments in Gymea Bay, NSW, Australia. Adverse biological effect values and potential ecological risk assessment were used to evaluate contamination of trace elements. Overall, the findings indicate that the bay had low contamination by trace elements. The highest concentrations of trace elements were found to be in the inner area of the bay, which displays levels with a considerable risk of contamination. This was because the sediments contained higher percentages of mud particles and organic matter. The lowest concentrations of trace elements were found to be at the edges of the bay, which had low risk of contamination, because these areas were dominated by high percentages of sand and low percentages of organic matter. In addition, waves and tides become more active in these sites, which can disturb and transport fine particles and trace elements, depositing them in the inner bay. The trace elements in Gymea Bay have accumulated over time from sources such as discharge points, fuel spillage, and exhaust fumes from vehicles and boats.

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