Assessment of environmental impacts of shipping on the marine coastal environment of New South Wales (NSW), Australia

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Declaration

I hereby declare that the work presented in this thesis has not been submitted for any other degree or professional qualification, and that it is the result of my own independent work.

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Date

Abstract

Australia is surrounded by a number of sea ports, many of which are in or near environmentally sensitive areas and engaged with extensive commercial and recreational activities. All these ports and shipping activities often release variety of pollutants (trace elements, nutrients and microplastics), demanding attention to understand their probable impacts on the surrounding ecosystems. In the present study a broad spectrum of contaminants, including trace elements and inorganic nutrients in water, sediment, oysters and seaweed, and microplastics in sediment and oysters of six sea ports, namely Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden of New South Wales (NSW), were investigated and compared with their background areas which were selected from the non-port areas of the same hydrogeological area.

Extensive review on trace elements and microplastics contamination in the sea port environment in Australia was carried out to identify the gaps which helped us to further design this study. Seawater samples at 30 stations from six ports in NSW, Australia were investigated to determine the Water Quality Index (WQI), Heavy metal Evaluation Index (HEI), Contamination Index (C_d) and newly developed Environmental Water Quality Index (EWQI). The study revealed medium water quality index, high and medium heavy metal evaluation index and high contamination index in almost all of the studied ports. Low level dissolved oxygen (DO) and higher dissolved solids, turbidity, faecal coliform, Cu, Fe, Pb, Zn, Mn, Cd and Co are mainly responsible for the poor water qualities of the port areas. Good water quality at the background samples indicated that port activities are the likely cause for poor water quality inside the port area. Likewise, sediment samples from the study ports were collected and analysed for trace element distribution. The study results revealed significant concentrations of As, Cu, Fe, Pb, Ni, Co and Zn in the surface sediments of the port areas which were much higher than the background values and the standards given by Australian and New Zealand Environment and Conservation Council (ANZECC/ARMCANZ, 2000) and other international guidelines including USA-ERM and CSQG-China. The maximum concentrations of Al, Bo, Co, Mo, Ba, Sn, Sr and Ti were also much higher than the background surface sediments, indicating enrichment of these metals at the study ports, although currently no guidelines exist for the concentration of these elements in sediments. However, geoaccumulation index (Igeo), enrichment factor (EF), pollution load index (PLI), potential ecological risk (PER) and sediment pollution index (SPI) also demonstrate

sedimentary metal pollution (Pb, Cu, Zn, Fe and Ni) in almost all the studied ports with significant pollution at Port Kembla and Port Eden.

Sydney rock oysters (*S. glomerata*) and seaweeds (*Ecklonia radiata*) from six major sea ports of NSW, Australia were further used as bioindicators to assess the distribution and concentrations of trace element accumulation in the sea ports. Substantial enrichment of Cu, Pb and Zn in the oysters at the sea ports were detected when compared to their background samples and the United States Environmental Protection Agency (USEPA) provisional tolerable intake standard. Enrichment of As, Al, Fe, Mn, Br, Sr were also found in the oysters at the port areas. The bioconcentration ratios (BCRs) of the trace elements illustrated significant Fe, Cu, Zn, As, Mn, Al, Pb and Cr accumulation in *S. glomerate*. The biota sediment accumulation factor (BSAFs) also suggested Cu, Mn and Zn accumulation at Port Yamba and Port Botany, indicating availability of these metals in the oysters as strong metal accumulators which is further supported by integrated metal contamination. However, significant levels of Zn, Fe, As, Al, Pb, B, Br, Si and Sn were also found in the seaweed of the studied ports most of which were higher compared to their background ecosystem. The BCRs results illustrated enrichment of Al, Fe, Mn, Zn, Pb, Cu, As and Ba in *E. radiata* whereas the BSAFs portrayed B enrichment in all sea ports along with bioaccumulation of As in Port Jackson and Pb in Port Botany.

Furthermore, the interrelationship of microplastics contamination in the sediments and oysters at the studied sea ports of NSW, Australia were investigated. The study results revealed a significant abundance of microplastic particles both in sediments and oysters of the sea ports with the higher abundance in oysters. The abundance of microplastics was 83–350 particles/kg dry weight in the sediments and 0.15–0.83 particles/g wet weight in the oyster at the studied seaports which were higher than their background areas in most ports, with exceptions to the background sediments of Port Botany, Port Kembla and Port Yamba and the background oyster of Port Kembla. Spherules, fibres and fragments were the three dominant categories of microplastics which were mostly white and transparent in colour and small in sizes (<1 mm) both in sediments and oysters. Fourier Transform Infrared Spectroscopy (FTIR) analysis results of the identified microplastics, in both sediments and oysters, demonstrated that polyethylene terephthalate (23% and 35% respectively) and nylon (20% and 29% respectively) were the two dominant polymer types of the study ports. The distribution, shapes and polymer types of the examined microplastics suggest that anthropogenic activities, industrial effluents, port activities and fishing inside and around the port areas were the likely major reasons for the microplastic pollution in the studied sea ports of Australia.

Overall, the obtained findings exposed uneven distribution of contaminants throughout the sea ports. Therefore, for effective management efforts, it is essential to adequately monitor the source, degree and impact of contaminants.

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Chapter 1: Introduction

1.1 Problem statement

Seaports play a significant role in global as well as Australia's economy by contributing to a large percentage of the global trade by volume and value (Shen et al., 2017, UNCTAD, 2015). Australia has a large number of seaports, which accommodate industry, commerce, tourism and recreation, resulting in aggravate marine and estuarine pollution from different port related activities (transport and storage of hazardous materials, industrial installation, recreational shipping etc.) (Bae et al., 2017, Birch, 2017, Bonanno and Orlando-Bonaca, 2018, Henriques et al., 2017). Trace elements, organochemicals, ballast water, garbage, ship paint, greenhouse gas emissions and microplastics are the major types of pollutants from different seaport activities, many of which are persistent and degrade slowly, therefore, accumulate in the port environment and eventually move into the food chain (Shen et al., 2017, Umo and Nitonye, 2015). Introduction of exotic species to the aquatic environment is another problem of intensive seaport activity (Onwuegbuchunam et al. 2017). All these pollutants are threatening the marine and estuarine ecosystems where they have substantial negative effects on faunal population as well as on commercial (fish, oyster) sectors (Bonanno and Martino, 2017, Jonathan et al., 2017, Kloff and Wicks, 2004, Pazi et al., 2017).

Recently, trace element pollution in marine and estuarine environment has become a critical issue and matter of global concern because of toxicity, numerous sources, persistence, slow degradation and accumulative behaviours (Alyazichi, 2015, Dural et al., 2007, Hu et al., 2011, Klavinš et al., 2000, Yuan et al., 2004). Trace elements in aquatic environments originate from both natural and anthropogenic sources and often reflect the ecological status of the environment. Natural sources of trace elements establish the background concentration, whereas anthropogenic activities, like shipping, industrial and urban activities, contribute to increased elemental concentration in marine and estuarine environment (Jiang et al., 2014). After entering the aquatic environment, trace elements tend to deposit in sedimentary environment through favouable physical, chemical and biological processes and eventually tend to accumulate in biota where they become detrimental to plants, animals and can pose serious threat to human health (Bonanno and Martino, 2017, Deboudt et al., 2004, Ikem and Egiebor, 2005, Islam et al., 2007, Jiang et al., 2014 , Roca et al., 2017, Stankovic and Jovic, 2012, Wang et al., 2013).

In the current decade, microplastics are another pollutant of concern for marine and estuarine environments. These may be produced from degradation of larger plastics by photo-degradation, mechanical action or biological processes. Primary microplastics, on the other hand, are generally in the industries for use in cosmetic products, pre-production pellets and synthetic fibres for clothes (Blumenröder, et al., 2017; Botterell et al., 2019; Carr et al., 2016; Napper et al., 2015; Napper and Thompson, 2016; Zhao et al., 2018). Increased demand and dependency on plastic products intensified annual plastic production and eventually plastic waste (Lots et al., 2017, Wang et al., 2019). After use, most of the plastic products are discarded and poorly managed as waste and transported to the marine environment via river, urban stormwater and wind, and retain and accumulate therein for years. In 2010, about 5-13 Mt of plastic wastes entered oceans either deliberately or accidentally (Jambeck et al., 2015, Kooi et al., 2017, Pan et al., 2019).

Microplastics are common near densely-populated areas, industrial and commercial areas and in different types of marine environments, such as beaches, estuaries, surface water and even in deep sea sediments (Besley et al., 2017, Leslie et al., 2013, Lots et al., 2017, Lusher et al., 2015, Van Cauwenberghe et al., 2015). However, the microplastics may be deposited in the sediment and can be ingested by marine biota such as small fish and zooplanktons (Blumenröder, et al., 2017, Kolandhasamy et al., 2018, Neves et al., 2015). Once ingested, the microplastics can be stored in the cells or tissues. Its hyper accumulation could have detrimental effect on the health of the aquatic organisms (Neves et al., 2015). Australian marine environment and neighboring Pacific islands are also significantly polluted with microplastics from urban storm water, river flow, floods, winds, shipping activities, recreational boating, fishing and offshore installations (Reisser et al., 2013, Rudduck et al., 2017, Ryan et al., 2009, Wilson and Verlis, 2017). Previous studies on marine plastics in Australia provide important baseline information for some selected areas (beaches, megafauna). However, data for the important marine and estuarine environment in Australia, for example, major sea ports, are limited (Caron et al., 2018, Reisser et al., 2013, Verlis et al., 2018, Verlis et al., 2013).

As a nation dependent on maritime trade, Australia's sea ports play an important role in the national economy by commodity exports and imports, tourism and fisheries and therefore, need proper attention for sustainable sea ports management. In the present study, background area was selected for each port to compare between the samples of the study sites and background sites. The background areas were selected from the non-port areas which were in the same hydrogeological area as the port but away from the influences of port activities.

1.2 Aims and objectives of the study

The present study aimed to investigate the distribution, loads and characteristics of broad spectrum of contaminants including trace elements and inorganic nutrients in water, sediment, oyster and seaweed, and microplastics in sediment and oyster at six seaports of New South Wales (NSW), Australia. This study also aimed to illustrate the impacts of seaport activities on the port environment compared with their background environment.

The specific aims of the study are

- To obtain a comprehensive dataset of sea ports' water quality by using different water quality evaluation indices, e.g., Water Quality Index (WQI), Heavy metal Pollution Index (HEI), Contamination Index (C_d) and Environmental Water Quality Index (EWQI).
- To assess the sediment quality and ecological state of the major sea ports by applying a wide range of environmental quality indices including the geoaccumulation index, pollution load index, enrichment factor, potential ecological risk index, sediment pollution index.
- To investigate the levels and patterns of trace elements concentrations in the sea port environments using oyster (*Saccostrea glomerata*) and seaweed *(Ecklonia radiata)* as bioindicators.
- To investigate the distribution, loads and characteristics of microplastic pollution (e.g., polymer type, color, size) in the sediments and oysters *(Saccostrea glomerata)* of the six major seaports along the NSW coastline of Australia.

1.3 Thesis outline

The thesis is organized as thesis by publication consisting of six chapters excluding the introduction, conclusion and recommendations chapters. The general discussion, objectives and thesis outlines are presented in **Chapter one**. In **Chapter two** trace elements contamination in marine and estuarine environment are thoroughly reviewed. Emphasis was given to the sources, distribution and level of trace elements in the marine and estuarine environment of Australia compared to other countries throughout the world. **Chapter three** represents experimental work on the impacts of seaport activities on the water quality of the surroundings environment. **Chapter four** chronicles the experimental evaluation of the sediments of the various seaport environments. In **Chapter five** Sydney rock oysters (*S. glomerata*) were used as a bioindicator to assess the distribution and levels of trace element accumulation in the seaports. The analysed results were then compared to their background samples and the United States Environmental Protection Agency (USEPA) provisional tolerable intake standards. In **Chapter six** seaweeds (*Ecklonia radiata*) from the sea ports of Australia were used as a bioindicator to assess the distribution and levels of trace element accumulation in the ports compared to the background ecosystem. Different accumulation indices and statistical analysis were used to identify trace element contamination in seaweeds. **Chapter seven** considered the microplastics contamination in the sediments and oysters from the seaports of Australia and compared to their background ecosystems. **Chapter eight** provides the conclusions and recommendations as indicated in the study outcomes.

1.4 List of publications

The following is a list of publications derived from this thesis.

Journal Articles

Jahan, S., Strezov, V., 2017. Water quality assessment of Australian ports using water quality evaluation indices. **PLOS One** 12, e0189284.

Jahan, S., Strezov, V., 2018. Comparison of pollution indices for the assessment of heavy metals in the sediments of seaports of NSW, Australia. **Marine Pollution Bulletin** 128, 295-306.

Jahan, S., Strezov, V., 2019. Assessment of trace elements pollution in the sea ports of New South Wales (NSW), Australia using oysters as bioindicators. **Scientific Reports** 9, 1416. https://doi.org/10.1038/s41598-018-38196-w

Jahan, S., Strezov, V., 2019. Assessment of trace elements pollution in sea ports of New South Wales (NSW), Australia using macrophytobenthic plant *Ecklonia radiata* as a bio-indicator. **Chemosphere** 218, 643-651.

Jahan, S., Strezov, V., Kan, T., Weldekidan, H., Kumar, R., Sarkodie, S.A., He, J., Dastjerdi, B., and Wilson, S. P. (2019). Interrelationship of microplastic pollution in sediments and oysters in a seaport environment of the eastern coast of Australia. **Science of the Total Environment** 695, 133924.

Jahan, S., Strezov, V., 2019. Impact of shipping on distribution of trace elements and petroleum hydrocarbons in the coastal basins of Australia: a review. **Marine and Freshwater Research** (Accepted).

Conference

Jahan, S., Strezov, V., 2018. Assessment of trace metal pollution in the water, sediments and biota in Port Jackson and Port Botany in Sydney. Environmental Institute of Australia and New Zealand Conference 2018, Sydney, Australia.

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Chapter 2: Impact of shipping on distribution of trace elements in the coastal basins of Australia: a review

Seaports play significant roles in the Australian economy. However, the intense marine traffic and various shipping activities carried out inside the ports or in their surrounding areas cause loading of various hazardous pollutants in the marine coastal bays. In this chapter, a review of trace elements contamination in the marine and estuarine environment of Australia are conducted. Emphasis was given to the impacts of seaport activities on the distribution and level of trace elements in the water, sediment and biota of the marine and estuarine environment of Australia and compared to other countries over the world.

Authors Contributions

Study Conception and Design: Vladimir Strezov and Sayka Jahan

Acquisition of Data: Vladimir Strezov and Sayka Jahan

Analysis and Interpretation of Data: Vladimir Strezov and Sayka Jahan

Drafting of Manuscript: Sayka Jahan

Critical Revisions: Vladimir Strezov

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Impact of shipping on distribution of trace elements in the coastal basins of Australia: a review

Abstract

This study surveys levels of trace elements in Australian seaport environments. Trace element toxicity in marine coastal environments is a growing threat to marine ecosystems as well as humans because of their dependency on the marine environment for food, economy and entertainment. Different activities contribute to discharges of trace elements into estuarine and marine environments. The elements of highest concern are As, Cu, Pb, Zn and Ni at Port Derwent with, Cd, Zn, Cu and Pb at Port Kembla as well as Zn and Cu at Port Botany Bay all exceeding the Australia and New Zealand Environment Conservation Council standards. Concentrations of some elements (Zn, Pb and Cu) in sediments at Port Kembla, Port Newcastle and the Derwent estuary are also higher than the Inter Sediment Quality Guidelines (ISQG). These findings provide baseline information on which to prioritise further research and formulate strategies to improve water quality in Australian port environments.

Keywords: Commercial shipping, pollutant distributions, harbour activities, Australian seaports.

2.1 Introduction

Trace metals are ubiquitous and major anthropogenic pollutants worldwide, in coastal and marine environments and mostly derive both diffuse and point sources (Brito et al. 2016). These elements are considered as potential threats to humans as well as ecosystems because of their toxicity, resistance and accumulative properties (Bonanno and Martino 2017, Li et al. 2016, Roca et al. 2017). A number of elements, such as Fe, Mn and Zn act as vital coenzymes in small amounts, however they become lethal to biota at high concentrations (Li et al. 2014). Other elements, namely Pb, Al and Cd are a concern even at low concentrations because of their high level of toxicity (Bonanno and Martino 2017, Rainbow 2007, Roctoa et al. 2017, Wang et al. 2013).

Generally, trace metals in marine waters have great potential to contaminate marine organisms, significantly affecting the ecosystems. Subsequently, these aquatic pollutants can be transferred and accumulated throughout the food chains (Bonanno and Orlando-Bonaca 2018). Trace metals can be deposited into marine environments in various ways, such as discharge from urban and industrial areas, dredging, aquaculture, mining activities, port operations, tourism and recreational boating (Bonanno and Orlando-Bonaca 2018).

Australian coastal and marine environments have been exposed to significant anthropogenic pressure for extensive period because of widespread industrialisation, development and mining activities which adversely impact the quality and sustainability of ecosystems along the coast and in estuaries (Birch and Rochford 2010). Significant metal and metalloid pollution from urban area, landfill, waste treatment plants, industries, leaded petrol and air pollution were also documented at Derwent estuary of Tasmania (Australia) (Gregory et al. 2013, Townsend and Seen 2012). Australia has an extensive system of seaports, varying from world-class resource export terminals to more traditional multi-cargo ports (Australian Ports 2014, Jahan and Strezov 2019). Although seaports make very significant contributions to the Australian economy, the intense shipping traffic and associated activities have negative influences on Australian coastal bays. In addition to commercial shipping, other diverse activities are carried out in ports or their surrounding areas which may cause further environmental effects; these include fishing, industrial concentration and handling of hazardous substances. Furthermore, the constant movements of many vessels in closed zones increases the occurrence of mishaps and accidental release of unsafe substances into the adjacent environments (Trozzi 2000). Past monitoring of trace elements suggests generally low pollutant concentrations in most of the coastal belt of Australia. Over the past decades, trace metal concentrations have increased in estuarine as well as marine ecosystems and are now a potential threat to aquatic organisms and humans through food chain accumulation (Sarma et al. 2011).

This study aims to review the sources and distributions of trace elements in selected Australian seaports (Fig. 2.1) throughout the 1960–2019 years of available data; the coordinates of the selected ports are shown in Table 2.1. The assessment is separated into three sections: levels of pollutants in (1) water (2) sediments and (3) biotas.

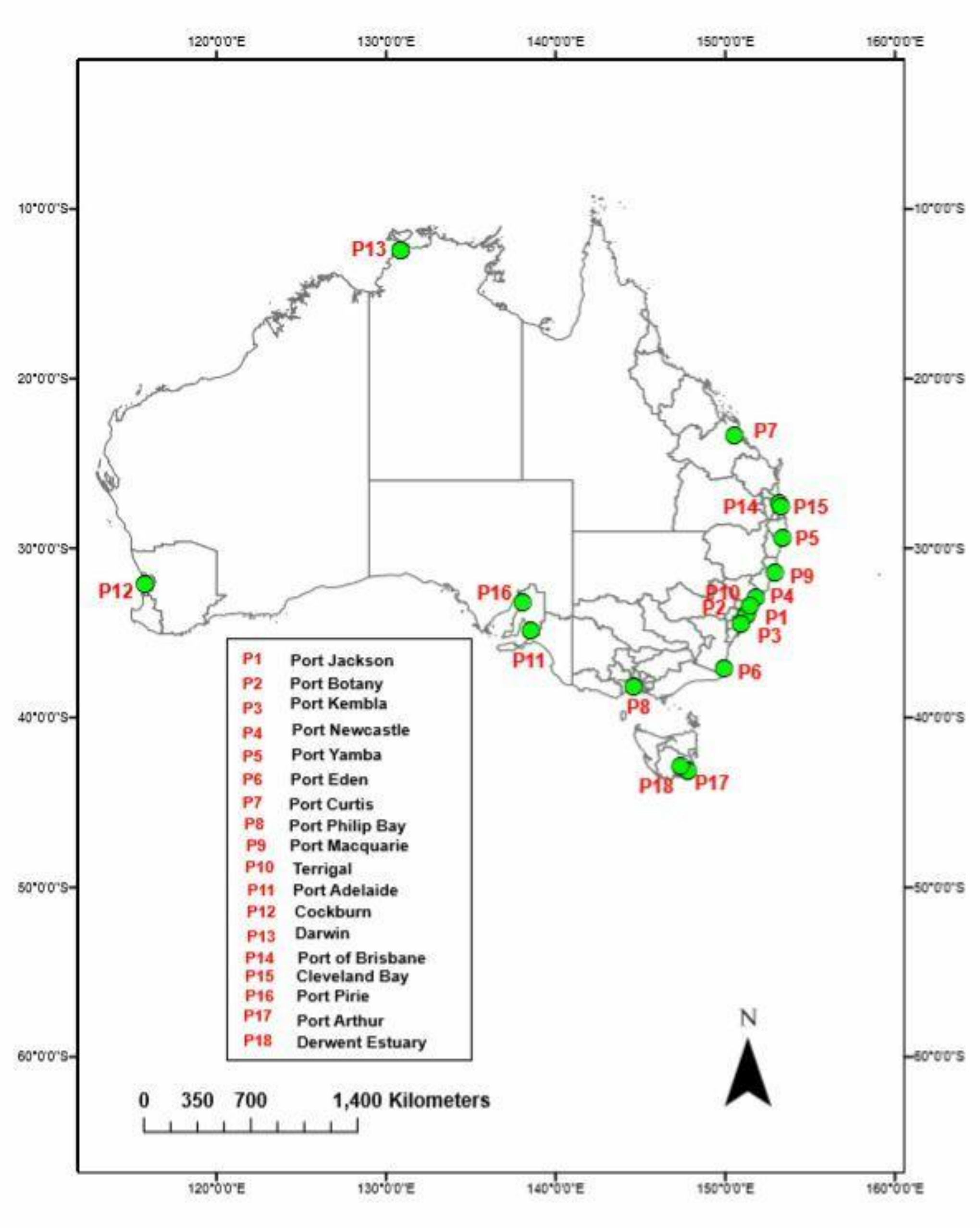

Fig. 2. 1 Map of Australia showing different study seaports

Table 2-1. Coordinates of studied Australian seaports

Location	Port Name	Latitude	Longitude
P1	Port Jackson	-33.861125	151.210578
P2	Port Botany	-33.965377	151.216999
P3	Port Kembla	-34.456653	150.883733
P4	Port Newcastle	-32.926636	151.782027
P5	Port Yamba	-29.435844	153.348809
P6	Port Eden	-37.071942	149.910301
P7	Port Curtis	-23.419685	150.5087948
P8	Port Philip Bay	-38.1430334	144.5793975
P9	Port Macquarie	-31.426633	152.893698
P10	Terrigal	-33.437895	151.43965
P11	Port Adelaide	-34.845177	138.498324
P12	Cockburn	-32.100816	115.760012
P13	Darwin	-12.414496	130.817515
P14	Port of Brisbane	-27.38358	153.161721
P15	Cleveland bay	-27.522496	153.263763
P16	Port Pirie	-33.172009	138.012477
P17	Port Arthur	-43.150614	147.768461
P18	Derwent Estuary	-42.884790	147.331624

In the present study, the environmental appraisal was conducted by comparing the revised levels of hazardous substances with the existing standard guidelines of the Australian and New Zealand Environment and Conservation Council (ANZECC/ARMCANZ 2000). The impacts on biotas were assessed based on the standards established by the Food and Agriculture Organization (FAO 2003) and provisional tolerable limit (PTI) values recommended by the United States Environmental Protection Agency (USEPA 2013), which rate the potential risk for human consumption of biota. The data presented in this review were derived from published peer-reviewed literature sources. The methods used to determine the contaminants, where available, the types of studied samples, types of data, timeframe of sampling and predictive modelling are compared in Table S2.1, Appendix A.

2.2 Water pollution

Water quality in the estuarine and marine environment of Australia has been degraded by various pollutants, such as trace elements, high nutrient loads, industrial and household chemicals, fecal bacteria and organic wastes over the years. The elements of most concern are Cu, Cd, Pb and Zn (Edgar 2001), whose concentrations often exceed the water quality guidelines of ANZECC/ARMCANZ (2000) and the Australian Food Standards Code NHMRC (1996).

In estuarine and marine environments, trace elements are released from different sources, such as industrial effluents, sewage discharges, mines as well as harbour activities and port operations; release of these substances can influence various biological processes and form potential cell mutagens and toxic compounds (Neff 1990, Stogiannidis and Laane 2015).

Sydney Harbour in Australia was once surrounded by industry, ship building and repair yards, as well as army and navy bases or facilities. Historically, it was significantly polluted by direct discharges from urban, recreational and industrial wastes (Hatje et al. 2001b, Revelante and Gilmartin 1978). The water quality of the Harbour has been improved with the adoption of the Clean Water Acts and Regulations of 1976, which prohibited the placing of materials into the harbour other than by licence. All types of industries, as well as military and other maritime facilities, have moved away from the foreshores, which has become a focus for visitors, tourists and leisure businesses. However, reports from the 1990s show that pollution persists in the Port Jackson estuary (P1) (Birch and Taylor 1999). Considerable study has been conducted to identify impacts of past and current man-made influences on the trace element levels in Port Jackson (P1). Most of these investigations have demonstrated the importance of periodic fluctuations in trace element dispersal in the port area, as summarised in Table 2.2, (Birch and Taylor 1999, Hatje et al. 2001a, Hatje et al. (2001b, 2003), Irvine and Birch 1998) .

The trace elements profiles show that Cd, Cu and Zn gradually increase with increasing salinity. The port then acts as a repository for minerals from rivers and wastewater (from domestic, commercial, industrial, and marine and communication services) that feed into the estuary. Concentrations of Ni and Mn are further influenced by tidal cycles and suspended particles, which are related to water circulation and re-deposition of bottom sediments (Hatje et al. 2003). As shown in Table 2.2, a recent study recorded lower amounts of Cd, Zn, Ni and Cu in Sydney Harbour (Lee et al. 2016). The decline in industrial activity and change to unleaded vehicle fuel are probable reasons for these reduced values. However, other pollutants persist because of excessive anthropogenic activities in and around the estuary (Birch et al. 2015).

Table 2-2. Salinity, suspended particulate matter (SPM) and dissolved trace metal concentrations in the Port Jackson estuary (P1)

Survey		Salinity	SPM(mg/l)	Ni (µg/l)	Cu (µg/l)	Zn (µg/l)	Cd (µg/l)	Mn (µg/l)	References
July 1999	Avg	28.4	5.9	0.87	1.35	Nd	0.03	39.2	Hatje et al. (2003)
n=8	Std.	5.2	3.8	0.41	0.28		0.02	41.9	
	Min	20.9	0.52	0.35	0.93		0.01	2.02	
	Max	34.2	10.7	1.45	1.77		0.05	101	
Aug 1999	Avg	30.8	4.4	0.90	1.45	Nd	0.06	22.6	Hatje et al. (2003)
n=8	Std.	3	2.8	0.47	0.32		0.03	23.1	
	Min	26	0.72	0.36	1.07		0.03	2.02	
	Max	34.4	8.5	1.61	1.85		0.10	58.9	
Sept 1999	Avg	31.7	5.1	0.91	1.73	Nd	0.07	15.9	Hatje et al. (2003)
n=8	Std.	2.9	3.7	0.41	0.23		0.03	18	
	Min	27	1.3	0.37	1.51		0.02	1.35	
	Max	34.9	11.5	1.38	2.07		0.10	48.3	
Jan 2001	Avg	33.9	7.5	0.80	1.98	6.47	0.04	8.14	Hatje et al. (2003)
n=12	Std.	1.2	4.2	0.41	0.48	1.99	0.01	8.57	
	Min	31.8	1.3	0.29	1.27	3.27	0.02	0.34	
	Max	35.1	13.1	1.41	2.55	9.66	0.06	22.0	
2003	Avg			0.86	1.68	6.47	0.04	20	Hatje et al. (2003)
n=8	Range			0.175–1.61	0.932–2.55	3.27–9.66	0.006–0.104	0.327–101	
2016	Avg			0.364	0.35	4.93	0.095		Lee et al. (2016)
UI									

n= no of samples, Nd= not detected UI= Unidentified

Port Botany (P2) is the only container seaport in NSW and the largest port for liquid and gas storage. The port is a major international maritime gateway and of strategic importance for economic growth and prosperity in NSW, serving 60% of Sydney's commercial shipping needs. Kinhill (1990) reported high amounts of Hg (2 μg/l) and Cu (11 μg/l) in Botany Bay, which exceeded the later established ANZECC/ARMCANZ (2000) guideline values (0.4 and 1.3 μg/l) respectively, which was further supported by Taylor (2003). The factors contributing to decreased water quality of the bay include the discharge of effluents from George and Cook Rivers, industrial operations, seaport activities (ballast, sewage and waste from ships, oil and chemical spills, spillage from dry bulk goods, washing operations) and airport operations (NSW EPA 2002).

Wollongong is another densely populated area which continues to be of interest for environmental research and monitoring because of Port Kembla (P3), the ninth largest port in Australia with extensive industries surrounding it. Since the 1970s, the water quality of this narrow coastal belt was poor because of the effluents and pollutants from urban activities along with heavy industries and port activities (steelworks, coal export terminal, copper smelter, fertilizer manufacturing plant). The concentration of certain metals e.g. Cd, Pb and Zn in the inner harbour was two to three times above the ANZECC (2000) guideline values, as shown in Table 2.3. The concentration of Cu in the inner harbour at that time was also higher than the guidelines (He and Morrison, 2001). However, with the introduction of pollution abatement programs from the 1970s to the 1990s, the levels of Zn, Fe and Cu have decreased, and the quality of the coastal environment improved, although the concentrations of these three pollutants were still above the ANZECC/ARMCANZ (2000) guidelines (He and Morrison, 2001). He and Morrison (2001) and Woods et al. (2007) confirmed notable improvements in the water quality at Port Kembla, which is the subject to regular monitoring.

Table 2-3. Concentrations (range, mean±std) of trace elements in the surface water of various ports of Australia.

Locations	Concentrations (µg/l)							References
Port Botany (P2)	**Cd**	**Pb**	**Zn**	**As**	**Ni**	**Cu**	**Fe**	
UI	<1	<5	<50	1.4	5-8	5-11		Taylor (2003)
Port Kembla (P3)	40	300	100			130	1210	Beavington (1975)a
n=2	50	1100	360			110	1960	b
n=2	13.3±4.8	13.8±4.0	6.3±1.9			6.5±1.7	40.4±29.6	Bowen (1979)
n=8 (1970s)	6.6±4.7	20.1±14.6	194.2±156.1			11.1±1.4	696±486	
(1990s)	4.6±1.3	8.6±1.9	51.8±29.8			7.8±4.2	228±198	He and Morrison (2001)
Port Curtis (P7) n=51	<1		0.17		0.34	0.51		Angel et al. (2010)
n=21	<1		0.31		0.54	0.72		Angel et al. (2012)
Port Philip Bay (P8) UI	<1	0.06 ± 0.02	0.25±1.05	2.8 ± 0.3	0.54±1.1	0.4±0.63	0.76 ± 0.44	Angel et al. (2010)
Derwent Estuary (P18) n=13		20	50	9		25		Farias et al. (2018)
ANZECC guidelines	2	5	50			5		ANZECC (1992)
ANZECC guidelines	0.7	2.2	7		7	0.3	-	ANZECC/ARMCANZ (2000)

a. Middle of harbour, b. Mouth of Allans Creek, n= No of Samples, UI= Unidentified, 99% protection level for standard value.

Port Curtis (P7), in Queensland, is one of Australia's foremost seaports, especially for coal exports. However, the largest aluminum refinery in the world, together with a cement kiln and aluminum smelters, as well as a large coal-fired power plant and other chemical plants are all located in the harbour area. The surrounding region is also associated with mining activities (Jones et al. 2005). A study by Jones et al. (2003) indicated that trace element concentrations in the Port Curtis (P7) estuary were low (see Table 2. 3), when compared to water quality guidelines (ANZECC/ARMCANZ, 2000). However, Cu and Zn concentrations in Port Curtis (P7) were consistently higher in 2012 than in 2010 (Angel et al. 2010, 2012) (Table 2.3). The major sources of trace element enrichment in Port Curtis have not been clearly defined as the port is linked with the ocean in several locations (Jones et al. 2005) .

Derwent Estuary (P18) in Tasmania is also known as Port Hobart. According to Coughanowr (1997) trace metal levels in Derwent Estuary (P18) are among the highest in Australia and mostly exceed national guidelines for Zn, Hg, Pb, Cd, Cu and As. Industrial activities associated with Zn and paper production as well as urban run-off were considered the probable main sources of metal contamination (Coughanowr, 1997). Over the past few decades, with the implementation of pollution reduction programs, metal emissions have decreased significantly. However, very high concentrations of Pb (20 µg/l), Zn (50 µg/l), As (9 µg/l) and Cu (25 µg/l), which are significantly above the ANZECC (2000) guidelines, were reported recently by Farias et al. (2018) - indicating persistent pollution in this estuary.

2.3 Sediment pollution

The pollutants in the coastal sediments of Australia have been extensively studied, especially in relation to the impact of sediment quality on biotic communities. Birch (1996, 1998, 2017), stated that trace element concentrations in Port Jackson (P1) sediments (see Table 2.4), are among the highest of all estuaries in Australia; they are only exceeded in four areas associated with smelters, large processing plants and discharges from mines.

Spooner et al. (2003) demonstrated significant spatial difference in the sedimentary Pb, As, Zn and Cu concentrations at Port Botany (P2) ($p < 0.0001$). Some surficial sediments were enriched in Zn, Cu, Pb and Cd. Birch (1996); Hayes et al. (1998); Irvine and Birch (1998) also identified the Cooks River and Georges River as major sources of Zn, Cu and Pb in Botany Bay. A recent study by Birch (2017a) illustrates sediments near Cooks River contained significant Zn (1832 µg/g), Pb (594 µg/g) and Cu (227 µg/g) concentrations. The Georges River inflow areas also contained high concentrations of Zn (401 µg/g), Pb (166 µg/g) and Cu (74 µg/g), while in Botany Bay the concentrations were Zn (295 µg/g), Pb (113 µg/g) and Cu (71 µg/g). The main sources of trace elements in this estuary originate from sewage overspill, direct fallout from berths and stormwater runoff. Stormwater is the dominant supplier of Pb received from dyes and transport emissions, whereas the sources of Zn and Cu could be from stable particles, electroplated metallic roofs, or Cu fittings (Birch 2017a). Batley et al. (1991) established links between sailing activities and Cu pollution in some areas of Botany Bay. Prior to establishing the State Pollution Control Committee (SPCC), manufacturing waste had been lawfully released into Botany Bay.

Bately and Low (1986) reported that sedimentary concentrations of Fe, Pb and Zn at Port Kembla (P3) were higher in concentrations than areas not affected by waste disposal of copper and steel industries surrounding the port (He and Morrison 2001). The large concentrations of Fe in the sediments at Port Kembla can be associated with the shipment and stockpiling of iron ore at the port. Dafforn et al. (2012) and Jafari (2009) studied the sedimentary trace metal distributions at Port Kembla and found high amounts of Pb, Cu and Cd. Table 2.4 shows that the sedimentary trace metal concentrations at Port Kembla are above the ISQG values of ANZECC guidelines with Cu (1737 µg/g) and Cd (11.7 µg/g) showing increasing trend. Another study by Birch (2017a) stated significant concentrations of Cu (about 69 µg/g), Pb (about 50 µg/g) and Zn (about 220 µg/g) in Lake Illawarra.

Newcastle is Australia's largest coal mining region, as well as having an important coal loading harbour, located at the mouth of the Hunter River. Birch et al. (1997) reported high contaminants concentrations in the Hunter River, which were also found by later studies in the same region (see Table 2.4). Birch and Taylor (2004) measured high Zn, Cu, Pb, Cr and Ni concentrations in Port Newcastle (P4). More recently, Birch (2017a) reported significant concentrations of Zn (387 µg/g), Pb (103 µg/g) and Cu (47 µg/g) in sediments of the Hunter River. The extensive industrial and commercial activities (e.g. iron, steel, petrochemical and pharmaceutical production) along with recreational and fishing activities, in and around the harbour, are considered the prime sources of pollutants in this area.

Table 2-4. Trace elements concentrations (range and mean) in the sediments (normalized <62.5μm) of the central New South Wales harbours.

Location	Cu (μg/g)	Pb (μg/g)	Zn (μg/g)	Cd (μg/g)	Cr (μg/g)	Co (μg/g)	Ni (μg/g)	Fe (%)	Mn (μg/g)	References
Port Jackson (P1)	9.3-1053	37.9-3604	108-7622	Bdl-24.3		2.2-54	5.0-245	0.5-10.6	26.6-578	Birch and Taylor (1999)
n=1700	188.1	364.4	651.2	0.8		8.3	21.7	3.2	118.4	
Port Jackson (P1) UI	188	364	651	0.8			21.8			Montoya (2015)
Port Jackson (P1) n=728-1178	133	210	486	1	77	5.3	15			Birch (2017)
Botany Bay (P2) n=119	17-457	29-924	76-2641	Bdl-12	17-185	7-28	13-122	<0.1-6.4		Birch et al. (1996b)
	70	155	393			16				
n=28	18-66									Dafforn et al. (2012)
n=43	71	113	295							Birch (2017a)
Hawkesbury River	17-203	19-174	68-272							Birch et al. (1998a)
(NSW) n=130-140	47	55	135							
n=252	36	55	136							Birch (2017a)
Hunter River (NSW) n=134	35-193	48-777	31-1638	Bdl-8	37-78	14-22	58-94	4.0-10	289-851	Birch et al. (1997)
n=120	47	103	387		21-167					Birch (2017a)
Port Newcastle (P4) UI	19-283	25-843	32-5161	Bdl-8		14-41	44-156			Birch and Taylor (2004)
Port Kembla Harbor (P3) UI	113	113	380	2						Bately and low (1985)
n=20-204		151	1209	4.5	203			7.3		He and Morrison (2001)
n=113	330	>150	357.5	1.22						Kachenko and Singh (2006)
n=95	324	114.5		11.7						Jafari (2009)
n=28	64–1,737									Dafforn et al. (2012)
n=120	69	50	220							Birch (2017a)
ANZECC ISQG (low-high) guidelines	65-270	50-220	200-410	1.5-10	80-370		21-52			ANZECC/ARMCANZ (2000)

Notes: n=No of Samples, UI=Unidentified, single value denotes mean, bdl- below detection limit.

Table 2.5 presents sedimentary trace element concentrations in the Australian ports and harbours (Fig 2.1). According to Jones et al. (2005) the sedimentary trace metal concentrations in Port Curtis (P7) are low, except for Cr and Ni which exceed the ISQG standard of ANZECC/ARMCANZ (2000) guidelines. The possible reason for their high concentrations is thought to be a natural source from underlying substrates. The maximum levels of Pb and Cd are also at the lower ISQG of ANZECC/ARMCANZ (2000) guidelines. However, a recent study by Angel et al. (2012) stated that the sedimentary concentrations of trace metals at Port Curtis are not elevated and are below ISQG standard of ANZECC/ARMCANZ (2000) guidelines (see Table 2.5).

Birch and Olmos (2008) conducted a study in Port Brisbane (P14) and found insignificant levels of Cu, Pb, Zn, Cd and Cr which are all below the low ISQG standard of ANZECC sediment quality guidelines (Table 2.5). Another study by Gracia et al. (2012), investigated the pollutants of the sedimentary environment at Port Brisbane measuring the total and organic carbon as well as nitrogen, ammonia and nitrate as major pollutants in the port environment. They determined that these pollutants mainly originated from urban stormwater.

Jones et al. (2003) and Townsend (2012) determined significant contamination, with Pb, Zn and Fe, in Derwent estuary sediments (P18). The main sources of pollution, since 1917, were identified to be paper mills and a zinc refinery, as well as stormwater from the urban areas. Previously, all contaminants (Cu, Fe, Zn, As, Cd, Pb, Hg and Se) were released directly into the Derwent estuary by direct industrial discharges. However, advanced water treatment technologies and other environmental precautions taken since 1981 have notably lowered the amount of chemicals released to the estuary (Coughanowr 1997). However, despite these efforts, recent investigations by Farias et al. (2018) indicate that the estuary continues to be polluted and is heavily contaminated by Cu, Pb and Zn (Table 2.5).

Some early studies on sedimentary trace element concentrations at other locations on the Australian coast are also presented in Table 2.5. Birch and Taylor (2004) revealed notable sedimentary Pb, Zn, and Cu contamination in Port Philip (P8). Identical investigations by Reichelt and Jones (1994) detected low Cu and Pb concentrations as well as high Zn concentration in Cleveland Bay (P15).

Table 2-5. Trace elements concentrations (range, mean) in the sediments (normalized<62.5µm) of Australian harbours other than central New South Wales.

Location	Cu (µg/g)	Pb (µg/g)	Zn (µg/g)	Cd (µg/g)	Cr (µg/g)	Co (µg/g)	Ni (µg/g)	Fe (%)	Mn (µg/g)	References
Corio Bay (Port Phillip) n=33	3-26	20-190	16-190	1-24	3-26		4-41			Fabris (1999)
Corio Bay (Port Phillip) UI	6-10	44-80	45-94	0.6-15	2-6		4-9			Birch and Taylor (2004)
Port Philip Bay (1994) (P8) n=36	5-860	5-350	8-1400							Birch and Taylor (2004)
Port Philip Bay (1996) (P8) n=36	1-62	2-197	13-830	<0.1-6	8-115		2-66	0.3-8.8		Birch and Taylor (2004)
Port Adelaide (P11) UI	11-293	10-329	30-403	<0.1-3.4		0.1-15				Birch and Taylor (2004)
Cockburn Sound (P12) n=79	6-20	5-43	3-56	<0.1-0.8	6-68		0.3-7	<0.1-1.1	2-47	Talbot and Chegwidden (1983)
Darwin Harbour (P13) UI	4-32	22-91	16-270	0.9-3						Birch and Taylor (2004)
Port of Brisbane (P14) n=83	30	57	157							Birch and Olmos (2008)
Cleveland Bay (P15) n=77	15-70	25-53	24-460							Reichelt and Jones (1994)
Spencer Gulf (Port Pirie) n=18	3-122	2-5270	11-16667	<1-267						Ward and Young (1981)
Port Pirie (P16) UI	Nd-170	Nd-5000	Nd-6000	Nd-150	Nd-40					Tiller (1989)
Port Curtis (P7) n=50	4-44	5-50	11-113	<0.10-0.24	13-85		4-33			Jones et al. (2005)
Port Curtis (P7) n=31	10	7	29	0.24	15		8			Angel et al. (2012)
Derwent Estuary (P18) n=35	262	1362	5526	41	78	41	23	46000		Jones et al. (2003)
n=6	101	408	1800					21100		Townsend and Seen (2012)
n=17	591	1880	14600							Farias et al. (2018)
ANZECC guidelines(Low-High)	65-270	50-220	200-410	1.5-10	80-370		21-52			ANZECC/ARMCANZ (2000)

Notes: n= No of Samples, UI= Unidentified, Single values are mean concentrations except.

2.4 Biotic pollution

Elevated levels of trace element bioaccumulation have been recorded in marine biota around the Australian coast (Fabris et al. 1994, Nicholson et al. 1991), with significant impacts on fish for example, lesions and eye damage (Gibbs et al. 1986).

Birch and Taylor (2002a, 2002b, 2002c) also investigated the toxicity of benthic animals in highly affected areas of Port Jackson (P1). A number of studies (McCready et al. 2005; Stark 1998; Twining et al. 2008) demonstrated that the diversity of benthic assemblages in Sydney Harbour (P1) has reduced significantly because of trace element contaminants. Recent investigations by Birch et al. (2014) stated that the levels of Pb, Cu and Zn in dried tissue of oysters from Sydney Harbour are 1419 µg/g, 8.9µg/g and 6518 µg/g respectively are all above the USEPA (2013) guidelines (Table 2.6).

Spooner et al. (2003) stated that in Port Botany (P2) the trace metals in biota, such as in oyster tissue, have high Zn, Cu and Cd concentrations. Others also indicated increased levels of trace metals in the oysters of Botany Bay (Brown and McPherson 1992; Mackey et al. 1975). Another study by Dafforn et al. (2012) also demonstrated very high Cu and Zn loadings in oysters from Port Botany tissues (Table 2.6).

Table 2-6. Trace elements concentrations in the biota of Australian harbours expressed in the range and mean values (µg/g).

Location	Biota	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Sydney Harbour (NSW) (P1)	Oyster n=76					1419				8.9	6518	Birch et al. (2014)
Botany Bay (NSW)	Oyster n=50	13	4.1			62	5.2			0.34	910	Spooner et al. (2003)
(P2)	Oyster n=21					60.14	36.88	3.43			282.86	Dafforn et al. (2012)
Port Pirie (SA) (P16)	Algae n=5	15-66.8 33.9	3.5-65.6 25.23	3-43.3 16.47	2.5-17.5 8.1	11.5-63.9 37.7	265-8712 3097	87.8-773 379.6	0.6-8.1 3.27	202-974 671.33	163-3162 1239.33	Chakraborty and Owens (2014)
Port Broughton (SA)	Algae n=9	22.3-23.3 22.8	0.08-0.21 0.145	1.5-1.8 1.65	1.5-2.3 1.9	2.6-3.3 2.95	162-175 168.5	32.7-41.8 37.25	0.3 0.3	2.5-3.5 23	15.5-15.9 15.7	Chakraborty and Owens (2014)
Glenelg Beach (SA)	Algae n=9	3.3-78.8 26.51	0.02-0.1 0.053	1.4-17.3 7.11	0.9-5.2 2.29	3.1-50.3 16.82	209-3634 1293.67	5.4-80.3 22.46	0.2-1.4 0.78	0.9-6.1 2.52	17.5-63 37.06	Chakraborty and Owens (2014)
Port Adelaide (SA) (P11)	Algae n=2	6.8-9.6 8.2	0.11-0.38 0.25	5.0-11.0 8	2.1-9.7 5.9	45.5-91.2 68.35	540-2756 1648	309-397 353	2.2-2.5 2.35	17.9-34.6 26.25	112-224 168	Chakraborty and Owens (2014)
Port Kembla (NSW) (P3)	Oyster n=26	1.80-2.98 2.47	0.20-0.53 0.35	Nd Nd	Nd Nd	37.15-65.16 49.56	Nd Nd	1.19-4.15 3.17	0.05-0.14 0.08	0.32-1.5 0.40	Nd Nd	Gall et al. (2012)
	Oyster n=240	34.1	0.9			10				4.5	130.3	Maher et al. (2016)
Port Curtis (QLD) (P7)	Oyster n=11	3.3-6.9	0.14-0.42		0.2-9.4	114-363	35-252		<0.2-9.3	<0.04-0.09	463-1400	Jones et al. (2005)
Reference conc. of Port Curtis	Oyster	11.2-15.7	0.14-0.26		<0.1-1.5	93-186	26-56		<0.2-0.9	<0.04-0.18	187-388	Jones et al. (2005)

Port Curtis (QLD) (P7)	Seagrass n=5	0.4-1.4	0.02-0.03		0.6-1.1	1.8-2.2	242-634		0.2-0.6	0.1-0.2	7-8	Jones et al. (2005)
Reference conc. of Port Curtis	Seagrass	0.2-0.3	0.01-0.02		0.4-0.7	0.3-0.5	103-162		0.2-0.3	0.07-0.12	2-3	Jones et al. (2005)
Derwent Estuary (P18)	Algae n=39	19				27				111	424	Farias et al. (2018)
Background Concentrations NSW	Oyster	1.88	0.54			21.6		2.53	0.13	0.085	277	Scanes and Roach (1999)
FAO			0.05							0.2		FAO (2003)
USEPA	PTI		0.025			0.05				0.025	0.3-1	USEPA (2013)

n= No of samples, UI= Unidentified, Nd= not detected. Single value denotes mean. PTI= provisional tolerable intake.

Jones et al. (2005) claimed the presence of high concentration of trace elements in biota (seagrass, oysters) at Port Curtis (P7). The Fe, As, Ni, Cr and Zn concentrations in oyster at Port Curtis were higher than their reference concentrations given by Jones et al. (2005) (Table 2.6). Moreover, the amount of Cu in the oysters at Port Curtis was 114-364 µg/g which is much higher than the reference concentrations 93-186 µg/g and the USEPA (2013) guideline concentration of Cu (0.05 µg/g) (Table 2.6). The very high amounts of Zn found in oysters (463-1400 µg/g) and seagrass (7-8 µg/g) at Port Curtis also exceed the reference concentrations (187-388 µg/g) for oysters and (2-3 µg/g) for seagrass given by Jones et al. (2005).

An attempt was also made to gain information on contaminants in fish tissue from the Port Kembla (P3). According to EPA (1994), an investigation of fish in April 1976 revealed notable amounts of cyanide and trace elements in fish. An investigation by Gall et al. (2012) explains that in Port Kembla the concentration of Cu (49.56 µg/g wet weight) and Pb (0.4 µg/g wet weight) in the tissue of oysters are above the background concentrations given by Scanes and Roach (1999); FAO (2003) and USEPA (2013) standards (see Table 2.6). Another study by Dafforn et al. (2012) reported that the concentration of Cu is between 64–1,737 and 76–956 µg/g in the sediments and oysters at Port Kembla. Maher et al. (2016) also stated that at Port Kembla the concentrations of As, Pb, Cu and Zn in oysters are considerably higher than the USEPA (2013) standard and the background concentration given by Scanes and Roach (1999) (Table 2.6).

Chakraborty and Owens (2014) studied the distribution of trace elements in biotic communities along the South Australian Coastline. According to this study the As concentration at Glenelg Beach is very high in brown algae and green algae shown in Table 2.6. At three sites around Port Pirie (P16) concentrations of Zn and Pb in seaweed are also higher (202-974 µg/g and 163-3162 µg/g) than USEPA (2013) guidelines (0.025 µg/g and 0.3-1 µg/g). In this study we used USEPA (2013) standard guidelines as there is no other guidelines for seaweed. Seaweed collected from Port Adelaide (P11) had accumulated 224 µg/g of Zn which exceeds the USEPA (2013) guidelines. The highest concentrations of Co, Cr and Cu in algae from Port Pirie (P16) are 43.3, 17.5, 63.9 µg/g while in Port Broughton and Port Adelaide (P11) concentrations of these trace elements range from 1.8-11 µg/g, 1.-9.7 and 2.6- 91.2 µg/g respectively (Table 2.6). Again, extremely elevated amounts of As, Pb, Zn and Cu have also been noted by Farias *et al.* (2018) in algae of the Derwent estuary (P18) (Table 2.6). In addition, concentrations of

Fe in algae from Port Pirie, Port Broughton, Port Adelaide and Glenelg are very high and range from 162-8700 µg/g; the maximum Mn accumulation (773 µg/g) was found in seaweed from Port Pirie.

2.5 Significance of metal concentrations

Tables 2.7 and 2.8 compare the levels of dissolved and sedimentary trace elements in marine coastal environment of Australia with other countries. In this review, most Australian studies have focused on marine pollution in coastal environments around the southeastern part of the continent.

The present studies have reported that levels of trace elements in various environmental components are improving, because of intensive environmental programs managed by government. Birch (1998) and the EPA (1994) explained that environmental quality in many marine coastal areas of Australia was improving, although constant losses of biotic communities and degraded water quality indicates that these environments are still extremely disturbed and requires continuous intensive monitoring strategies (Birch 1998). This review has also revealed that Pb, Cd, Cu, Zn and Ni are the major pollutants detected in the coastal aquatic environments of Australia.

Table 2-7. Comparison of surface water metal concentrations (range and mean) (µg/g) in Australian harbours and other countries around the world.

Location	Ni	Cu	Cd	Zn	Mn	References
Port Jackson, Australia (P1)	0.175–1.61	0.932–2.55	0.006–0.104	3.27–9.66	0.327–101	Hatje et al. (2003)
North Australian coast and Estuaries	0.116–0.552	0.151–1.04	0.002–0.034	0.018–0.498	Nd	Munksgaard and Parry (2001)
Torres Strait and Gulf of Papua	0.940–4.60	0.036–0.986	<0.001–0.029	Nd	Nd	Apte and Day (1998)
Open Coastal Pacific Ocean	0.200	0.090	0.010	0.200		Batley (1996)
New South Wales coast, Australia	0.180	0.031	0.002	0.022	Nd	Apte et al. (1998)
Port Phillip Bay, Australia	0.540–1.10	0.400-0.630	<0.005–0.070	0.250–1.05		Fabris and Monahan (1995)
Archelos estuary, Greece	2.76	0.31	Nd	2.05	5.2	Dassenakis et al. (1997)
Weser estuary, Germany	3.75	2.98	0.16	7.03	7.68	Turner et al. (1992)
Six estuaries, Texas, USA	Nd	0.100–3.20	Nd	0.300–18.0	Nd	Benoit et al. (1994)
Mexican Coast	0.17-0.32	0.015-0.044	0.052-0.093	0.13-0.17	Nd	Pérez-Moreno et al. (2016)
Port Manzanillo, Mexico	0.03	0.05	0.039	Nd	Nd	Bejarano-Ramirez et al. (2017)
Tweed estuary, UK	Nd	0.49–4.7	0.007–0.033	0.43–1.90	Nd	Laslett (1995)
Humber estuary, UK	Nd	0.75–3.6	0.049–0.22	3.6–15	Nd	Laslett (1995)
Humber estuary, UK	2.50–12.0	1.80–10.1	0.050–0.450	3.00–20.5	Nd	Comber et al. (1995)
Mersey estuary, UK	2.00–10.5	0.80–4.95	0.01–0.11	6.50–28.0	Nd	Comber et al. (1995)
Scheldt estuary, Netherlands	Nd	0.300–2.22	0.010–0.030	0.600–23.0	Nd	Zwolsman et al. (1997)
Black Sea Coast of Turkey	0.02-1.80	0.00-0.86	0.00-0.016	Nd	0.00-1.72	Akbal et al. (2011)
Tay estuary, Scotland	0.230–0.900	0.450–1.90	0.002–0.120	0.400–8.00	0.001–24.0	Owens and Balls (1997)
Coast of Bay of Bengal, Bangladesh	0.2-2	0.2-5	0.5-5	2-5	0.2-10	Kibria et al. (2016)
Bohai Sea, China	Nd	1.23-8.24	0.052-0.466	11.1-35.4	Nd	Pan et al. (2012)
Guidelines values[a]	70	1.3	5.5	15	Nd	ANZECC/ARMCANZ (2000)

Single value presents mean. Nd= not determined.

[a] Trigger values (ANZECC/ARMCANZ 2000) for marine water with a species protection level of 95%.

Table 2-8. Sydney Harbour and global normalized sedimentary (<62.5 µm) metal concentrations (µg/g).

Location	Cd	Cu	Ni	Pb	Zn	References
Sydney Harbour (P1)	0–24.3	9–1,053	5–245	38–3,604	108–7,622	Montoya (2015)
Port Kembla (P3)	5.6	1468	-	484	1209	He and Morrison (2001)
Hong Kong	0.1–5.3	1–4,000	5–220	9–260	17–790	Montoya (2015)
Quanzhou Bay, China	0.3–0.9	25–120	16–46	34–101	106–242	Montoya (2015)
Lima Estuary, Portugal	-	16-406	46-447	19-64	59-398	Montoya (2015)
Port of Barcelona, Spain	0.4-2.8	71-531	18-34	86-589	183-1133	Montoya (2015)
Izmir Bay, Turkey	0.02-0.36	-	-	44-73	-	Kucuksezgin et al. (2006)
San Pablo Bay, San Francisco, USA	0.1-0.4	25-49	27-45	15-27	48-79	Montoya (2015)
Port Manzanillo, Mexico	0.01-0.022	0.53-0.75	0.12-0.17	0.08	0.60-1.26	Bejarano-Ramirez (2017)
South-American Estuary, Argentina	0.428	17.96	8.46	7.12	41.98	Serra et al. (2017)
Montevideo Harbour, Uruguay	-	59-135	26-34	44-128	174-491	Montoya (2015)
Bahrain	19.14	48.3	-	99	52.2	Freije (2015)
UAE	-	-	1010	-	-	Naser (2010)
Coast of Bay of Bengal, Bangladesh	1.5-10	65-270	21-52	50-200	200-410	Kibria (2016)
Coast of India	-	30.23	52	-	125	Fernandes et al. (2017)
Bohai Bay, China	0.52	-	-	48.18	-	Xu et al. (2012); Gao et al. (2014)
ANZECC sediment quality guidelines Low	1.5	65	21	50	200	ANZECC/ARMCANZ (2000)
ANZECC sediment quality guidelines High	10	270	52	220	410	ANZECC/ARMCANZ (2000)

The major threats to the marine environment of Australia are interconnected and many key sources of threats lie in the extensive maritime activities and inland catchments. Therefore, integrated strategic planning for coastal management is of the utmost importance along with integrated catchment management which is equally important for the sea and land. Overall the key challenges to marine environments in Australia (such as water quality, ecosystem change, low fishing capacity, biodiversity loss and climate change) require long-term monitoring. In comparison with selected international estuaries reported in Table 7 and 8, Australian estuaries and ports have the maximal concentrations of Cd, Pb and Zn as well as the highest average concentration of Cu. Estuaries elsewhere, such as Hong Kong, has a maximum concentration of Cu (4000 µg/ g) and Lima, Portugal has a higher concentration of Ni (447 µg/g).

2.6 Conclusion

This study reviewed the historical concentrations of trace elements at major Australian ports. The following conclusions can be drawn from this survey:

- The reported contaminants peaked in the 1960s-1970s, when industrial activities flourished around marine and estuarine environment. The levels of contaminants were related to the industrial and recreational (boating, cruise ship) activities operating at each location as well as contributions from refuse materials and urban runoff.
- The introduction of different Environmental Acts during the 1980s and their adoption by industries has significantly reduced pollution levels of marine and estuarine environment.
- Although there is evidence of improvements, many recent studies have confirmed that pollution still persists in marine coastal environments.
- Contamination with trace elements, such as As, Cu, Mn, Pb, Ni, Cd, Zn and Co showed notable enrichment at most sites suggesting anthropogenic contribution.
- In port environments (Port Jackson (P1), Port Kembla (P3), Port Newcastle (P4) and Port Derwent (P18)) where pollutant distribution is now unlikely, closer monitoring is needed to assess the degree of contamination and its probable effects, to assist in formulation of suitable and efficient management initiatives.
- This review also compiles important baseline information for further monitoring of environmental impacts at Australian ports and the need for continuous improvement of their environmental performance.

2.7 References

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Chapter 3: Water quality assessment of Australian ports using water quality evaluation indices

The ecological sustainability and biological productivity of coastal and marine ecosystems largely depend on the coastal water quality. However, the coastal marine water quality is declining continuously due to the elevated concentration of various pollutants from different point and non-point sources. This chapter was designed to assess the impacts of seaport activities on the water quality of the port's environment. The study examines the extent of physicochemical and biological constituents present in the port water and compared with their background environment which was selected from the same hydrogeological area but far from industrial and port activities. A number of water quality indices of different international and national standards were applied to assess the surface water collected from the seaport environment.

Authors Contributions

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Water quality assessment of Australian ports using water quality evaluation indices

Abstract

Australian ports serve diverse and extensive activities, such as shipping, tourism and fisheries, which may all impact the quality of port water. In this work water quality monitoring at different ports using a range of water quality evaluation indices was applied to assess the port water quality. Seawater samples at 30 stations in the year 2016-2017 from six ports in New South Wales (NSW), Australia, namely Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden, were investigated to determine the physicochemical and biological variables that affect the port water quality. The large datasets obtained were designed to determine the Water Quality Index, Heavy Metal Evaluation Index, Contamination Index and newly developed Environmental Water Quality Index. The study revealed medium water quality index and high and medium heavy metal evaluation index at three of the study ports and high contamination index in almost all study ports. Low level dissolved oxygen and higher level of total dissolved solids (TDS), turbidity, fecal coliforms, Cu, Fe, Pb, Zn, Mn, Cd and Co are mainly responsible for the poor water qualities of the port areas. Good water quality at the background samples indicated that various port activities are the likely cause for poor water quality inside the port area.

Key words: Sea port, Water quality indices, Trace elements.

3.1 Introduction

Large number of seaports are situated along the coastal belt of Australia that are engaged with different commercial activities, such as transportation of passengers, livestock, coal, iron ore, steel and different business products (IMO, 2013, National Ports Strategy, 2011). Regardless of their size, the environmental impact of seaports largely depends on the type of commercial activities (Gomez et al., 2015). Seaports are very complex systems with a wide range of environmental particulars, including releases to water, air and soil, waste production, noise and dredging, amongst others (Darbrato et al., 2005). In port areas or in their vicinity, several activities, such as commercial fishing, industrial installations, storage of hazardous materials, may cause further environmental impacts. Deballasting of waters from ships has been shown to impact distribution of pollutants and pathogens with adverse health and environmental impacts (Darbrato et al., 2005). Finally, the continuous movement of ships in a confined area and the intense traffic increase the frequency of accidents often causing risk of release of hazardous materials in the port area (Trozzi and Vaccaro, 2000).

The ecological sustainability and biological productivity of coastal and marine ecosystems largely depend on the coastal water quality. The coastal regions are believed to have richer biodiversity than the open ocean regions (Gray, 1997). However, the coastal marine water quality is declining continuously due to the elevated concentration of various pollutants, among which total dissolved and suspended solids, nutrient and organic compounds (Shahidul and Tanaka, 2004) often cause turbidity (Orpin et al., 2004) and significant reduction in dissolved oxygen levels (Sanchez et al., 2007). The distribution of trace metal pollutants does not have direct impact on the optical properties of water; however, their presence influences the other properties of water, viz., pH, temperature, total dissolved solid and turbidity (Swain and Sahoo, 2017). Although some contaminants (trace metals, biological and nutrients) occur naturally in the environment, elevated pollutant concentrations in the coastal port areas are generally the consequence of effluent discharge from shipping activities, cargo handling, container loading and storage, and vehicle marshalling, urban storm water and agricultural and industrial run-off (Haynes and Johnson, 2000, Goonetilleke et al., 2009, Guerra-García and García-Gómez, 2005). There is an abundant volume of work that investigates concentration of pollutants in sediments around various ports in Australia. However, there is only limited work published on the pollutants present and dissolved in the water. Jonathan et al. (2011) suggest that water profile stores the pollution sequence in a more reliable way, and further states that beach water quality deteriorates more than the sediments (Jonathan et al., 2011). Although sea ports act as a major industrial activity and the central part of the land-sea interface in the coastal zone of Australia, relatively little attention has been given to these areas, where different shipping operations may have considerable impacts on the port environment (Bateman, 1996).

The aim of this study was to generate the most reliable and large data for water quality and trace metal concentrations of the water in Australian ports. The present study considered to use different water quality modeling which is a powerful tool for the comprehensive interpretation of complex water quality interactions (Ambrose et al., 2009). The study was designed to obtain Water Quality Index (WQI), Heavy Metal Evaluation Index (HEI), Contamination Index (C_d) and Environmental Water Quality

Index (EWQI) to present the large complex datasets in a more comprehensive and understandable approach. This study also considered the significance of tides on the distribution of pollutants and impacts of different port activities on the water environment. Moreover, in this study, analysis of variance (F-test) was used to determine the similarities or dissimilarities between sampling sites and correlation among the physicochemical parameters and trace metals were also analysed to determine the degree of dependency of the parameters.

3.2 Materials and methods

3.2.1 Study site

New South Wales (NSW), which is economically the most important state in Australia, has a number of sea ports, out of which Port Jackson, Port Botany, Port Newcastle, Port Kembla, Port Eden and Port Yamba are the largest commercial ports (Harris and O'Brien, 1998). The sampling localities in this study were all the six important ports of NSW, Australia which are engaged with different shipping activities. Port Jackson of Sydney Harbour is engaged with passenger shipping, recreational boating and water sports (Hatje et al., 2003) and is generally a well mixed estuary (Hatje et al., 2001b) because of low freshwater discharge and tidal turbulence (Revelante and Gilmartin, 1978). Port Botany, located in the mouth of George River, is now the site of Sydney's two major stevedoring and bulk liquid facilities. Container, crude oil and bulk liquid operations (fossil fuel, chemical and bio-fuel) are the major activities of Port Botany (Harris and O'Brien, 1998). Port Kembla Harbour is a major export location for coal mined in the southern and western regions of NSW with many facilities and berths including the grain terminal, bulk liquids, oil, various products berths (steel berth) and multi-purpose berths (fertiliser, pulp & steel products). Moreover, the port is important for importing iron ore, dolomite, limestone, sulphur, copper, phosphate rock and petroleum products and exporting iron and steel, coal, coke, tinplate and copper cables (Harris and O'Brien, 1998). The Port of Newcastle is the world's largest coal export port that also deals with raw materials for steelworks, fertiliser and aluminium industries, grain, steel products, mineral sands and woodchips (Harris and O'Brien, 1998) and is known as one of Australia's largest ports by throughput tonnage (Bateman, 1996). Port Yamba is Australia's eastern most sea port is the home of the 2nd largest fishing fleet of NSW and handles a range of imports and exports, such as container liquid berth-livestock and explosive products. The Port of Eden is a small seaport, located in the South

Coast region of NSW, it is one of the largest fishing fleets in NSW, Australia. Woodchip export is currently the major trade for the port, while the principal imports are break bulk and machinery and equipment, mainly for the oil and gas industry (Harris and O'Brien, 1998). The map of the study area and coordinates details of the sampling location points are listed in Fig 3.1 and Table 3.1.

Table 3-1. Sample site identification

Study area	**Site Id**	**Coordinates**	**Study area**	**Site Id**	**Coordinates**
Port	1 Bg	S 33.853570, E 151.208512	Port	1	S 32.925416, E 151.778577
Jackson	2	S 33.859807, E 151.209741	Newcastle	2	S 32.925539, E 151.782635
	3	S 33. 859842, E 151.212707		3	S 32.924978, E 151.786634
	4	S 33.857741, E 151.215940		4	S 32.923327, E 151.790202
	5	S 33.859411, E 151.221616		5 Bg	S 32.924313, E 151.793066
Port	1	S 33.954812, E 151.193165	Port	1Bg	S 29.431120, E 153.341446
Botany	2	S 33.957034, E 151.196641	Yamba	2	S 29.432980, E 153.342746
	3	S 33.958707, E 151.197874		3	S 29.433824, E 153.343594
	4	S 33.976960, E 151.226426		4	S 29.435538, E 153.345395
	5 Bg	S 33.979771, E 151.228915		5	S 29.434685, E 153.346981
Port	1 Bg	S 34.437268, E 150.902012	Port Eden	1	S 37.072537, E 149.909572
Kembla	2	S 34.445780, E 150.900463		2	S 37.072786, E 149.907408
	3	S 34.463832, E 150.896941		3	S 37.071524, E 149.907529
	4	S 34.464195, E 150.898728		4	S 37.071228, E 149.905944
	5	S 34.465885, E 150.900251		5 Bg	S 37.074487, E 149.910094

Bg=Background

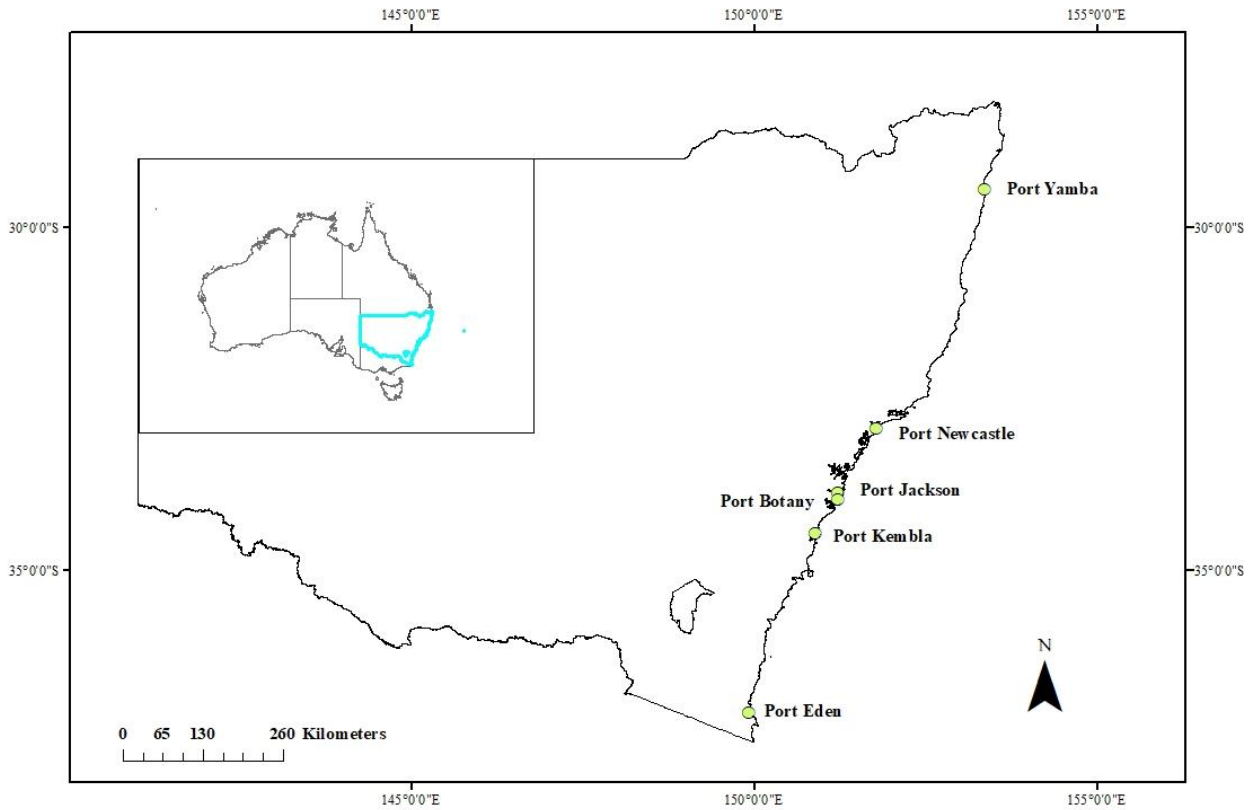

Fig. 3. 1 Map of the study area showing study ports.

3.2.2 Sampling procedure and analysis

The port water sampling was carried out during the period of December 2016 to March 2017. From each port, five water samples were collected from different points during the period of high and low tides, among which one was background sample collected from outside of the port area. The sampling positions were recorded by a GPS. Composite water sample was prepared from each point by mixing water from different depths (0-10 m depth), which was collected using Niskin water sampler. The Niskin water sampler was previously cleaned with deionised water and conditioned for at least 15 minutes at each depth of water collection.

Samples were collected in clean screw capped polypropylene bottles without any preservatives and preserved at 4^{o}C. On-site measurement of pH, dissolved oxygen (DO) and temperature were performed using EUTECH EcoScan pH6, EUTECH CyberScan DO 300 meters. The turbidity and conductivity were measured using HANNA HI 98703 turbidimeter and EUTECH CyberScan CON 400 conductivity meter. All instruments were calibrated prior to each sampling day. To reduce error five replicated measurements were taken for quality assurance purposes at each sampling site. Fecal coliform was analysed following the USEPA approved IDEXX Laboratories Colilert test kit procedure (Croteau et al., 1999). The National Association of Testing Authorities (NATA) and Australian accredited Envirolab Services analysed all the remaining inorganic, organic and standard water quality parameters (Envirolab, 2015). The samples were filtered in the laboratory before testing for the dissolved parameters in compliance to the approved methods. For trace metal analysis filtered samples were acidified with nitric acid to <2 pH (Rice et al. 2012), and then samples and blank were analysed for Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn, Hg, Be, V, B, Co, Mo, Sb, Ba, Bi and Sn using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS, Optima 2100 DV ICP System, Perkin Elmer). Quality control was performed in accordance with NATA guidelines for method validation (NATA, 2012) and measurement uncertainty (NATA, 2009) by analysing certified reference material AC-E with a composition of 14.75% Al_2O_3; 2.54% Fe_2O_3 and 0.06% MnO_2. The recoveries were 100.9% for Al, 93.1% for Mn and 98.2% for Fe.

3.2.3 Water quality assessment

Sample water quality was assessed, and quality indices were calculated as outlined below.

3.2.3.1 Water quality index (WQI) calculation

WQI expresses the overall water quality of a particular source at a certain time using a ‘single value’ based on selected water quality variables (Yogendra and Puttaiah, 2008). The WQI incorporates nine parameters including temperature, dissolved oxygen, pH, phosphate, nitrate, total dissolved solids, biological oxygen demand (BOD) and fecal coliform (Abbasi and Abbasi, 2012). The index is calculated from Q value and weight factor W, where Q indicates the level of water quality relative to any single parameter and the weight factor represents the relative importance of the single parameter to the overall water quality. The overall water quality ranking criteria falls under five categories which are very bad when WQI is < 25, bad when WQI is 26-50, moderate when WQI is 51-70, good when WQI is 71-90 and very good when in the range of 91-100 (Gupta et al., 2003, Nikoo et al., 2011).

$$WQI = \sum W_i Q_i = W_{Temperature} Q_{Temperature} + W_{DO} Q_{DO} + W_{pH} Q_{pH} + W_{Nitrate} Q_{Nitrate} + W_{Turbidity} Q_{Turbidity} + W_{TDS} Q_{TDS} + W_{Phosphate} Q_{Phosphate} + W_{BOD} Q_{BOD} + W_{Fecal\ Coliform} Q_{Fecal\ Coliform} \quad \text{.......(i)}$$

3.2.3.2 Contamination index (C_d)

The Contamination index (C_d) was calculated separately for each analysed sample of water, as a sum of the contamination factors of individual components exceeding the upper permissible value. The index relates the quality of water to human health risk and is calculated as:

$$C_d = \sum_{i=1}^{n} C_{fi} \quad \text{.......(ii)}$$

Where $C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1$; C_{fi}, C_{Ai} and C_{Ni} represents contamination factor, analytical value and upper permissible concentration of the i^{th} component respectively and *N* denotes normative value (Prasanna et al., 2012, Edet and Offiong, 2002) and hence C_{Ni} is taken as maximum allowable concentration (MAC).

The calculated values are grouped into low (C_d <1), medium (C_d =1-3) and high (C_d >3) contamination (Backman et al., 1998).

3.2.3.3 Heavy metal evaluation index (HEI)

HEI describes water quality condition in response to anthropogenic trace metals and is calculated by (Edet and Offiong, 2002):

$$HEI = \sum_{i=1}^{n} \frac{H_c}{H_{mac}} \quad \text{.......(iii)}$$

Where, H_c is monitored value and H_{mac} is maximum admissible concentration of the i^{th} parameter, n= number of parameters considered.

The HEI values are grouped into low contamination (HEI< 400), Medium concentration (HEI = 400-800) and high contamination (HEI > 800) (Edet and Offiong, 2002).

3.2.3.4 Environmental assessment

The environmental assessment was performed by comparing the measured concentrations of the trace elements with the available trigger values recommended by

ANZECC guidelines for marine water and with internationally published guidelines including USEPA and United Kingdom Department for Environment, Food and Rural Affairs. All the comparative standard guidelines (ANZECC/ARMCANZ, 2000, USEPA, 2009, DEFRA, 2014) are listed in Table S3.1 in Appendix B.

3.2.3.5 Environmental water quality index

The environmental water quality assessment index is a newly proposed index by (Ali et al., 2017) which is calculated by multiplying the concentration of each contaminant measured in the water samples with the corresponding hazard intensity to determine the water quality impact. The hazard intensity of each parameter was determined according to the total score assigned by the Toxicological Profiles of the Priority List of Hazardous Substances prepared by the Agency for Toxic Substances and Disease Registry (ATSDR), the Division of Toxicology and Environmental Medicine, Atlanta, USA (ATSDR, 2015). The total score of each trace element given by ATSDR was multiplied by its analysed concentration and products of all considered trace elements were added to calculate the trace element toxicity index (TETI). The environmental water quality index (EWQI) was calculated by dividing the water quality index (WQI) by the trace element toxicity index (TETI) (See Table S3.2 in Appendix B).

Environmental water quality index $\mathrm{EWQI} = \frac{\mathrm{wQI}}{\sum_{i=1}^{n} C_i * Ts_i}$..................................(iv)

Where, *WQI*= water quality index; TETI=$\sum_{i=1}^{n} C_i * Ts_i$; C_i = Concentration of individual trace element; TS_i = Total Score (Agency for Toxic Substances and Disease Registry) of individual trace element.

3.2.4 Statistical analysis

For statistical analysis Microsoft Excel, ArcGIS and SPSS 24 softwares were used. Analysis of variance was conducted to determine the effects of tides on pollutant distribution and the significant variations between study sites and background site. Correlation analysis was also performed to measure the realtionships among analyzed parameters. A number of single and multiple element indices and Australian New Zealand water quality guidelines were used to determine pollution and ecological state of the port water.

3.3 Results and discussion

The descriptive statistics of the eight physicochemical and one biological parameters of water quality with their observed standard deviations for each site were calculated as shown in Table 3.2 and used to assess the quality of port water.

3.3.1 pH

The pH values in five out of the six ports ranged from 7.6 to 8.3, which are within the standard values, except for Port Eden where the water pH ranged from 6.92 to 7.89 and was not affected significantly by the tides.

3.3.2 Dissolve Oxygen (DO)

The Dissolved Oxygen (DO %) values for most of the water samples were markedly lower during high tide, except for Port Eden where DO was significantly affected by the low tide. Most of the background samples had higher DO levels than the port water samples and, out of six ports; three ports (Port Jackson, Port Newcastle and Port Yamba) had standard levels of DO according to ANZECC, 2000 guidelines (ANZECC/ARMCANZ, 2000). The other three ports (Port Botany, Port Kembla and Port Eden) had DO levels lower than the standard guidelines. At Port Eden the DO was significantly low (36.1, 52.3, and 23.6) at three points inside the port area during low tide likely due to intensive commercial fishing activities and hydrocarbon contamination from imported petroleum products inside the main port (Pollard and Rankin, 2003).

3.3.3 Total Dissolved Solids (TDS) and Turbidity

Total Dissolved Solids (TDS) of the port water were significantly affected by the tide, showing higher values during low tide comparing to the high tide for the same site. The water in all ports, except for Port Kembla and Port Newcastle, had higher turbidity values than the background site water, which indicates impact of port activities on the water environment.

3.3.4 Biological Oxygen Demand (BOD_5)

Almost all ports had standard BOD_5 levels, except for Port Botany and Port Eden. The three major sampling points at Port Eden had very high BOD_5 levels. According to Pollard and Rankin (2003) Port Botany and Port Eden are moderately polluted by organic waste (Pollard and Rankin, 2003).

3.3.5 Fecal coliforms

The presence of fecal coliforms in the port area was detected during both high and low tides. Port Jackson, Port Botany, Port Kembla and Port Eden were positively affected by high tide, whereas low tide increased the fecal coliforms in the water at Port Newcastle and Port Yamba. Among all ports, the number of fecal coliforms was significantly higher in the water at Port Jackson, Port Yamba and Port Eden than the corresponding background samples, which indicates the impact of cruise ships, fishing fleet and recreational boating on the port environment.

The WQI for the port water quality during both high and low tides were reported as good, except for Port Botany and Port Eden (Table 3.2). The WQI analysis revealed that Port Botany and Port Eden were the two most affected sites of seaports investigated in this study. Out of nine parameters considered for this study, DO (%) and fecal coliforms have high weight value exhibiting the maximum influence in WQI calculations (Table 3.2). Port Botany and Port Eden experienced lower DO and higher fecal coliform concentrations, thus signifying the moderate port water quality

Table 3-2. Water quality index parameters.

Parameter			**pH**	**DO %**	**TDS mg/l**	**Turbidity NTU**	**Temp °C**	**Phosphate mg/l**	**Nitrate mg/l**	**BOD mg/l**	**FC /100ml**	**Conductivity ms**	**WQI**	**Water Quality**
Study Area	Tide	Weight Factor	0.11	0.17	0.07	0.08	0.1	0.1	0.1	0.11	0.16			
Port	H		7.75 ± 0.095	75 ± 8.72	43393 ± 953.66	0.505 ± 0.15	23.3	0.009 ±0.0012	0.035 ± 0.014	0.73 ± 0.25	212 ± 201	51 ± 1.65	75.78 ± 3.11	GGGG
Jackson	L		7.66 ± 0.064	81.4 ± 2.68	49325 ± 12604	0.63 ± 0.009	25.4	0.011 ± 0.0015	0.037 ± 0.012	0.57 ± .096	6 ± 5.55	49 ± 0.85	80.33 ± 7.2	GGGG
	B		7.70 ± 0.007	85 ± 7.07	45450 ± 6764.18	0.53 ± 0.25	24.4	0.013 ± 0.0028	0.034 ± 0.03	0.65 ± 0.070	3.1 ± 4.38	51 ± 0.64	81.1 ± 9.12	GG
Port	H		7.64 ± 0.78	67.18 ± 6.04	46120 ± 4093	2 ± 1.41	24	0.0084 ± 0.0024	0.072 ± 0.107	1.1 ± 0.25	410 ± 428.10	49 ± 0.45	73.21 ± 2.42	GGGG
Botany	L		7.65 ± 0.017	70.78 ± 1.56	45690 ± 5445	2 ± 0.59	26.1	0.0097 ± 0.002	0.066 ± 0.003	2 ± 0.95	287 ± 482.25	50 ± 0.43	76.24 ± 5.71	MGGG
	B		7.72 ± 0.035	70.50 ± 0.78	42965 ± 1477.85	0.27 ± 0.064	25	0.0048 ± 0	0.0315 ± 0.006	0.8 ± 0.28	502 ± 709.23	51 ± 0.28	68.91 ± 1.57	GG
Port	H		7.88 ± 0.25	75 ± 6.98	40720 ± 818.10	0.29 ± 0.105	22.8	0.010 ± 0.004	0.014 ± 0.014	1 ± 0.13	507 ± 375.72	52 ± 0.32	74.93 ± 2.89	GGGG
Kembla	L		7.9 ± 0.028	76.87 ± 5.27	41219 ± 363.87	0.19 ± 0.015	23	0.010 ± 0.004	0.010 ± 0.011	1 ± 0.44	35 ± 41.71	52 ± 0.20	80.20 ± 2.7	GGGG
	B		7.70 ± 0.25	76 ± 7.63	40600 ± 1357.65	0.44 ± 0.17	22.6	0.013 ± 0.002	0.0048 ± 0	0.48 ± 0.002	401 ± 176.09	52.3 ± 0.14	75.21 ± 1.14	GG
Port	H		7.8 ± 0.23	82.08 ± 5.02	40335 ± 1654.36	0.74 ± 0.15	24	0.006 ± 0.0005	0.004 ± 0.0006	0.9 ± 0	672 ± 397	52 ± 0.61	74.69 ± 0.38	GGGG
Newcastle	L		7.9 ± 0.02	83.45 ± 5.76	46703 ± 1352.7	0.55 ± 0.14	24.2	0.0065 ± 0.0015	0.0046 ± 0.0012	0.9 ± 0	1003 ± 0	52 ± 0.60	75.87 ± 1.84	GGGG
	B		8.11 ± 0.27	85.7 ± 6.08	42744 ± 3285	0.89 ± 0.24	24.2	0.0048 ± 0	0.005 ± .0002	1 ± 0.35	706 ± 420	52 ± 1.56	74.89 ± 3.01	GG
Port	H		7.7 ± 0.26	75.6 ± 3.40	85860 ± 2441	0.92 ± 0.29	22.4	0.006 ± 0.0009	0.0048 ± 0	0.9 ± 0	444 ± 511	53 ± 0	77.37 ± 4.65	GGGG
Yamba	L		7.7 ± 0.086	81 ± 3.86	74248 ± 24422	0.81 ± 0.41	22.3	0.0038 ± 0.005	0.0042 ± 0.0007	1 ± 0.31	1003 ± 0	53 ± 0	74.12 ± 0.72	GGGG
	B		8.3 ± 0.077	80.2 ± 3.4	87580 ± 17239	0.30 ± 0.042	22.4	0.005 ± 0.042	0.0049 ± 0	0.9 ± 0	25 ± 131.17	53 ± 0	81.52 ± 1.41	GG
Port Eden	H		7.72±0.36	87.8±4.32	67125±8822	0.1925±0.060	19.8	0.014±0.008	0.043±0.038	0.9±0	899.875±205.50	54.525±0.330	75.76±0.860	GGGG

L	7.40±0.36	57.67±22.90	53100±14651	3.68±3.70	20.2	1.554±2.518	0.013±0.0082	89±129.038	570.125±418.13	54.85±0.822	51.98±16.47	MMMG
B	7.60±0.36	88.5±0.424	50400±10323	0.70±0.29	20.1	0.278±0.226	0.058±0.0215	6.50±5.031	366.25±503.85	54.7±0.707	74.52±1.382	GG

H = High tide, L = Low tide, B = Background, G = Good, when WQI=71-90, M = Moderate, when WQI=51-70.

The impact of tides on the water quality parameters was tested with the statistical t-test, where $P > 0.05$ advocates no significant difference of the tidal conditions, as shown in Table 3.3. Although the t-test results presented no significant difference between the tidal conditions, some of the water quality parameters (DO, turbidity, fecal coliform) showed variations with tide, as presented in Table 3.2.

Table 3-3. Test of significance of tides on water quality parameters

Study Area	P -value	Pearson correlation
Port Jackson	0.174	0.9999
Port Botany	0.115	0.9999
Port Kembla	0.4839	0.9999
Port Newcastle	0.1537	0.9999
Port Yamba	0.1654	0.9999
Port Eden	0.16067	0.9999

Significant, if $P < 0.05$.

The concentration of trace metals in the port water and the background sites are given in Table 3.4. The concentration of Se, Hg, Be, Bi and Sn were all below the detection limits of the measuring equipment employed in the study. The mean concentrations of Ag, Al, As, Ni, V and B were all within the ANZECC and other international guidelines. The maximum concentration of Cu in all the studied ports water was much higher than ANZECC guidelines and exceeded other international guidelines with the highest concentration (0.04 mg/l) in Port Yamba. Moreover, the mean concentration of Cu also exceeded the ANZECC guidelines, except for Port Kembla and Port Newcastle. Very high concentrations of Fe were found in the port water of Botany, Port Newcastle, Port Yamba and Port Eden though the others also exceeded the UK, (2014) guidelines (DEFRA, 2014). All background samples, except for Port Jackson, also showed high concentrations of Fe. In the port water of Newcastle, Yamba and Eden the maximum concentration of Mn was higher than the background sample. The maximum concentration of Pb in the water of Port Botany (0.007) and Port Yamba (0.005) exceeded the ANZECC (0.0022) guidelines but was within the UK (0.025) and USEPA, 2009 (0.0081) guidelines (USEPA, 2013). In addition, all the background samples had much lower concentration of Pb compared to the port area. According to the ANZECC guidelines, the water in all the studied ports, except Port Kembla, contained very high concentrations of Zn, which exceeded the guidelines. However, if the EPA (0.081) and UK (0.041) guidelines are considered, the values were all within the standards. Furthermore, all the background samples have very low concentrations of Zn except the background sample of Port Jackson. Among all ports, only the water of Port Eden contained very high concentration of Cd and Co that exceeded the ANZECC guidelines but were absent in the background water.

The presence of excess concentration of dissolved Cu and Fe in Port Yamba water indicates the impacts of trade with livestock, explosive products and organic waste from recreational boating and fishing fleet. The intensive activities of fishing fleet break bulk and machinery and equipment from oil and gas refinery and preservative chemicals from the export of wood chips at Port Eden are likely contributors to high concentrations of Zn, Mn, Fe, Cd and Co in the port water (Gubelit et al., 2016).

Table 3-4. Trace metals concentrations in sample water.

Study Area	Port Jackson				Port Botany				Port Kembla				Port Newcastle				Port Yamba				Port Eden			
Analytes (mg/l)	Min	Max	Mean	Bg	Min	Max	Mean	Bg	Min	Max	Mean	Bg	Min	Max	Mean	Bg	Min	Max	Mean	Bg	Min	Max	Mean	Bg
Ag	Bd	Bd	Bd	Bd	Bd	0.001	0.001	Bd	Bd	0.004	0.003	0.003	Bd	Bd	Bd	Bd	Bd	0.001	0.001	Bd	Bd	0.001	Bd	Bd
Al	0.014	0.028	0.019	0.018	0.018	0.151	0.113	0.02	0.001	0.037	0.01	0.02	0.003	0.125	0.028	0.004	0.022	1.17	0.214	0.03	0.013	0.016	0.015	Bd
As	0.003	0.004	0.003	0.003	0.002	0.008	0.004	0.005	0.002	0.005	0.003	0.003	0.002	0.004	0.0033	0.003	0.002	0.005	0.0029	0.002	0.002	0.006	0.0032	0.0035
Cd	Bd	0.001	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	0.001	0.007	0.001	Bd
Cr	Bd	0.001	0.001	Bd	0.001	0.002	0.001	Bd	Bd	0.001	0.001	Bd	Bd	0.001	0.001	Bd	0.001	0.002	0.001	Bd	Bd	0.001	Bd	Bd
Cu	0.003	0.004	0.0035	0.003	0.001	0.009	0.003	0.0025	Bd	0.004	0.002	Bd	Bd	0.005	0.0021	Bd	Bd	0.04	0.009	Bd	Bd	Bd	Bd	Bd
Fe	0.022	0.077	0.042	0.005	0.015	0.531	0.1	0.018	0.008	0.036	0.017	0.012	0.008	0.191	0.0514	0.013	0.016	0.27	0.143	0.112	Bd	0.094	0.082	0.016
Mn	0.002	0.004	0.003	0.003	0.002	0.006	0.005	0.0025	0.001	0.009	0.003	0.0015	0.001	0.034	0.0087	0.001	0.009	0.044	0.015	0.01	0.001	0.051	0.01	0.0045
Ni	Bd	0.001	0.001	Bd	Bd	0.001	0.001	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	0.009	0.0016	0.001
Pb	0.001	0.002	0.001	0.001	0.001	0.007	0.002	0.001	Bd	0.001	0.001	Bd	Bd	0.001	0.001	Bd	Bd	0.005	0.0008	Bd	Bd	0.001	Bd	Bd
Se	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	0.002	0.002	Bd	0.001	0.005	0.0027	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd
Zn	0.009	0.038	0.015	0.023	0.004	0.025	0.012	0.0075	Bd	Bd	Bd	Bd	0.01	0.02	0.01	Bd	0.011	0.035	0.018	Bd	0.001	0.029	0.0075	0.002
Hg	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd
Be	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	0.001	Bd	Bd
V	0.003	0.007	0.004	0.004	0.004	0.01	0.006	0.005	0.003	0.004	0.004	0.003	0.004	0.005	0.004	0.004	0.003	0.008	0.0045	0.003	0.004	0.005	0.004	0.004
B	4.22	4.57	4.4	4.45	4.16	4.62	4.4	4.21	4.41	4.6	4.53	4.53	4.42	4.86	4.59	4.68	4.55	4.8	4.71	4.63	3.99	4.57	4.36	4.29
Co	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	0.001	0.001	Bd	Bd	0.002	Bd	Bd
Mo	0.008	0.01	0.0089	0.008	0.01	0.013	0.011	0.012	0.009	0.013	0.011	0.01	0.006	0.01	0.0083	0.009	0.008	0.01	0.0092	0.009	0.008	0.01	0.0084	0.008
Sb	Bd	0.001	0.001	0.001	Bd	0.001	0.001	Bd	Bd	0.001	0.001	0.001	Bd	0.001	0.001	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd
Ba	0.007	0.008	0.0075	0.008	0.008	0.015	0.011	0.008	0.006	0.008	0.007	0.006	0.009	0.013	0.0092	0.005	0.01	0.011	0.011	0.011	0.005	0.029	0.0093	0.007
Bi	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd
Sn	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	Bd	0.001	0.001	Bd	Bd	0.001	0.001	0.001	0.002	0.006	0.0032	0.0045	0.001	0.001	0.001	0.001

Bd- Below detection, Bg- Background. Detection limit : Ag, As, Cd, Cr, Cu, Mn, Ni, Pd, Zn, Sn, Bi, Sb, Co, Mo, V, Ba = <0.001; Al, Fe= <0.005; Se= <0.002; Hg=<0.0005;

The presence of excessive amount of Cu, Fe, Pb and Zn in Port Botany confirm the impacts of the port activities which are associated with trade of crude oil, fossil fuel, chemicals and bio-fuels. Moreover, the trade of coal, steel products, fertilisers, mineral sands and preservative chemicals from woodchips in Port Newcastle may be sources of excess amounts of Cu, Fe, Zn, Mn in the port water. Finally, effluent from shipping activities, storage of hazardous products in the port vicinity are often overlooked (Goonetilleke et al., 2009) while they may be also the sources of metals in the studied port areas.

The variation of trace metals between the different locations by means of ANOVA was also found insignificant at 5% level as $P > 0.05$, as shown in Table 3.5.

Table 3-5. Significance analysis in metal concentrations between background and port water

Study Area	F	Df	P
Port Jackson	0.00024	36	0.9877
Port Botany	0.00092	36	0.9758
Port Kembla	0.00001648	36	0.9967
Port Newcastle	0.00007617	36	0.993
Port Yamba	0.002448	36	0.9608
Port Eden	0.01649	36	0.8985

Significant, if $P < 0.05$.

Table 3.6 presents correlation between the water quality parameters and selected trace metals. Significant correlation at 5% significance ($P < .05$) was observed between TDS with Al, Cu and Zn. Strong positive correlations were also found between turbidity with As, Pb and V. Al showed strong positive correlation with Cu, Fe, Zn and Ba whereas V is positively correlated As, Mn.

Table 3-6. Correlation matrix between elements

	pH	TDS	Turbidity	Conductivity	Al	As	Cu	Fe	Mn	Pb	Zn	V	B	Mo	Sb	Ba
pH	1.000															
TDS	-0.345	1.000														
Turbidity	-0.713	0.086	1.000													
Conductivity	0.561	0.542	-0.561	1.000												
Al	-0.516	**0.890***	0.489	0.329	1.000											
As	-0.396	-0.363	**0.881***	-0.658	0.081	1.000										
Cu	-0.415	**0.994***	0.089	0.476	**0.871***	-0.376	1.000									
Fe	-0.585	0.850	0.588	0.189	**0.978***	0.179	**0.837***	1.000								
Mn	-0.008	0.880	0.079	0.691	0.827	-0.242	**0.827***	**0.799***	1.000							
Pb	-0.557	-0.360	**0.881***	-0.755	0.071	**0.962***	-0.348	0.154	-0.366	1.000						
Zn	-0.449	**0.949***	0.207	0.334	**0.849***	-0.250	**0.954***	**0.874***	**0.836***	-0.266	1.000					
V	-0.730	0.063	**0.973***	-0.535	0.482	**0.864***	0.069	0.543	0.009	**0.907***	0.124	1.000				
B	**0.7632***	-0.053	-0.251	0.490	-0.097	-0.072	-0.144	-0.074	0.403	-0.338	-0.028	-0.381	1.000			
Mo	-0.364	-0.252	0.356	-0.300	0.021	0.424	-0.230	-0.071	-0.434	0.594	-0.413	0.555	-0.649	1.000		
Sb	0.250	**-0.990***	-0.003	-0.641	**-0.869***	0.422	**-0.976***	**-0.801***	**-0.888***	0.421	**-0.898***	-0.257	0.018	0.215	1.000	
Ba	-0.495	0.603	0.775	0.044	**0.871***	0.498	0.567	**0.921***	0.690	0.414	0.657	0.713	0.098	-0.007	-0.552	1.000

"***** bold" denotes significant correlation values.

Moreover, Cu showed strong positive correlations with Fe, Mn and Zn. Furthermore, Fe is positively correlated with Zn and Mn and Pb is strongly correlated with V. Sb showed strong negative correlations with most of the trace metals while Mo did not significantly correlate with any parameter. From the above correlation analysis, it is found that, TDS and turbidity have significant positive correlations with many trace metals (Al, As, Cu, Pb, Zn, V and B).

Table 3.7 presents the results of the water quality indices based on trace metals used to assess the quality of the port water and to compare with different countries' standards and with the background water. According to ANZECC, USEPA and UK guidelines, the contamination index (C_d) was high almost for all ports, except for some points at Port Botany, Port Kembla and Port Newcastle. However, Table 3.7 shows that sampling point 2 of Port Botany had a low contamination index with respect to ANZECC trigger values standards but high contamination index according to the USEPA and UK standards. Similarly, sampling points 1, 2, 4 and 5 at Port Kembla and all sampling points at Port Newcastle showed variations in contamination index according to different country standards. The background sample of Port Kembla was low and medium contaminated according to UK and ANZECC standards, while the other points showed variations in contamination according to different standards shown in Table 3.7. The background area of Port Kembla exhibited lower contamination than the other sampling points. Almost all sampling points at Port Newcastle, including the background area, represented low and medium contamination according to ANZECC standards, whereas they depicted high contamination according to USEPA and UK standards, except for the background area that was medium contaminated during high tide. Port Yamba and Port Eden portrayed high contamination for all standard guidelines.

The heavy metal evaluation index (HEI) shows that all sampling points at all ports were determined to be of low pollution, except for points 3 at Port Botany and Port Yamba and point 1 at Port Eden, which were classified as medium and high-polluted areas during low tide, according to the UK standard (Table 3.7). These are the same areas, which were classified as highly polluted according to the C_d. The other points of Port Botany, Port Kembla, Port Yamba and Port Eden, classified as high and medium contaminated according to C_d, were calculated as lower level pollution according to HEI.

The results inform that the various indices do not consistently predict the impact of various port activities on the water environment. The indices are designed to consider different attributes in the water quality for water quality assessment. Even though the WQI considers wider impacts of pollution on the water quality, it neglects the toxicity of metals present in the water. Likewise, C_d and HEI do not consider the toxicological impacts of the nutrients, physicochemical and biological parameters. To overcome this problem a separate new index based on the elemental toxicological impact, termed as trace element toxicity index (TETI), is used in this work. Table 3.7 provides the individual toxicological estimates for tested elements based on their concentrations measured in each location and the relative toxicological weight. TETI indicates that B had the highest impact on the toxicological profiles of all studied areas followed by Al, Zn, Ba, As, Mn, Mo, Cu, V, Co and Pb. In addition to these findings, Port Jackson had high concentration of Se, whereas Cd and Cr were present only in the water of Port Yamba and Port Eden. Furthermore, TETI results state that Port Yamba had the highest index value followed by Port Botany, Port Newcastle, Port Kembla, Port Jackson and Port Eden. Additionally, in almost all ports the TETI value was high in the middle of the port area in comparison to the other points and the background area.

The proposed TETI only considers toxic elements in the water, while it overlooks the other fundamental water quality parameters used for WQI calculation. To overcome the gap of various index parameters, Environmental Water Quality Index (EWQI) is introduced that incorporates WQI and TETI indices.

Table 3-7. Comparison of the contamination indices (C_d, HEI, WQI, TETI and EWQI) estimated, based on different standards and measured port water chemistry.

Study Area	Tide	C_d (ANZEEC)	C_d (USEPA)	C_d (UK)	C_d Level	HEI (ANZEEC)	HEI (USEPA)	HEI (UK)	HEI Level	WQI	Water Quality	TETI	EWQI
Port Jackson background	H	14.69	22.0949	70.94	HHH	21.77	28.0949	79.948	LLL	83.1	G	2021.5	0.041
	L	7.82	7.1	20.9	HHH	11.82	11.1	27.9	LLL	70.2	G	2024.15	0.034
Port Jackson	H	7.93-11.71	6.63-15.54	21.08-47.57	HHH	12.93-17.72	11.63-20.55	29.08-56.57	LLL	71.16-77.65	G	1931.2-2021.3	0.038-0.04
	L	6.52-7.96	5.82-13.11	16.87-55.97	HHH	11.65-14.61	9.82-22.85	23.87-63.97	LLL	71.04-87.15	G	1917.19-2072.5	0.036-0.041
Port Botany background	H	4.36	2.07	9.55	HMH	8.36	5.07	16.55	LLL	70.02	G	1922	0.036
	L	6.95	3.99	15.07	HHH	12.95	6.99	23.07	LLL	82.45	G	2078	0.039
Port Botany	H	0.27-13.46	4.89-21.67	18.55-72.07	LHH-HHH	4.73-17.46	7.89-25.68	25.55-80.7	LLL	71.15-76.70	G	1953.7-2096	0.034-0.039
	L	3.85-30.35	14.5-168.61	48.11-526.25	HHH	7.85-17.34	17.5-172.61	55.27-535.25	LLL-LLM	69.45-81.81	M*-G	1923.8-2443	0.030-0.042
Port Kembla background	H	3.094	-2.46	-2.73	HLL	9.094	1.54	5.263	LLL	74.4	G	2090.5	0.035
	L	1.83	4.48	-2.19	MHL	3.83	5.48	17.8	LLL	76.01	G	2015.6	0.037
Port Kembla	H	1.81-12.75	0.9-8.84	6.34-30.97	MMH-HHH	3.81-17.75	3.87-11.84	12.35-37.97	LLL	72.86-77.96	G	1978-2021	0.036-0.039
	L	1.41-5.7	1.35-6.09	5.16-18.12	MHH-HHH	3.41-9.7	3.35-7.9	11.16-21.36	LLL	77.67-83.05	G	1970-2050.3	0.038-0.04
Port Newcastle	H	-0.92	1.58	4.85	LMH	0.078	2.58	8.85	LLL	77.03	G	1996	0.036
background	L	-0.92	4.15	15.09	LHH	0.078	6.15	19.09	LLL	72.76	G	2041	0.039
Port Newcastle	H	0.92-1.43	4.7-10.29	13.85-31.03	LMH-MMH	0.078-3.54	6.13-11.9	19.85-36.04	LLL	74.25-78.88	G	2012-2045	0.035-0.039
	L	1.41-16.6	4-59.46	16.67-187.6	MHH-HHH	3.41-19.6	7-62.46	22.67-192.8	LLL	74.44-78.55	G	2024-2165	0.034-0.038

Port Yamba background	H	33.29	40.06	136.55	HHH	41.29	46.06	143.54	LLL	81.52	G	2041	0.039
	L	19.61	20.37	75.01	HHH	27.61	26.37	82.01	LLL	79.53	G	2135	0.037
Port Yamba	H	50.39-101.59	18.95-54.05	72.53-183.1	HHH	58.39-110.58	24.95-61.05	79.53-191.1	LLL	72.08-83.41	G	2131-2236	0.033-0.039
	L	48-67-220.43	44.41-594.5	162.6-1859	HHH	56.67-229.43	51.42-601.5	170.6-1867	LMH-LLL	73.11-74.66	G	2229-3002	0.024-0.033
Port Eden background	H	10.05	-5.92	-6.15	HLL	19.056	0.076	0.846	LLL	73.54	G	1914	0.038
	L	49.554	4.133	25.68	HHH	58.55	11.133	33.688	LLL	75.5	G	1897	0.039
Port Eden	H	2.17-10.5	5.92-5.96	6.10-6.16	LLL-HLL	2.66-6.82	0.033-0.074	0.09-0.89	LLL	70.6-76.46	G	1932-2019	0.037-0.038
	L	0.55-316.99	4.13-158.3	6.11-502.2	LLL-HHH	9.95-326	0.048-165.3	0.89-510.2	LLM-LLL	47.62-82.21	M*-G	1914-2006	0.024-0.042

H=High contamination, M=Medium contamination, L=Low contamination, G=Good water quality, M*=Moderate water quality.
C_d=contamination index, HEI=heavy metal evaluation index, WQI-water quality index, TETI=trace element toxicity index, EWQI=environmental water quality index

The EWQI clearly represents the impact of port activities on the water environment where the higher EWQI value represents better quality. Table 3.7 states that all ports have similar EWQI values, except for some points at Port Botany, Port Yamba and Port Eden, which have lower values unveiling the comparative bad water quality of those ports.

Evaluation of the four indices used to determine pollution level reveals the important contaminants and anthropogenic inputs of metals and other pollutants in the study areas. Although all four indices specify varying levels of contamination in the studied areas their outcomes are not uniform. This is because each index considers different pollutants of importance for their calculated results. For instance, WQI index considers nine parameters which are physicochemical, nutrients and one biological parameter and disregards the toxicity of metals in the aquatic system. Based on the WQI only one case for Port Botany and three cases for Port Eden during low tide exhibited medium water quality, mainly due to high turbidity, low DO and fecal coliforms, while for all of the other sampling sites the water quality was good. Both HEI and C_d disregard the physicochemical and biological impacts on water quality and consider the trace metals or hydrocarbons in relation to the recommended national guideline threshold values. In this study the HEI index showed that one sampling site at Port Botany, Port Eden and Port Yamba had water quality of medium contamination and one site in Port Yamba of high contamination. In all cases this was a result of significant Fe concentrations and relative to the UK and USEPA guidelines. The C_d index in most showed high contamination due to either the Cu content relative to the ANZECC guidelines or Fe content relative to the USEPA and UK guidelines. These findings clearly showcase the limitations of each index and limitations of the international water quality guidelines, which are, firstly non-standardized between different countries and, secondly, do not provide guidelines for a number of pollutants. The newly established EWQI attempts to overcome the limitations of the current water assessment indices and considers all pollutants ranging from physicochemical, biological and the individual toxicity levels of each trace element. The EWQI index in this study presented that the trace element of most importance of the water quality in the studied ports is B, as shown in Table S3.3 in Appendix B. B appears in high concentrations in the water samples, has total score of 438 according to the ATSDR (ATSDR, 2015) assessment, but is not considered in any of the international guidelines, hence it is not accounted for in either of the WQI, C_d or HEI indices.

3.4 Conclusions

This study examines the extent of physiochemical and biological constituents present in the port water. The extensive study on pollutants of different port land uses and the comparison with the respective background area advocates a number of important considerations in the port water environment in NSW, Australia. The water quality index (WQI) analysis of the port area unveiled that the lower DO levels, higher turbidity and fecal coliforms markedly reduced the water quality of Port Botany and Port Eden. The trace metal concentrations in the port water provide baseline information for understanding the pollution levels, such as the high concentrations of Cu at Port Jackson, high concentrations of Cu and Pb at Port Botany and high concentrations of Cu and Zn at Port Kembla. Furthermore, Port Newcastle had high concentration of Cu and Mn; Port Yamba was enriched with Cu, Mn and Pb, while Port Eden had very high concentrations of Cu, Mn, Cd and Co. Contamination index and heavy metal evaluation index also revealed the level of contamination and heavy metal index. The contamination index presented high contamination levels in all of the studied ports areas. In addition, the heavy metal evaluation index depicted Port Botany, Port Yamba and Port Eden as high and medium polluted areas. Different water quality indices used in this study, apply different water quality indicators that help assess the overall water quality of the port areas. WQI considers physicochemical, biological and nutrients but overlooks the toxicological indicators whereas; C_d and HEI consider only the toxicological parameters neglecting the physicochemical, biological and nutrient pollution. The study further explains the EWQI, which incorporates all the physicochemical, biological and toxicological indicators to assess the quality of the port water in a more comprehensive way. This research work points out that on an average the quality of the port water is good, except for Port Botany, Port Yamba and Port Eden, and recommends regular monitoring and management of port activities accounting for both biological and chemical toxicological profiles of the discharging activities.

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Chapter 4: Comparison of pollution indices for the assessment of heavy metals in the sediments of seaports of NSW, Australia

Marine sediments often act as pollutant traps and scavengers for metals. As a result, they present excellent evidence of past anthropogenic impacts. Sediments are ideal for long term environment studies and provide indications of the relationship between natural and anthropogenic sources of pollution which may enter the food chain. This chapter evaluated the sediment quality of the seaports and compared to their background environments. Considering the sediment is a reservoir and repository for historical environmental pollutants, a broad spectrum of contaminants, including trace elements, inorganic nutrients and organic carbon were assessed and evaluated with a number of pollution indices and sediment quality guidelines values (SQGVs).

Authors Contributions

Study Conception and Design: Vladimir Strezov and Sayka Jahan

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Analysis and Interpretation of Data: Vladimir Strezov and Sayka Jahan

Drafting of Manuscript: Sayka Jahan

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Comparison of pollution indices for the assessment of heavy metals in the sediments of seaports of NSW, Australia

Abstract

Sediments samples from six seaports of NSW, Australia were analysed for the presence of metal contamination. Geoaccumulation index (Igeo), enrichment factor (EF), pollution load index (PLI), potential ecological risk (PER) and sediment pollution index (SPI) along with multivariate statistical analysis were used to identify the pollution pattern and possible sources of metals in the ports. The results demonstrate Cu, Pb and Zn pollution (Igeo > 5) at most sites and enrichment of As, Ni, Mn (EF > 3) and other metals. The PER recommends serious pollution at Port Kembla and Port Eden. By contrast, PLI and SPI demonstrate high contamination in all ports with exception of Port Botany and Port Yamba. PCA and cluster analysis detected major groups of elements in which three distinct clusters of pollutants and sites were apparent by dendrogram which portray simple and effective baseline scenarios for port activity-related quality assessment of surface sediments.

Key Words: Seaport; Metals; Sediments quality; Pollution indices; PCA; HCA.

4.1 Introduction

The global economy is significantly influenced by the activities of seaports contributing 80% of the global trade by volume and over 70% by value (UNCTAD, 2015, Shen et al., 2017). Marine seaports which underpin industry and commerce are also intensively used for tourism and recreation (Niemi et al., 2004, Birch and McCready, 2009, Birch, 2017b). However, intensive economic and recreational activities also cause environmental pressures from metal pollution, oil spills, ballast water, garbage, ship paint, greenhouse gas emissions and other pollutants (UNCTAD, 2015, Shen et al., 2017). Trace metal pollution in port environment is now a global environmental concern because of toxicity, wide sources, persistence, slow degradation and rapid accumulative behaviours (Klavinš et al., 2000, Yuan et al., 2004, Dural et al., 2007, Hu et al., 2011, Alyazichi, 2015). Trace metals discharged into the port environments are generally eliminated from the water column by binding with suspended particles and are ultimately deposited as bottom sediments under favourable hydraulic conditions (Zeng and Wu, 2009, Hosono et al., 2010, Zhang et al., 2013, Zhang et al., 2014). Accordingly, sediments are considered as the most important sinks and play a pivotal role in the dissemination of metals, with significantly higher elemental concentration than in the water column (Li et al., 2001, Ridgway and Shimmield, 2002, Hung and Hsu, 2004, Xia et al., 2011, Wang et al., 2012, Mashiatullah et al., 2015). Thus, sediments are considered as repositories for historical environmental pollutants (Xia et al., 2011). Specifically, metal distribution characteristics in sediment cores can show time-dependent historical variations of metal concentrations and can provide useful information on metal accumulation and alteration from a past period (Jain et al., 2008, Wang et al., 2010, Alvarez et al., 2011, Ma et al., 2013, Tang et al., 2016, Wang et al., 2016).

Trace metals entering the marine environment mostly settle down and adsorb onto sediments together with organic matter, Fe/Mn oxides, sulphides and clay (Wang and Chen, 2000). Marine sediments often act as pollutant traps and scavengers for metals. As a result, they present excellent evidence of past anthropogenic impacts (Guevara et al., 2005). To some extent, trace metal contents in sediment can represent the quality of the water body. Sediments cannot bind metals permanently although they are some of the endmost sinks for trace metals input into the aquatic environment. Under variable hydraulic conditions and through various remobilization processes some sediment bound metals might be released again into the water body. Therefore, sediments play an important role in the transport and storage of potentially hazardous trace metals (Ruilian et al., 2008).

Considering sediments are pollutant traps they are valid for long term studies (Mostafa and El-Naggar, 2003, Zaghden et al., 2007) and act as indicators for the relationship between natural and anthropogenic variables as they pass pollutants to the food chain (Calman et al., 1996, Hassanshahian et al., 2010). The retention capacity of sediment may be related to its physicochemical properties, such as grain size and organic matter (Abdallah et al., 2016).

However, in the assessment of environmental health, the use of sedimentary indicator is often poorly utilized, deemphasized and misspent (Rainbow, 2006). Traditionally, water columns and biological indicators are the preferred media for assessment of the marine and estuarine health (Rainbow, 1995, Rainbow, 2006). As water is dynamic with highly variable short- and long-term properties, analysis of large number of samples is required to spatially and temporally characterize water quality with confidence (Birch and Olmos, 2008). Moreover, low chemical concentrations in water, and complex and expensive analysis often compromise data quality and interpretation

(Birch and Taylor, 2000, Bubb et al., 1990, Siaka et al., 1998, Zhuang and Gao, 2014). On the other hand, analysis of flora and fauna is often difficult due to significant variations in the chemistry of tissues between individuals, species, gender, organs and age (Birch, 2017a).

In recent years the status of aquatic environments has been assessed through sediment analysis rather than other traditional media. Sediment provide extensive habitat and store large contaminants which has a substantial influence on the biological health in the marine environment. However, for a comprehensive assessment of aquatic systems sediments should be used in combination with other screening tools (Belin et al., 2014). Sediments have advantage over other indicators because they record and combine environmental events over time within the aquatic system, commonly referred to as 'the memory of sediments (Birch, 2007, Birch et al., 2013). Furthermore, sediments not only provide useful spatial and temporal information but allow predictions of future environmental change and status from the integration of environmental events over time (Birch et al., 2010, Birch et al., 2012, Birch et al., 2013). Additionally, sediments greatly affect the quality of overlying and interstitial water through physical (re-suspension), (Peterson et al., 1997, Simpson et al., 2000), biological (bio-turbation), (Reible et al., 1996) and chemical (desorption and benthic diffusion) processes (Birch, 2017a, Rivera-Duarte and Flegal, 1994). Finally, compared to other indicators of marine and estuarine health, sediment studies are less time consuming and inexpensive to measure the environmental conditions (Maher et al., 1999, Birch et al., 2000, Birch, 2003).

Recently sediment quality monitoring of trace metals has been conducted for contamination assessment in the ports of NSW which were reported as high to moderately polluted areas (Birch, 2017). Birch (2017) stated that trace metal concentrations in sediments of the Sydney estuary are some of the highest reported in NSW and Australia. McCready et al., (2000, 2004, 2006a, 2006b, 2006c) revealed significant metals and nutrient contamination in the sediments of Sydney Harbour estuary. Spooner et al. (2003) demonstrated significant concentrations of Zn, Cu, Pb and As in surficial sediment of Port Botany. Dafforn et al. (2012) investigated high concentrations of trace metals (Cu, Pb and Cd) in the sediment of Port Kembla. Another study by Birch and Gillis (2006) explained the non-dredged part of the Port Newcastle has a higher level of sedimentary trace metals. Although a number of studies have been conducted in the ports of NSW or elsewhere, they were mainly based on analysis of some selective elemental concentrations of the sediments, using limited sediment quality indices to quantify the environmental state of the sediments. The present study analysed large sets of trace elements and assessed the sediment quality using a wide range of environmental quality indices and compares the indices to determine the most effective method for assessing sediment quality.

The aim of this study was to apply a wide range of environmental quality indices including the geoaccumulation index (Igeo), pollution load index (PLI), enrichment factor (EF), potential ecological risk index (PER), sediment pollution index (SPI), factor analysis and multivariate statistical analysis to assess the sediment quality and ecological state of the major ports of NSW, Australia and determine the most accurate and suitable quantitative assessment method for analysis of the sediment quality. This will impart a tool for prime stakeholders, including marine and estuarine managers, government and the public in connection to protecting aquatic biota and environment.

4.2 Materials and methods

4.2.1 Study site

The study areas in this work were the six dominant ports in NSW, Australia, namely Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden, which are away from one another and are engaged with different shipping activities (Jahan and Strezov, 2017). Port Jackson of Sydney is a premier port of Australia, well known for passenger shipping, recreational boating and water sports (Hatje et al., 2003). The area is floored with a clean, flood delta sand, containing <10% mud, which extends ~2 km into the embayment from the entrance. Port Botany, located in the mouth of George river is mainly engaged with container, crude oil and bulk liquid operations (fossil fuel, chemical and bio-fuel) (Harris and O'Brien, 1998). The depositional environment of Port Botany is characterised by bay sediments and tidal deltaic sediments composed of mostly fine to medium grained sand (Roy and Crawford, 1981). Port Kembla is a major export location for coal mined in the southern and western regions of New South Wales with many facilities and berths including the grain terminal, bulk liquids, oil, various products berths (steel berth) and multipurpose berths (fertiliser, pulp & steel products). The port is important for importing iron ore, dolomite, limestone, sulphur, copper, phosphate rock and petroleum products and exporting iron and steel, coal, coke, tinplate and copper cables (Harris and O'Brien, 1998). The surface sediments of Port Kembla are coarse grained sediments (slightly gravelly sands and gravelly sands) is affected by the presence of large amounts (up to 80%) of calcium carbonate derived mainly from coralline algae

(Bosher, 1977). The Port of Newcastle is the world's largest coal export port that also receives raw materials for steelworks, fertiliser and aluminium industries, grain, steel products, mineral sands and woodchips (Harris and O'Brien, 1998) and is known as one of Australia's largest ports by throughput tonnage (Bateman, 1996). The port is the economic and trading centre for the Hunter Valley and much of New South Wales and is a critical supply chain interface for the movement of cargo (Clarson, 2017). The Hunter River channel sediment is derived from the relict marine and aeolian dune sand deposits. Fine sediments transported by the river system are trapped in Fullerton Cove (mud basin) and deposited on the middle shelf mud belt (Roy, 1977). Port Yamba is located at the mouth of the Clarence River in the Northern New South Wales and is Australia's most eastern sea port. Port Yamba is home port of the New South Wales' 2nd largest fishing fleet and handles a range of imports and exports, such as container liquid berth-livestock and explosive products. The Clarence River is the largest catchment area on NSW Tasman Sea coast comprising mainly of clayey mineral rich sandy sediments (Smith, 1996). Port of Eden is a small seaport, located in the Twofold Bay of South Coast region of New South Wales, Australia. The port is home to one of the largest fishing fleets in New South Wales. Woodchip export is currently the major trade for the port, while the principal imports are break bulk, and machinery and equipment, mainly for the oil and gas industry (Harris and O'Brien, 1998). Based on texture and composition (lithology and calcium carbonate content) surficial sediments of Twofolds Bay are mainly fine quartz sand in the inner bay area, with a zone of coarse sand along the southern and outer parts of the bay (Hudson, 1991). The coordinates and details of the sampling location points are listed in Table 4.1 and shown in Fig 4.1.

Table 4-1. Coordinates of sampling locations.

Study Area	Site Id	Coordinates	Study Area	Site Id	Coordinates
Port Jackson	1Bg	33◦51'18.6"S 151◦12'22.1"E	**Port Newcastle**	1	32◦55'31.6"S 151◦46'44.9"E
	2	33◦ 51' 37.1"S 151◦12' 34.7"E		2	32◦55'24.4"S 151◦47'24"E
	3	33◦51' 28.6"S 151◦12' 56.6"E		3Bg	32◦55'29.3"S 151◦47'34.8"E
Port Botany	1	33◦58'55.6"S 151◦12'32.1"E	**Port Yamba**	1Bg	29◦25'14.1"S 153◦20'20"E
	2	33◦57'27.5"S 151◦11'54.8"E		2	29◦26'7.2"S 153◦20'42.9"E
	3Bg	33◦59'15.1"S 151◦13'52.9"E		3	29◦26'0,8"S 153◦20'43.9"E
Port Kembla	1Bg	34◦25'27.3"S 150◦54'23.1"E	**Port Eden**	1	37◦04'19.8"S 149◦54'32.3E"
	2	34◦28'30.7"S 150◦54'39.9"E		2	37◦04'17.4"S 149◦54'27.8"E
	3	34◦28'05.8"S 150◦54'02.7"E		3Bg	37◦04'14.7"S 149◦54'38.4"E

Bg=Background point

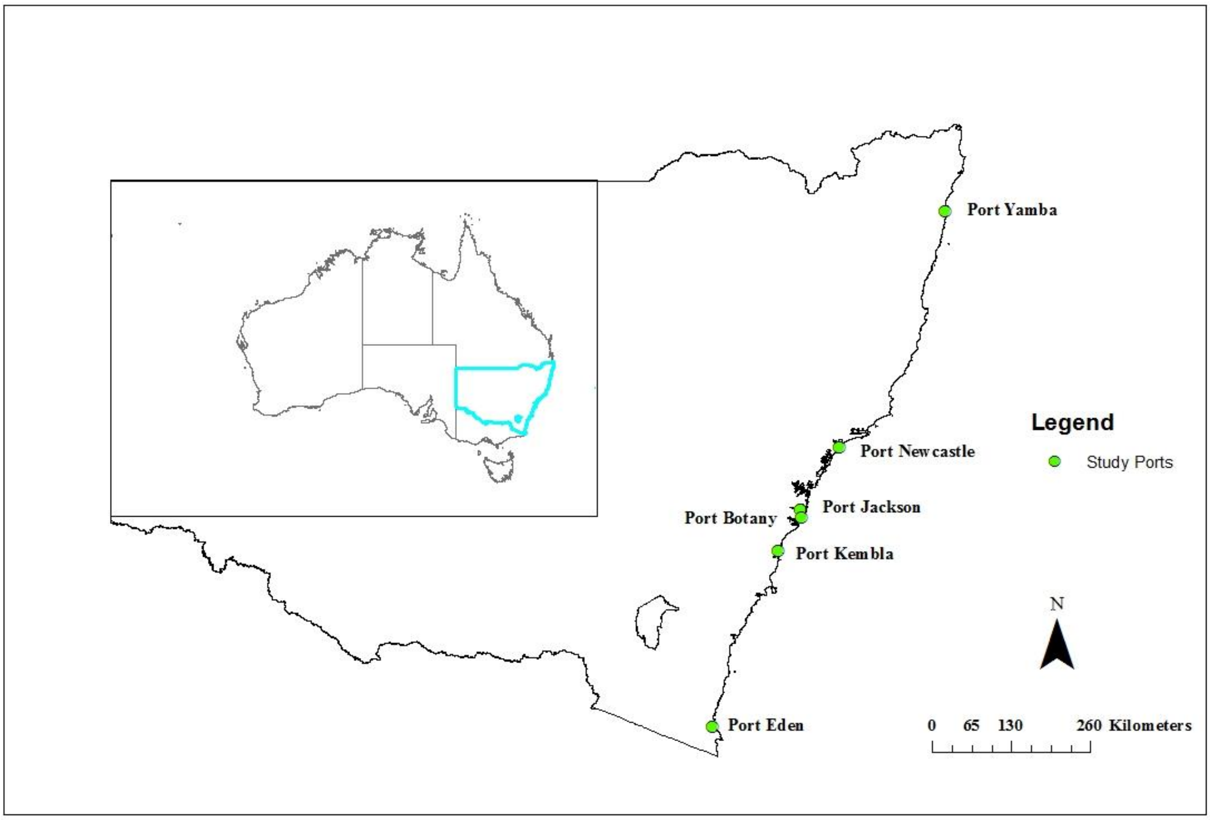


Fig. 4. 1 Map of the study area showing study ports of NSW

Sediment samples from the six sea ports were collected for trace metal analysis during the period of April – May 2017 using a stainless steel Ekman Grab Sampler. From each individual port three composite surface sediment samples were collected at water depths ranging from 1 to 10 m, one of these was a background sample (Same hydrogeological area but away from any influences of the port activities). Two replicate samples were collected from each sampling point in order to obtain a composite sample and ensure that the sample sediments were not contaminated by collection procedure. Replicate samples were collected at a distance of approximately 1 m apart. After sampling, the sediment samples were packed and carried to the laboratory in iced-boxes and stored at 4° C until analysis. The sediment samples were then submitted for analysis of trace metals, grain size, total organic carbon, nitrite, nitrate, ammonia, sodium, potassium and calcium.

4.2.2 Metal analysis

The sediment samples were air dried at room temperature (20°C), crushed, sieved by 160 µm mesh soil seive and then stored in polyethylene bags for further analysis. The samples were then diluted with water to prepare sample solutions. Sample solutions and blanks were analyzed for Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, Zn, Hg, Be, V, B, Co, Mo, Sb, Ba, Bi, Sn, Si, St, Rb, U and Ti with Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) and inductively coupled plasma-mass spectrometry (ICP-MS, Optima 2100 DV ICP System, Perkin Elmer). Hg was determined by Cold Vapour AAS.

Quality control was performed in accordance with NATA (National Association of Testing Authorities) guidelines for method validation (NATA, 2012) and measurement uncertainty (NATA, 2009) by analysing certified reference material AC-E with a composition of 14.75% Al_2O_3; 70.61% SiO_2; 2.54% Fe_2O_3 and 0.06% MnO_2. The recoveries were 100.9% for Al, 100.2% for Si, 93.1% for Mn and 98.2% for Fe.

For the measurement of total organic matter, sediment samples were dried at 70°C for 24 h and then combusted for 4 h in an oven at 550°C. Total organic matter, as explained by Abrantes et al. (1999), was measured by the following equation:

Total organic matter (TOM,%)= (B-C/B)*100……………………………………………(i)

where *B* and *C* are the weights of dried sediment before and after combusting in the oven, respectively.

4.2.3 Grain size analysis

As the surface area of sediments is grain-size dependent and controls the adsorption of metals, metal concentrations were normalised to grain size in order to interpret metal concentrations in sediments between areas (Blomqvist et al., 1992, Hanson et al., 1993).

The sediment grain size of all samples was analysed by first drying in an oven at 120°C for 24 hours and then sieving to particle size of <2000 µm (i.e. gravel-free). The sediment fractions were determined using laser detection on a Malvern Mastersizer 2000 with a 300RF lens, The samples were dispersed in water and 30 s of ultrasonication was used to break up agglomerated particles. A total of four measurements were made for each sample and averaged to determine the final value. The distribution abundances within the 0.2–2000 µm grain size range were calculated by the Malvern built-in software.

4.2.4 Inorganic measurement

Moisture content of the sample sediments were determined by heating at 105±5 °C for a minimum of 12 hours. Nitrite and nitrate were determine colourimetrically based on APHA NO^{2-} B and analysed following water extraction. Total Nitrogen (TN) was determined from the sum of Total Kjeldahl Nitrogen (TKN) and oxidised nitrogen. Ammonia and phosphate were also determined colourimetrically based on APHA 4500-NH3 F and EPA365.1 and APHA 4500 P E respectively.

4.2.5 Statistical analysis

For statistical analysis microsoft excel and SPSS 24 software were used. The data were subsequently analyzed using the multivariate statistical tools principal component anlysis (PCA) and hierarchical cluster analysis (HCA) using both cases and variables to develop groups and identify links between elements and sampling sites. The PCA and HCA were used to indentify the possible sources of trace metals in the sediments and group them based on their similarities. For PCA, only PCs with eigenvalue >1 were retained and variables were centered as mean (Kaiser, 1960). Varimax rotation was applied to component loadings > 0.5 to facilitate the interpretation of the outcomes (Loska and Wiechuła, 2003). HCA was also performed on mean centred data and presented as a dendrogram plotted with linkages between groups using squared Euclidean distance.

Finally, a number of single and multiple element indices and Australian New Zealand sediment quality guidelines (ANZECC/ARMCANZ, 2000) were used to determine trace metal pollution and ecological state of the port sediment.

4.2.6 Geo-accumulation index

The geo-accumulation index (Igeo) represents the pollution intensity of individual sampling locations. The Igeo is a quantitative measure of the degree of contamination in sediments (Förstner et al., 1990) and it is calculated by the following equation:

$$\text{Igeo} = \log_2\left[\frac{Cn}{1.5\times Bn}\right] \quad \text{......(ii)}$$

where C_n is the examined elements in the sediment and B_n is the geochemical background of a given element.

Muller (1979) classified the sediments based on the Igeo value, as: Igeo > 5 = extremely contaminated, 4–5 = strongly to extremely contaminated, 3–4 = strongly contaminated, 2–3 = moderately to strongly contaminated, 1–2=moderately contaminated, 0–1=uncontaminated to moderately contaminate and <0 = uncontaminated.

4.2.7 Pollution Load Index

Tomlinson et al. (1980) proposed Pollution Load Index (PLI) calculated through Contamination Factor (CF) of each metal with respect to the background value in the sediment (Angulo, 1996), by applying the following equation.

$$PLI = (CF1 \times CF2 \times CF3 \times \ldots \ldots \ldots . \times CFn)^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(iii)$$

where $CF = C_{metal} / C_{background}$ and n = number of metals. PLI, an aggregative explanation for the overall level of trace metal pollution in sediments which ultimately evaluate the contamination status. An area with PLI value >1 is polluted whereas PLI value <1 indicates no contamination (Tomlinson et al., 1980, Ray et al., 2006, Badr et al., 2009). The calculation of PLI doesn't considers the lithogenic and sedimentary inputs of metals which is a limitation.

4.2.8 Enrichment factor (EF)

Enrichment factor (EF) is generally conducted to ascertain whether metals in sediments were of anthropogenic origin (Hornung et al., 1989, Dickinson et al., 1996, Abrahim et al., 2007). The EF method normalizes the measured trace metal, trace elements, rare earth elements and actinides content with respect to a sample reference metal, such as Fe, Sc or Al (Ravichandran et al., 1995, Ashraf, 2011, Ibrahim et al., 2014, Ashraf et al., 2016). In the present study, Fe was selected as the normalization element to account for the metal variations with respect to the variations of grain sizes.

EF was calculated according to the following equation:

$$EF = (C_x/Fe_x)_{sample}/(C_{ref}/Fe_{ref})_{background\ Sample} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(iv)$$

where C_x is the concentration of an element in the sample, Fe_x is the concentration of Fe in the sample; C_{ref} is the concentration of an abundant and common element in the average sediment, and Fe_{ref} is the concentration of Fe in the average sediment (Turekian and Wedepohl, 1961).

According to the EF values, each sample falls into one of the five tiers, as proposed by (Sutherland, 2000). The elemental ratios indicate depletion to minimal enrichment when EF < 2 or moderate enrichment if the values fall between 2 and 5. If the EF value falls in the range between 5 and 20, 20–40, and > 40, it is considered significantly enriched, very highly enriched, and extremely enriched, respectively.

Generally, if the enrichment factor is close to or < 1 it shows that the main source of trace elements in the sediments originates from crustal or marine environments. The enrichment factor value becomes significantly larger than 1 when the main source is from anthropogenic contribution.

4.2.9 Potential ecological risk index (PER)

PER index was also introduced to assess the contamination degree of trace metals in the present sediments. PER were proposed by Guo et al. (2010) and is calculated with the following calculations:

PER = $\sum$E……………………………………………………………………………(v)

E = TC

C = C_a/C_b

where C is the single element pollution factor, C_a is the content of the element in samples and C_b is the reference value of the element. The sum of C for all examined metals represents the integrated pollution degree (C) of the environment. E is the potential ecological risk index of an individual element. Ti is the toxic-response factor of an individual element, which is determined for Cu = Pb = 5, Zn =Mn= 1, Cr=2, Cd=30, As = 10 and Ni = 6 (Hakanson, 1980, Fu et al., 2009, Guo et al., 2010, Chen et al., 2014, Cao et al., 2015). PER is a comprehensive potential ecological index, which equals to the sum of E. It illustrates the potential ecological risk caused by the overall contamination.

4.2.10 Metal provenance

Further assessment of the metal provenance in the sediment was conducted using the principal component analysis. In order to eliminate the grain size effects, metal/Fe contents were used during the process. Moreover, all the analyses were based on the standardized data set.

4.2.11 Sediment pollution index

Sediment pollution index (SPI) was conducted to evaluate the sediment quality on the basis of the most important parameters extracted by PCA (Shin and Lam, 2001). Twelve variables (Zn, Pb, Bo, Cr, Fe, As, Ba, Ti, Cu, Ni, Mn and Si) with high PCA loadings were extracted and were applied in the SPI calculation. The following modified arithmetic weighted formula (Schintu and Degetto, 1999) was used to calculate the SPI:

$$SPI = (\sum q_i w_i)^2 / 100 \quad \text{(vi)}$$

Where q_i is the sediment quality rating of the variable i, and the rating was based on the percentile in the data set, and w_i is the weight attributed to the variable i, based on the proportion of eigenvalues obtained from the PCA. The SPI was divided into five ranks: $0 \leq SPI \leq 20$ shows excellent sediment quality, $21 \leq SPI \leq 40$ is good, $41 \leq SPI \leq 60$ is average, $61 \leq SPI \leq 80$ is poor, and $81 \leq SPI \leq 100$ is bad.

4.3 Results and discussion

4.3.1 Sediment properties

Textural characteristics of the sediments of the six study ports were analysed as presented in Table 4.2. The results demonstrated that, except for the background sediment of Port Jackson and Port Eden, the sediments of other ports belong to the medium sand group (57.17–79.45%). All ports, except for Port Yamba and Port Eden, had less than or equal to 10% fine sand, while only Port Jackson had as high as 63% coarse sand at the background site, with the rest being 25% or less.

Sediment transportation and sedimentary processes are the most important factors which influence the distribution of fine-grained sediments in the marine ecosystem (Tavakoly et al., 2014). As all the study ports are almost natural bays, they are expected to be sandy, because most natural bays are dominated by sandy sediments, with some exceptional occurrences of gravel (McManus et al., 1998).

Among inorganic nutrients the mean concentration of Na in the port sediment ranged from 2200 to 4300 mg/kg with the lowest concentration at Port Yamba and the highest concentration at Port Eden. The mean concentration of Ca in the port sediments ranged from 430 to 110,500 mg/kg with the highest concentration at Port Kembla and lowest concentration at Port Yamba. However, the concentration of S and K ranged from

315 to 1200 mg/kg and 145 to 705 mg/kg with the highest concentration at Port Eden. In addition, the concentration of TOC is also very high (4000 mg/kg) at the sediment of Port Eden compared to the other ports and background areas. Moreover, the sediment of Port Eden has also very high concentration of TN (285 mg/kg).

Table 4-2. General characteristics of the study area sediments

Parameter	Port Jackson		Port Botany		Port Kembla		Port Newcastle		Port Yamba		Port Eden	
mg/kg	Bg	Mean	Bg	Mean	Bg	Mean	Bg	Mean	Bg	Mean	Bg	Mean
Na	4400	3600	3200	2650	2900	3600	2700	3000	2400	2200	4000	4300
Ca	8400	9000	4100	5030	14000	110500	14000	13300	340	430	87000	32500
S	470	350	250	315	260	730	240	380	280	350	530	1200
K	290	220	160	160	120	280	280	210	150	145	270	705
Moisture	18	15.5	16	16	11	14.5	14	15	14	15	13	15.5
Fine sand (125-250 µm) %		9.01	8.54	8.78	1.4	10.08	9.66	8.78	32.42	33.56	58.06	30.4
Medium sand (250-500 µm) %	18.54	65.23	57.17	60.12	74.2	65.56	77.05	79.45	64.47	62.03	16	62.1
Coarse sand (500-1000 µm) %	63.01	25.04	33.82	29.85	24.39	26.8	13.27	12.07	3.02	6.08	23	7.4
very coarse sand (1000-2000 µm) %	18.44	-	-	-	-	-	-	-	-	-	-	-
TOC	1100	550	300	400	Bd	750	Bd	550	300	250	700	4000
TKN	220	71.5	48	80.5	13	202.5	27	94.5	48	47	160	285
NO_2	Bd	Bd	7.5	Bd	Bd	Bd	Bd	5.4	1	0.2	Bd	Bd
NO_3^-	Bd	4	1.6	Bd	Bd	2.1	1.5	1.3	0.5		Bd	Bd
TN	220	126	57	81	14	153	28	100	49	47.5	160	285
NH_3	4.7		1.9	1.6	Bd	Bd	Bd	0.75	0.8	0.9	0.8	1.4
PO_4^{3-}	0.8	Bd	0.8	0.8	Bd	Bd	Bd	Bd	Bd	0.8	Bd	Bd

Bg=background; Bd=Below detection.

4.3.2 Trace metal concentrations

The concentrations and background values (mean±std and maximum) of metals in the sediments of the study ports are presented in Table 4.3. The concentrations of Ag, Cd, Se, Hg, Be, Bi and Sb were all below the detection limits of the instrument. The results reveal Mo (40±52.21 mg/kg) and Rb (2±0 mg/kg) are only present in the sediments of Port Eden among all six ports but absent in the background sample. The mean concentrations of Cr, Mn and Ni for all ports were all within the ANZECC and other international guidelines, except for Port Kembla where the Ni concentration in the port sediment was higher than the ISQG lower value of the ANZECC standard guidelines. The maximum concentration of Al was much higher in all of the sediments than the background area (shown in Table 4.3) with the highest (2500 mg/kg) concentration recorded at Port Eden. As was found only in the sediment of Port Jackson, Port Eden with higher concentration of As at Port Kembla and Port Eden than the standards given by ANZECC and USA-ERL. However, the maximum concentrations of Cu (2200 mg/kg) and Fe (79000 mg/kg) in Port Eden were also much higher than the standards given by ANZECC, USA-ERM and CSQG-China (Table 4.3). The maximum concentrations of Pb and Zn in the sediments of Port Kembla (120 and 290 mg/kg) and Port Eden (410 and 3800 mg/kg) also exceed the ISQG standard given by ANZECC and other international guidelines. V and Ti were present in the sediments at all six study ports but among them their maximum concentrations are significantly higher at Port Jackson (14 and 65 mg/kg), Port Kembla (17 and 62 mg/kg) and Port Eden (15 and 86 mg/kg). On the contrary, Port Eden sediment contained notable amounts of B and Co (20 mg/kg), Mo (77mg/kg) and Ba (60 mg/kg), (Table 4.3). In addition, high concentration of Sn was present in Port Kembla (24 mg/kg) and Port Eden (54 mg/kg) sediment. Moreover, very high concentrations of Sr were present in the sediment of Port Kembla (1100 mg/kg) and Port Eden (270 mg/kg). The contributors to the high concentrations of metals in the port sediment are associated with the excessive industrial and port activities at Port Kembla, and intensive activities of fishing fleet, export of break bulk, machinery and equipment for oil and gas refineries, preservative chemicals and wood chips at Port Eden.

Table 4.4 summarizes the mean and maximum concentration of metals in the measured sediments compared with other international ports reported in the previous studies. The mean concentrations of Pb (165 mg/kg), Cu (1195 mg/kg) and Zn (2345 mg/kg) in the surficial sediment of Port Eden are the highest compared to the worldwide harbours listed in Table 4.4.

Table 4-3. Metals concentrations (mg/kg in dry weight) in sediment samples

Heavy Metals	Port Jackson		Port Botany		Port Kembla		Port Newcastle		Port Yamba		Port Eden		ANZECC (ISQG)		USA		China	
mg/kg	**Bg**	**Mean±Std** **Max**	**Bg**	**Mean±Std** **Max**	**Bg**	**Mean±Std** **max**	**Bg**	**Mean±Std** **Max**	**Bg**	**Mean±Std** **max**	**Bg**	**Mean±Std** **max**	**Low**	**High**	**ERL**	**ERM**	**CSQ** **G 1**	**CSQ** **G 11**
Al	850	895±7.07 900	280	930±28.28 950	200	1250±212.13 1400	220	1550±777.82 2100	430	383±77.78 440	490	2250±353.55 2500						
As	-	6 6	-	-	-	18.5±19.90 32	-	4	-	-	-	29±29.69 50	20	70	8.2	70		
Cr	4	4 4	-	2±1 3		11±2.82 13	1	4	-	1	1	31±16.97 43	80	370	81	370	80	150
Cu	6	6±1 7	2	2 2	-	59±24.75 76	-	4 4	-	1	2	1195±1421 2200	65	270	34	270	35	100
Fe	7900	7300±141.42 7400	480	765±247.48 940	970	8000±777.81 8800	870	5300±565.68 5700	1100	760±198 1100	4300	46000±46669 79000			20000	40000		
Mn	34	110 110	3	6±2.82 8	14	201±182.43 330	4	185±49.49 220	14	5±1.41 6	11	73±45.96 110			460	1100		
Ni	1	3±1 3	-	-	-	20±19.79 34	-	3 3	-	-	2	12±4.24 15	21	52	20.9	51.6		
Pb	16	18 18	3	2	1	74±65.76 120	-	24 24	-	1	6	165±205.06 410	50	220	47	218	60	130
Zn	110	85±7.07 90	6	7±3.53 9	5	235±77.78 290	1	78±2.83 80	3	3 3	10	2345±2057 3800	200	410	150	410	150	350
V	11	13.5±0.70 14	1	2.5±0.70 3	3	13.5±4.95 17	2	7.5±0.707 8	-	1	3	13±2.82 15						
Bo	5	4±0 4	-	-	-	7.5±3.55 10	-	4.5±0.70 5	-	-	3	14.5±7.77 20						
Co	-	1	-	-	-	2±0 2	-	2±0 2	-	-	-	12±11.31 20						
Mo	-	-	-	-	-	-	-	-	-	-	-	40±52.32 77						
Ba	45	4.5±2.12 6	-	2±0 2	-	7±1.41 8	-	13.5±0.70 14	-	-	3	42±25.45 60						
Sn	-	-	-	-	-	16±11.31 24	-	3±1.41 4	-	-	2	37±24.04 54						
Sr	47	56±4.24 9	25	28±32.52 51	92	610±692.96 1100	48	80±0 80	4	4.5±0.70 6	490	245±35.35 270						

U	-	-	-	-	-	0.75±0.212 0.9	-	0.15±0.70 0.2	-	-	0.2	0.55±0.35 0.8
Ti	28	56±12.72 65	7	17±7.77 22	13	47±21.92 62	5	37.5±0.70 38	13	10±1.41 13	7	73±19.09 86
Rb	-	-	-	-	-	-	-	-	-	-	-	2±0

Bg=Background value, "-" = below detection. ANZECC/ARMCANZ (2000), Long, et al. (1995), CEPA (2002). **High and Low** represents threshold concentrations linked to low and high biological impact. **ERL** refers to Effect Range Low. **ERM** refers to an Effect Range Median concentration.

Table 4-4. Study area and global metal concentrations in total surficial sediment (mg/kg dry wt.)

	Cd	Co	Cr	Cu	Ni	Pb	Zn	References
Port Jackson	Bd	1	4)	6.00-7	2.0-3	18	80-90	This work
	Bd	1	4	7	3	18	85	
Port Botany	Bd	Bd	1.00-2	0-2	Bd	2	4.0-9	This work
	Bd	Bd	1	2	Bd	2	7	
Port Kembla	Bd-0.6	2	9.00-13	41-76	6.0 -34	27-120	180-290	This work
	0.6	2	11	59	20	74	235	
Port Newcastle	Bd	2	3.00-4	4	3	24	76-80	This work
	Bd	2	4	4	3	24	78	
Port Yamba	Bd	Bd	Bd-1	1	Bd	1	3	This work
	Bd	Bd	1	1	Bd	1	3	
Port Eden	Bd-0.6	4.0-20	19-43	190-2200	9.0-15	120-410	890-3800	This work
	0.6	12	31	1195	12	165	2345	
Hong Kong, China	0.1 - 5.3		5-560	1.0-4000	5.0-220	9-260	17.0-790	Zhou et al., 2007
	0.33		49	119	25	54	148	
Quanzhou Bay, China	0.3-0.9		51-122	25-120	16.0-46	32-101	106-242	Yu et al.,2008
	0.59		82	71	33	68	180	
Tamaki Estuary	0.1-1			21-47		51-122	138-272	Abrahim and Parker,2008
Auckland, New Zealand	0.28			35		73	207	
Qua Iboe Estuary			0.01-0.02	43-45	21	43-46	102-104	Udofia et al.,2009
Niger Delta, Nigeria			0.014	44	21	45	102	
Lima Estuary			24-84	16-406	1.0-46	19-64	59-398	Cardosa et al.,2008
Viana do Castelo, Portugal			57	45	14	37	111	
Port of Barcelona	0.4-2.8		39-110	71-531	18-34	86-89	183-1133	Guevara-Ribaetal., 2004
Barcelona, Spain	1.22		68	183	25	189	391	
Gulf of Gemlik		13-24	71-181	23-58	35-165	0.1-67	88-185	Ünlü et al., 2008
Sea of Marmara, Turkey		19	117	41	110	29	128	
San Pablo Bay	0.1-0.4		15-39	25-49	27-45	15-27	48-79	Lu et al., 2005
San Francisco, USA	0.21		21	39	37	22	65	
Montevideo Harbour			79-253	59-13	26-34	44-128	174-491	Muniz et al.,2004
Uruguay			161	89	30	85	312	
Gulf of Paria Venezuela			10.0-40 29	5.0-22 14	5.0-24 18	1.0-37 13	48-158 89	Rojas de Astudillo et al., 2005

Bd= below detection.

The sediments in Port Kembla contain moderate concentration of Ni compared to the other harbours. The study results also demonstrate the second highest concentration of Co at Port Eden in comparison to the other harbours listed in Table 4.4.

The significant differences in the calculated parameters between the background and study area were determined by ANOVA. Prior to the analysis, the normality and homogeneity variance assumptions were checked and, when necessary, a log(1 + x) transformation data was utilized. The variation of trace metals between the different locations by means of ANOVA was found significant ($P < 0.05$) for Port Kembla ($P = 0.024$), Port Newcastle ($P = 0.04$) and Port Eden ($P = 0.005$) (Table 4.5) which demonstrates the impact of port activities on the sedimentary environments of the ports.

Table 4-5. Significance analysis in metal concentrations between the background and port sediments.

	F	Df	P
Port Jackson	0.0351	37	0.85
Port Botany	0.206	37	0.65
Port Kembla	5.503	37	0.024
Port Newcastle	4.25	37	0.04
Port Yamba	0.021	37	0.88
Port Eden	8.91	37	0.005

Significant if $P < 0.05$

Correlation analysis was also performed on the normalized data set to test the relationship between the environmental parameters (Table 4.6). According to the Pearson statistical analysis ($P < .05$) Cr shows strong positive relationship with Al and As, whereas Cu shows strong positive correlation with As and Cr. Fe is positively correlated with Al, As, Cr and Cu. In contrast, Ni shows strong positive relation with As, Cr, Cu and Fe. Significant positive relationships are also found between Pb and Al, As, Cr, Cu, Fe, Mn and Ni.

Table 4-6. Correlation matrix for metals, sand and TOC in surface sediments from studied ports of NSW.

	Al	***As***	***Cr***	***Cu***	***Fe***	***Mn***	***Ni***	***Pb***	***Zn***	***V***	***Bo***	***Co***	***Mo***	***Ba***	***Sn***	***Sr***	***Ti***	***TOC***	***Fsand***	***Msand***	***Csand***
Al	1.00																				
As	0.76	1.00																			
Cr	**0.87***	**0.96***	1.00																		
Cu	0.78	**0.92***	**0.97***	1.00																	
Fe	**0.82***	**0.95***	**0.94***	**0.90***	1.00																
Mn	0.69	0.79	0.67	0.52	0.77	1.00															
Ni	0.70	**0.96***	**0.90***	**0.86***	**0.84***	0.78	1.00														
Pb	**0.87***	**0.98***	**0.96***	**0.88***	**0.96***	**0.86***	**0.93***	1.00													
Zn	**0.87***	**0.97***	**0.98***	**0.94***	**0.99***	0.76	**0.88***	**0.98***	1.00												
V	0.79	**0.88***	**0.83***	0.70	**0.87***	**0.91***	**0.82***	**0.92***	**0.88***	1.00											
Bo	**0.83***	**0.98***	**0.95***	**0.90***	**0.98***	**0.83***	**0.92***	**0.99***	**0.98***	**0.89***	1.00										
Co	0.78	0.77	**0.88***	**0.92***	**0.83***	0.39	0.68	0.77	**0.85***	0.51	**0.81***	1.00									
Mo	0.61	0.62	0.76	**0.85***	0.73	0.14	0.47	0.59	0.73	0.35	0.64	**0.94***	1.00								
Ba	**0.94***	**0.85***	**0.91***	**0.85***	**0.93***	0.73	0.75	**0.92***	**0.94***	0.79	**0.92***	**0.88***	0.73	1.00							
Sn	0.76	**0.89***	**0.93***	**0.94***	**0.82***	0.55	**0.90***	**0.86***	**0.87***	0.62	**0.87***	**0.89***	0.73	**0.82***	1.00						
Sr	**0.83***	**0.89***	**0.88***	0.78	0.79	**0.81***	**0.93***	**0.92***	**0.86***	**0.89***	**0.87***	0.60	0.37	0.77	**0.82***	1.00					
Ti	**0.83***	**0.91***	**0.88***	0.78	**0.94***	**0.86***	**0.80***	**0.94***	**0.94***	**0.98***	**0.93***	0.64	0.51	**0.86***	0.67	**0.85***	1.00				
TOC	**0.83***	**0.85***	**0.95***	**0.97***	**0.91***	0.47	0.73	**0.85***	**0.93***	0.67	**0.86***	**0.96***	**0.92***	**0.90***	**0.87***	0.70	0.78	1.00			
Fsand	-0.21	0.07	0.09	0.30	0.12	-0.39	0.00	-0.06	0.06	-0.36	0.05	0.45	0.59	0.03	0.28	-0.30	-0.21	0.29	1.00		
Msand	0.33	0.13	0.04	-0.12	0.20	0.64	0.13	0.28	0.17	0.31	0.27	0.01	-0.26	0.37	0.03	0.22	0.27	-0.07	-0.42	1.00	
Csand	0.11	0.00	-0.02	-0.16	-0.13	0.22	0.08	0.04	-0.05	0.34	-0.07	-0.44	-0.49	-0.16	-0.20	0.35	0.19	-0.22	-0.87	-0.04	1.00

Bold* denotes significant relation.

However, Zn shows strong positive correlation with Al, As, Cr, Cu, Fe, Ni and Pb, whereas V shows positive relation with As, Cr, Fe, Mn, Ni, Pb and Zn. Analysis results explain that the occurrence of B is strongly related with all the studied metals, except for Mo. In addition, Co shows positive correlation with Cr, Cu, Fe, Zn and Bo, while Mo shows relation with Cu and Co. The occurrence of Ba is related with the occurrence of Al, As, Cr, Cu, Fe, Pb, Zn, Bo and Co, while the occurrence of Sn is related with As, Cr, Cu, Fe, Ni, Pb, Zn, Bo, Co and Ba. Furthermore, Sr shows positive relationship with Al, As, Cr, Mn, Ni, Pb, Zn, V, Bo and Sn and Ti shows strong positive correlation with Al, As, Cr, Fe, Mn, Ni, Pb, Zn, V, Bo, Ba and Sr. Finally, the occurrence of Al, As, Cr, Cu, Fe, Pb, Zn, Bo, Co, Mo, Ba and Sn are strongly related with the occurrence of TOC.

The I_{geo} index and Enrichment Factor calculated for the different metals are presented in Table 4.7. The results show that Port Jackson and Port Botany are moderately contaminated with Mn and Al (as I_{geo}=1-2) whereas Port Kembla is extremely contaminated with Cu and Pb (as I_{geo}> 5), strongly to extremely contaminated by Zn (I_{geo}=4-5), strongly contaminated by Mn (as I_{geo}=3-4) and moderately to strongly contaminated by Al, Cr, Fe and Ba (I_{geo}=2-3). Port Newcastle is extremely contaminated by Zn, strongly to extremely contaminated by Mn and Pb, strongly contaminated by Ba and moderately to strongly contaminated by Al and Ti (I_{geo}=2-3). The I_{geo} index reveals that Port Yamba is not significantly contaminated by any metal while Port Eden is extremely contaminated by Cu and Zn (as I_{geo}> 5), strongly to extremely contaminated by As, Cr and Pb (I_{geo}=4-5), strongly contaminated by Ba (I_{geo}=3-4) and moderately to strongly contaminated by Fe, Mn and Ti (I_{geo}=2-3).

The enrichment factor analysis presented in Table 4. 7 shows that the sediments of Port Jackson are heavily enriched with As, Mn, Ni (EF > 3), while Port Botany and Port Yamba sediments are not enriched with any metal. The study results explain that Port Kembla is heavily enriched with Cu, Pb and Zn (EF > 5) while Port Newcastle is heavily enriched with Mn, Pb and Zn (EF > 3). Extremely high enrichment factor for Cu and Zn (EF > 21) was found at the sediments of Port Eden which demonstrate the high degree of metal enrichment from anthropogenic activities.

Table 4-7. Geoaccumulation index and Enrichment factor of different metals in the surface sediment of the study ports.

	Igeo index										**Enrichment Factor**						
	Al	**As**	**Cr**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**	**Ba**	**Ti**	**As**	**Cr**	**Cu**	**Mn**	**Ni**	**Pb**	**Zn**
Port Jackson	-0.51	2.00	-0.58	-0.58	-0.70	1.11	-0.42	-0.96	-3.91	0.42	6.49	1.08	1.08	3.50	3.25	1.22	0.84
Port Botany	1.15		0.42	-0.58	0.09	0.42	-1.17	-0.36	0.41	0.70		1.25	0.63	1.25	0.00	0.42	0.73
Port Kembla	2.06	-4.02	2.87	5.30	2.46	3.26	5.62	4.97	2.22	1.27	0.01	1.33	7.15	1.74	2.43	8.97	5.70
Port Newcastle	2.23	1.42	1.42	1.58	2.02	4.95	4.00	5.70	3.17	2.32	0.66	0.66	0.66	7.59	0.49	3.94	12.80
Port Yamba	-0.75		0.30	0.30	-1.12	-2.07		-0.58		-0.96		1.45	1.45	0.52	0.00	1.45	1.45
Port Eden	1.61	4.27	4.37	8.64	2.83	2.15	4.20	7.29	3.22	2.80	2.71	2.90	55.85	0.62	0.56	2.57	21.92

Table 4-8. PER and PLI of different metals of sampling site in the surface sediments of the study area

Study Area	**E**								**PER**	**PLI**
	As	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cr**	**Mn**		
Port Jackson	60	5	18	5.625	0.7727	-	2	3.24	94.63	1.18
Port Botany	0	5	0	3.333	1.1666	-	4	2	15.5	1.62
Port Kembla	0.925	295	120	370	47	180	22	14.36	1049.28	6.57
Port Newcastle	40	20	18	120	78	-	8	46.25	330.25	5.30
Port Yamba	0	5	0	5	1	-	2	0.35	13.36	0.82
Port Eden	290	2987.5	36	137.5	234.5	-	62	6.64	3754.14	11.79

PER= potential ecological risk index, PLI= pollution load index.

The potential ecological risk of one metal or a combination of multiple metals was determined using potential ecological risk index (PER). The calculated PER values can be categorized into 5 classes of potential ecological risks: low grade (PER < 150), moderate (150 < PER < 300), severe (300 < PER < 600) and serious (PER > 600) (Hakanson, 1980). The calculated PER values of the current study show that Port Kembla and Port Eden are in serious ecological risk (as PER > 600) and Port Newcastle is in severe risk (PER > 300). As PER values for the other ports are below 150 therefore, they are not under the potential ecological risk areas (Table 4.8).

Pollution load index (PLI) for the ports is shown in Table 4.8, which is an aggregative explanation for the overall level of trace metal pollution in the sediments. The calculated PLI values of the study areas clearly indicate the studied ports are heavily polluted (PLI > 1) by metals except for Port Yamba (PLI < 1).

In this study the principal component analysis (PCA) was performed to group the pollutants and identify the differences in the contamination levels of trace metals in the six studied ports of NSW. By extracting the eigenvalues and eigenvectors from the correlation matrix, three significant principal components were determined, as shown in Table 4.9, where the results of the PCA for the data of surface sediments (PCA loadings > 0.4) are shown in bold, while the eigenvalues, percent of variance and eigenvectors are given for the first three principal components.

The first eigenvalues produced 79.87% of the total variance, demonstrating they were the most important factors. The first generated factors had the highest weights (> 0.9) for Zn, Pb, Bo, Cr, Fe, As, Ba, Ti, Cu, Ni and moderate weights (0.89-0.69) for Sr, Al, Sn, V, Co, Mn and Mo, therefore, demonstrate the anthropogenic sources of the factors and indicate the adverse impacts of the port activities. The second group of components which created 9.43% of the total variance did not show any significant factors, while in the third group only one factor (Si) had moderate weight (0.80).

Table 4-9. Varimax normalization rotated loading for three factors obtained according to pollutants in the sediment samples of the studied sea ports.

	PC1	PC2	PC3
Eigen value	14.38	1.69	1.28
Variance (%)	79.87	9.43	7.09
Cumulative (%)	79.87	89.3	96.39
Eigenvectors			
Zn	**0.995**		
Pb	**0.991**		
Bo	**0.988**		
Cr	**0.982**		
Fe	**0.972**		
AS	**0.969**		
Ba	**0.947**		0.318
Ti	**0.928**		
Cu	**0.927**	-0.357	
Ni	**0.907**		-0.375
Sr	**0.894**		
Al	**0.893**		
Sn	**0.892**	-0.31	
V	**0.883**	0.395	
Co	**0.844**	-0.47	
Mn	**0.789**	**0.586**	
Mo	**0.687**	-0.655	
Si	0.396	0.41	**0.807**

The sediment pollution indexes (SPI) were calculated to evaluate the sediment quality of the study areas based on the most important parameters extracted by PCA. The quality rating of the individual variables was calculated from the percentile of the variable in the dataset. The weight of each variable was also calculated by multiplying relative eigenvalues with the relative loading values obtained from PCA (Table 4.10). Table 4.11 shows that for Fe bad quality (SPI > 100) sediments are found in almost all ports, except for Port Botany and Port Yamba. The SPI of the other elements presented a general good sediment quality with the mean value of <39 in almost all port areas. However, Zn and Cu (SPI > 90) at Port Eden strongly suggests bad sediment quality at the port area.

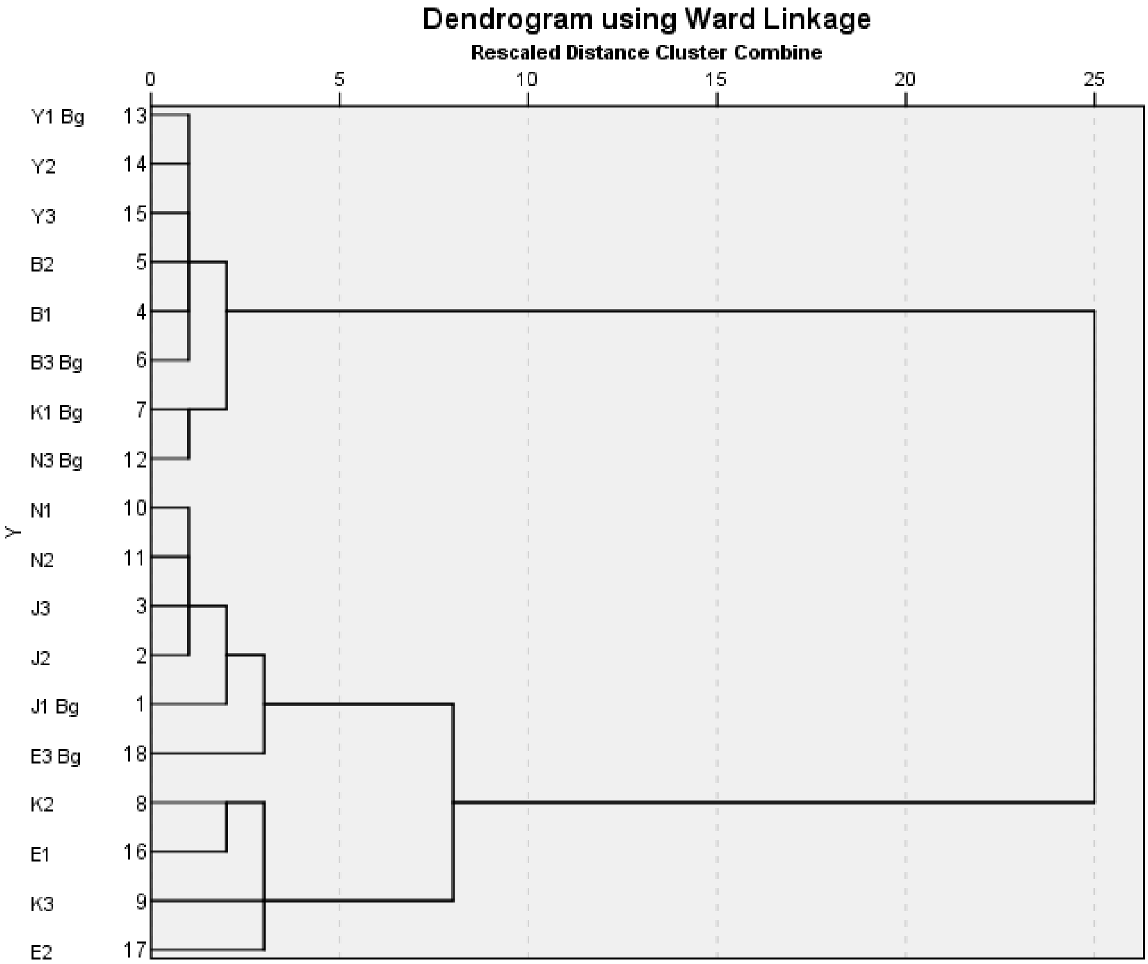
Table 4-10. Weight for the variables selected from the principal component analysis (PCA) for the calculation of sediment pollution index

PC	**Eigen value**	**Relative Eigen value**	**Variable**	**Loading value**	**Relative loading value**	**Weight (Relative Eigen value*Relative Loading Value)**
1	14.38	0.828818444	Zn	0.995	0.103581095	0.08584992
			Pb	0.991	0.103164689	0.0855048
			Bo	0.988	0.102852384	0.08524595
			Cr	0.982	0.102227774	0.08472826
			Fe	0.972	0.101186758	0.08386545
			AS	0.969	0.100874453	0.08360661
			Ba	0.947	0.098584218	0.08170842
			Ti	0.928	0.096606288	0.08006907
			Cu	0.927	0.096502186	0.07998279
			Ni	0.907	0.094420154	0.07825717
			Total	9.606	1	
2	1.69	0.09740634	Mn	0.586	1	0.09740634
3	1.28	0.073775216	Si	0.807	1	0.07377522

Table 4-11. Sediment Pollution Index

	Zn	**Pb**	**Bo**	**Cr**	**Fe**	**As**	**Ba**	**Ti**	**Cu**	**Ni**	**Mn**	**Si**
Port Jackson	0.1900	0.0030	0.0000	0.0002	1349.318	0.0009	0.0002	0.1287	0.0008	0.0001	0.4133	0.1102
Port Botany	0.0001	0.0000	0.0002	0.0000	1.6465	0.0000	0.0000	0.0007	0.0000	0.0000	0.0000	0.0314
Port Kembla	2.6049	0.2600	0.0026	0.0055	2880.886	0.0153	0.0012	0.0510	0.1425	0.0245	3.8332	0.0054
Port Newcastle	0.0720	0.0150	0.0005	0.0002	316.109	0.0002	0.0078	0.0144	0.0002	0.0001	2.0783	3.1350
Port Yamba	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0001	0.0000
Port Eden	405.2900	1.9904	0.0153	0.0690	148827.039	0.0588	0.1178	0.3416	91.3543	0.0056	0.0809	0.3483

Hierarchical cluster analysis as a multivariate statistical technique was applied on the Euclidean distances and the dendrogram of the sampling stations, as shown in Fig 4.2. Dendrograms assist with the interpretation and understanding of the sampling stations with respect to the analysed metal concentrations and their sources. The dendrogram of the sampling stations show three clusters of metal concentrations and sampling stations. The first cluster includes all the sampling stations of Port Yamba and Port Botany with the background stations of Port Newcastle and Port Kembla, therefore, represents low metal contamination area. Cluster 2 includes all the sampling stations of Port Jackson, two stations of Port Newcastle (N_1 and N_2. without background) and the background station of Port Eden ($E_{3\ Bg}$) representing moderate enrichment of metals. Cluster 3 comprises of the remaining stations of Port Kembla (K_2, K_3) and Port Eden (E_1, E_2), which have very high enrichment of trace metals and therefore, evidence the impacts of port activities on the area.



Bg=Background point of Ports; J1, J2, J3= Sampling points of Port Jackson; B1, B2, B3= Sampling points of Port Botany; K1, K2, K3= Sampling points of Port Kembla; N1, N2, N3= Sampling points of Port Newcastle; Y1, Y2, Y3= Sampling points of Port Yamba; E1, E2, E3= Sampling points of Port Eden.

Fig. 4.2 Dendrogram showing cluster of sampling stations based on analysed variables.

All indices (EF, Igeo, PLI, PER and SPI) used in the present study specify varied levels of contamination in the studied areas although their end results are not consistent. This is because each index appraises different pollutants of importance for their evaluation. For instance, the enrichment factors use terrestrial element (Fe in this study) for normalization in the calculation of enrichment factor seems to unearth contamination better (as it considers more metals and sites) than Igeo, PLI and PER. Moreover, sediment pollution index (SPI) evaluates the most important parameters extracted by PCA and rates them individually from the percentile of the variable in the dataset which demonstrates Fe as the major pollutant followed by Zn and Cu at Port Eden. The EF index in most ports showed high enrichment of Cu followed by Zn at Port Eden whereas Igeo index identified extreme contamination of Cu, Zn, As, Cr and Pb in the same area. Besides PER index identified Port Eden as a serious ecologically risk area which was a result of significant concentrations of Cu followed by As, Zn and Pb. These findings clearly showcase the limitations of each index. However, the use of multivariate statistical tools (PCA and HCA) can overcome some of the limitations of the indices. They can assess the impact of multiple contaminants and their relative importance in the pollution of the environment. In the present study PCA identified Zn as the most important element followed by Pb, B, Cr and Fe in all study ports which portray the generalized results for different areas. The HCA analysis can solve the problem by presenting the clusters of contributing elements with their sources, presented as dendrogram. Among all the analysis methods this can be the simplest and effective method for presenting the contaminants at different places with their relation to one another.

4.4 Conclusions

Concentrations and spatial distributions of trace metals (Al, As, Cr, Cu, Fe, Mn, Ni, Pb, Zn, V, B, Co, Mo, Ba, Sn, Si, Sr, and Ti), inorganic nutrients and organic carbon were analysed for the surface sediments of six important sea ports of NSW. The study results demonstrate that, the surface sediments of Port Eden contain significant concentrations of trace metals followed by Port Kembla, Port Jackson and Port Newcastle. The concentrations of As, Cu, Fe, Pb, Ni, Co and Zn in the surface sediments of the port areas were much higher than the background values and the standards given by ANZECC and other international guidelines. The maximum concentrations of Al, B, Co, Mo, Ba, Sn, Sr and Ti were also much higher than the background surface sediments, indicating enrichment of these metals at the study ports, although currently no guidelines exist for the concentration of these elements in sediments. The significance of variations among background and study areas strongly suggests that port activities are contributing to metal contamination in the environment. The different sediment quality indices used in the present study reveal different aspects of pollution. The geo-accumulation index suggests that Port Kembla, Port Newcastle and Port Eden are extremely contaminated (as I_{geo}> 5) by Cu, Pb and Zn, whereas the EF focuses on the anthropogenic impacts on the sedimentary environment suggesting that As, Cr, Cu, Mn, Ni, Pb and Zn in the port sediments mainly originate from inputs of anthropogenic origin. The PER values represent integrated degree of contamination that illustrates ecological risk, reporting that Port Kembla and Port Eden are at serious ecological risk (as PER > 600), followed by Port Newcastle as a port in severe risk (PER >300). The PLI is also a summative indication of overall metal pollution indicating that all of the study ports are heavily polluted (PLI > 1) by trace metals except for Port Yamba (PLI < 1). The calculated SPI reveals poor quality (SPI >90) sediments in almost all ports except Port Botany and Port Yamba. The principal component analysis states that the three major component groups comprise about 96.39 % of the total variance with the dominance of first components group (76.87%). Finally, the dendrogram which distinctly presents the cluster of sampling stations based on analysed variables, clearly displays that among three cluster groups the third cluster which comprises Port Kembla and Port Eden are highly enriched with metals (Pb, Zn, Sr, Si) compared to other clusters. The comparative analysis among all the indices demonstrates that the dendrogram is the most effective and simplified way to describe, compare and correlate the sedimentary status of different stations.

4.5 References

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Chapter 5: Assessment of trace element pollution in the sea ports of New South Wales (NSW), Australia using oysters as bioindicators

Due to extensive sources, persistent nature and toxicity, trace elements are considered some of the main contaminants with substantial effects on marine and estuarine biota. Oysters are considered to be one of the best bioindicators for coastal pollution studies due to their specific life traits, such as a sessile and filter-feeding behaviour, a wide geographical distribution, abundance, sedentary and their relative resilience to pollutants. In this chapter Sydney rock oyster (*S. glomerata*) was used as a bioindicator to assess the distribution and levels of trace element accumulation in the seaports. The analysed results were then compared to their background samples and the United States Environmental Protection Agency (USEPA) provisional tolerable intake standards.

Authors Contributions

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Assessment of trace element pollution in the sea ports of New South Wales (NSW), Australia using oysters as bioindicators

Abstract

In this study Sydney rock oysters (*S. glomerata*) from six major sea ports of NSW, Australia were used as bioindicators to assess the distribution and levels of trace element accumulation in the ports. Substantial enrichment of Cu, Pb and Zn in the oysters of the sea ports were detected when compared to their background samples and the United States Environmental Protection Agency (USEPA) provisional tolerable intake standard. Enrichment of As, Al, Fe, Mn, Br, Sr were also found in the oysters at the port areas. The bioconcentration ratios of the trace elements illustrated significant Fe, Cu, Zn, As, Mn, Al, Pb and Cr accumulation in *S. glomerate*. The biota sediment accumulation factor suggested Cu, Mn and Zn accumulation at two of the ports (Port Yamba and Port Botany), indicating availability of these metals in the oysters as strong metal accumulators. In addition, integrated metal contamination illustrated notable Fe, Zn, Cu and Al contamination at port environment, whereas cluster analysis portrayed interconnection between the contaminants and the study sites.

Key Words: Trace elements, Bioaccumulation, Oyster, Seaports, Australia.

5.1 Introduction

Trace element contamination is considered as one of the major issues in marine and estuarine environments due to their diverse sources, persistence, bioaccumulation, non-degradability and harmful effects on biota (Pan and Wang, 2012, Wang et al., 2013, Wang et al., 2014, Kumar et al., 2015, Le et al., 2016, Yin and Wang, 2017). The ecological status of the aquatic environment can be evaluated by analysing the distribution of trace elements in water, sediments and marine organisms (Bazzi, 2014). In most cases, contaminated site assessment typically demands analysis of water and sediments to measure total trace elements concentrations, but often this is not a sufficient predictor of trace element toxicity to biota (Jahan and Strezov, 2019, Topcuoglu et al., 2003). To overcome the problem, biomonitoring offers advantage as marine organisms' (oysters, mussels, and clams) evident greater spatial tolerance to elemental toxicity compared to water and sediments. They have, therefore gained universal acceptance as a reliable medium to detect sources of biologically available trace element contamination

(Bazzi, 2014, Spooner et al., 2003, Yin and Wang, 2017). However, bivalve molluscs are considered to be one of the best bioindicators for coastal pollution studies due to their specific life traits, such as a sessile and filter-feeding behaviour, a wide geographical distribution, abundance, sedentary and a relative resilience to pollutants (Goldberg, 1986, Yin and Wang, 2017). Moreover, mollusc bivalves have the potential to accumulate chemical compounds at levels of 10^3 at 10^5 times more than other species (Meng et al., 2017). Hence, since the 1970's a Worldwide scheme for monitoring ocean health by using mussels and oysters has been introduced (Goldberg, 1975; Watling and Watling, 1976; Phillips, 1977; Davies and Pirie, 1980).

The specific ability of oysters to accumulate pollutants makes them candidate species for biomonitoring contaminant exposure to their potential biological effects (Goldberg, 1986, Oliver et al., 2001, Valdez Domingos et al., 2007, Yin and Wang, 2017). Furthermore, oysters are often used as sentinel organisms due to their rapid adaptive capacity to the new environment. In Australia an integrated approach, including analysis of oysters as bioindicator and for quantification of elements in biota, was analysed to monitor the impact of trace elements on port ecosystems (Nasci et al., 1999, Séguin et al., 2016). As a common food source, it also urges investigation of the impact of marine activities on trace elements accumulation in oysters.

Australian sea ports, which accommodate industry, commerce, tourism and recreation, often exacerbate trace elements contamination from different port related activities (transport and storage of hazardous materials, industrial installation, recreational shipping etc) (Batley, 1987, Birch et al., 1996, Birch and Taylor, 1999, Creighton and Twining, 2010, Jahan and Strezov, 2018, Roach, 2005). This influences the growth rate and fecundity of marine biota and ultimately reduces the population diversity (Creighton and Twining, 2010, Ellis et al., 2017, McCready et al., 2006, Stark, 1998, Twining et al., 2008) and reduces their suitability as a food source for humans (Ahdy et al., 2007).

Among oysters, *S. glomerata* has been evidenced to be one of the most suitable organisms for biomonitoring chemical contamination in coasts and estuaries (Thompson et al., 2011). They are widely used as a sentinel organism for its capacity to concentrate pollutants, its idleness, its limited ability to metabolize accumulated contaminants, its abundance, persistence, and ease of collection. Therefore, make them useful stable bioindicators for environment change (Luna-Acosta et al., 2017). In the present study *S.*

glomerata was used as the bioindicator to investigate the levels of trace element contamination in port environments and as also applied by Goldberg et al. (1983) and Thompson et al. (2011). Evidence also suggested that *S. glomerata* is widely distributed species along the coastal belts of NSW that also acts as a suitable candidate species to compare between sites (Lanlan et al., 2016,Thompson et al., 2011).

The objective of this study was to assess the trace elements concentrations in the oysters of NSW sea ports to determine the variations of trace element bioaccumulation in the oysters under different port activities and to explore the level of trace element pollution in oysters which ultimately provides a scenario of stress on port environments. Finally, the present study typifies a new perspective for biomonitoring and risk assessment of trace elements in aquatic ecosystems using principal component and hierarchical cluster analysis methods.

5.2 Materials and methods

5.2.1 Study site

The field study was conducted at the six major sea ports in NSW, Australia, namely Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden (Fig. 5.1). These ports are away from each other and are engaged with different shipping activities (23 km -1198 km). Port Jackson of Sydney Harbour, which accommodates cruise shipping, pleasure boating and water sports, is a well-mixed estuary (Jahan and Strezov, 2017). Port Botany is another important port of Sydney mainly engaged with shipping of containers, crude oil, fossil fuel, chemicals and bio-fuels. Port Kembla is a prime export location for coal, grain terminal, bulk liquids, oil, fertiliser, pulp and steel products. The port is important for export and import of different mineral ores and petroleum products. Port Newcastle is the world largest port for coal export by tonnage that is also engaged with export and import of raw materials for steelworks, fertiliser and aluminium industries, grain, steel products, mineral sands and woodchips. Port Yamba is the eastern most sea port of New South Wales located at the mouth of the Clarence River. It is the 2nd largest fishing port of New South Wales dealing with container liquid berth-livestock and explosive products. The Port of Eden is located in the South Coast region of New South Wales, Australia. The Port is the largest fishing port of New South Wales also engaged with export and import of woodchips, break bulk, machinery and equipment for the oil and gas industry (Jahan and Strezov, 2018, Harris and O’Brien, 1998). The study locations are shown in Fig. 5.1.

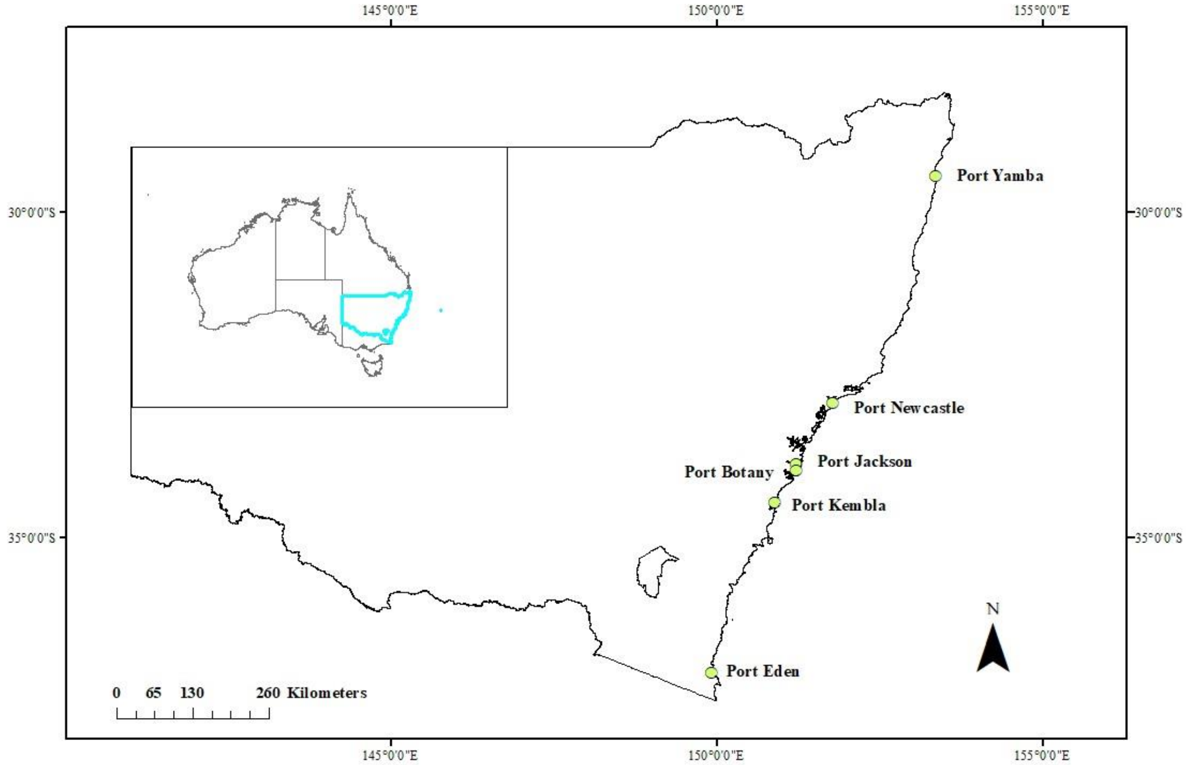

Fig. 5. 1 Map of the study area showing study ports of NSW

5.2.2 Sample collection and processing

Oyster samples known as Sydney rock oyster (*S. glomerata)* of different shell sizes (3cm -7cm) were collected from the six sea ports from April - June 2017. Three sampling points from each port were selected based on the availability of Sydney rock oyster to collect samples. Among the three points, two were from port areas and one was from a background site (selected from the same hydrogeological but non-port area). In this study, >40 indigenous oysters from each sampling point were collected by hand from dock columns and rocks in surface water (0 –1 m). Immediately after collection, the oysters were stored in bags in a cooler box with ice and transported to the laboratory. About 20 oyster samples were selected from each sampling point and their tissues and shells were separateted. The tissues were then dried in an oven at 105 ± 5 °C for 8 hours to a constant weight (Baltas et al., 2016). The soft tissue, after the removal of the liquid, was then weighted. Prior to analysis, the dried samples were ground. For each sampling point, the powdered sample was divided, and the analysis repeated twice.

5.2.3 Analytical procedure

The oyster tissue samples (0.05g) were digested in 1 mL concentrated HNO_3 acid at 80°C on the hot plate for 24 hours until the samples were completely digested. The sample solutions were then diluted three times with Milli-Q water. Metals and major element (Ag, Al, As, Cd, Cr, Cu, fe, Mn, Ni, Pb, Se, Zn, Hg, Be, V, B, Co, Mo, Sb, Ba,Bi, Sn, Si, Br, Sr, Rb, U, Ti, I) concentrations (Séguin et al., 2016) in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700X and Varian vista-pro ICP-AES) respectively, while mercury was determined by cold vapour atomic absorption spectroscopy (CV-AAS) to reach the PQLs (practical quantitation limits). Quality and accuracy of the experimental procedure and the equipment was ensured using replicate analyses, certified referennce material (CRM) (oyster tissue, SRM 1566b) and sample spikes. The recovery percentage of all trace metals in CRM were 90-110% and the analytical precision expressed as coefficients of variance was <10% for all the metals based on replicate analysis. The detection limit of the method (MDL) was estimated as the standard error of 10 blank replicates (Federal Register, 1984). The recovery percentage and detection limits of all trace elements are presented in Table S5.1 in **Appendix D.**

5.2.4 Data Processing

5.2.4.1 Bioconcentration Ratio (BCR)

Bioconcentration is a process in which biological organisms absorb a chemical compound from their surrounding environment through different body parts (Jonathan et al., 2017). It is a quantitative measure of the biota's bioaccumulative capacity (Zalewska and Suplińska, 2012). The measured bioconcentration ratios also form the base for assessing the risk of adverse effects of hazardous substances on specific biota (IAEA, 2014). The extent of bioconcentration is calculated by using the formula (1) (Arnot and Gobas, 2006):

$$BCR = \frac{C_{Organism}}{C_{Water}} \quad \text{.....(1)}$$

where $C_{Organism}$ is the concentration (mg/kg) of an element in the oyster, which was measured in this study, while C_{Water} is the concentration (mg/l) of the same element in the water of the same study locations, which was derived from the mean values from Table 3-4. of chapter three. When the BCR is >1, bioaccumulation is considered.

5.2.4.2 Biota sediment accummulation factor (BSAF)

Biota sediment accumulation factor (BSAF) is the ratio between the concentration of element in a biota to the concentration of same element in sediment (Thomann et al., 1995). The BSAF for each element in the sample is calculated with equation (2):

$$BSAF = \frac{C_{Organism}}{C_{Sediment}} \quad \text{.........(2)}$$

where $C_{Organism}$ and $C_{Sediment}$ are the concentrations(mg/kg) of trace elements in the oyster and in sediment (Negri et al., 2006). Typically, BSAF value >1 indicates bioaccumulation of trace element. In this work, the sedimentary metal concentrations for the same sea ports, study locations and the same time of sampling were derived from Table 4-3. of chapter four.

5.2.4.3 Integrated metal contamination (IMC)

The severity of metal pollution can be determined using the integrated metal contamination equation (3) given by Liu and Wang (2012).

$$IMC = \sum_{i=0}^{m} C^{i}_{Contaminated} - C^{i}_{Clean} \quad \text{.........(3)}$$

Where $C^{i}_{Contaminated}$ is the concentration(mg/kg) of i metal in a contaminated oyster obtained from the port area, C^{i}_{Clean} is a reference value (mg/kg) for the i metal in oyster obtained from the background site of each port, while m is the number of metals investigated, which is m=13 for this calculation.

5.2.5 Statistical analysis

Statistical analysis was performed by using Microsoft excel and SPSS version 24. Analysed metal concentrations were presented as normalized concentration for standardized weight and length. The normality distribution of data were tested by Kolmogorov-Smirnov test and then normalized and analyzed using the multivariate statistical tools principal component analysis (PCA) and hierarchical cluster analysis (HCA) using both cases and variables to develop groups and identify links between elements and sampling sites by dendrogram as described by Jahan and Strezov (2018). The PCA and HCA were used to indentify the possible sources of trace elements in the sediments and group them based on their similarities. For PCA, only PCs with eigenvalue

>1 were retained and variables were centered as mean (Kaiser, 1960). Varimax rotation was applied to component loadings greater than 0.5 to facilitate the interpretation of the outcomes (Loska and Wiechuła, 2003).

5.3 Results & discussion

Bioaccumulation pattern and normalized concentrations of trace elements (whose concentrations are significantly high) in the soft tissue of the oysters (30-40g and 5-7 cm) (*Saccostrea glomerata*) are shown in Table 5.1. The concentrations of As in Port Jackson, Port Botany, Port Kembla and Port Eden range from 5 to 9 mg/kg which are significantly higher than their background concentrations (1.88 mg/kg) in oysters of the NSW coast given by Scanes and Roach (1999), and are also higher than the standard quality guidelines for bivalve molluscs (4 mg/kg) given by FAO (1989). However, in Australia and New Zealand, the regulation appllied to seafood is related to inorganic As. This is because marine organisms and plants, such as shellfish, molluscs and seaweed, can contain high levels of As, but mostly in organic arsenosugar forms (Andrewes et al., 2004).

The Cu concentrations in the oysters of all ports were found to be higher than the USEPA (provisional tolerable intake) (USEPA, 2013) standard (0.05 mg/kg) and FAO standard quality guidelines for bivalve molluscs (20 mg/kg) (FAO, 1989). The highest concentration of Cu was detected at Port Yamba (61 mg/kg), which is above the standards and is identified as unsafe food (Pazi et al., 2017). Cu enrichment in the oysters at Port Botany, Port Kembla, Port Newcastle and Port Yamba compared to their background sites demonstrates the impacts of port activities which are associated with trade of coal, steel products, crude oil, fossil fuels, chemicals, fertilisers, mineral sands, preservative chemicals from wood chips and storage of hazardous products in the port vicinity (Jahan and Strezov, 2017). However, Cu concentrations found in oysters are also associated with higher assimilation efficiencies and bioavailability in the port environment. The normalized Pb concentrations in the studied *S. glomerata* species at Port Kembla exhibited six-fold increase when compared to the maximum permissible limits recommended by Food and Drug Administration (FDA, 1993) and recommended as unsafe for human consumption.

Table 5-1. Comparison of the studied trace elements concentrations (normalized concentration mean±SD. for 30-40g standardized weight and 5-7cm length) in *S. glomerata* with that of the maximum permissible limits set forth by various organizations.

Parameters	mg/kg dry wt.	Al	As	Cr	Cu	Fe	Mn	Pb	Zn	Bo	Si	Br	Sr	Ti
Port Jackson	Bg	14	7	Bd	16	240	3	2	43	5	40	53	14	Bd
	Study point	21±7.2	8.5±1	Bd	6±6.5	560±440	5.5±3.8	2±0	45±12	4±0	35±7	53±1.4	155±162	Bd
Port Botany	Bg	17	5	Bd	1	510	Bd	Bd	26	4	40	87	14	Bd
	Study point	12±4.9	5±1	Bd	14±14	160±250	8	Bd	17±6	5±0	25±7	60±13.4	10±2	Bd
Port Kembla	Bg	32	4	Bd	13	140	3	Bd	23	4	30	68	180	Bd
	Study point	68.5±26.8	7.5±2.5	2±0	18±5	790±0	10±4	7±5	51±2.8	4±1.2	55±7	64±12.7	51±49.5	13±15.6
Port Newcastle	Bg	19	Bd	Bd	1	21	7	Bd	16	7	60	56	33	5
	Study point	15±2.1	Bd	Bd	10.5±5	70±38	4.5±1	Bd	35±5	3±0	25±4.2	56±2.8	51±58	Bd
Port Yamba	Bg	70	Bd	Bd	Bd	45	10	Bd	11	Bd	50	64	16	Bd
	Study point	99±82.7	Bd	Bd	40±29.7	220	23.5±5	Bd	13±3.3	5±1.4	65±49.5	55±2	7±1.4	2±1.7
Port Eden	Bg	65	10	Bd	13	250	2	Bd	12	5	50	Bd	140	2
	Study point	41±15	8±2	Bd	3±1	260±125	2.5±1	Bd	45.5±10.6	6±2.8	40±0	Bd	32±21.9	1±0
Background concentration[a]	NSW		1.9		21.6		2.5	0.09	277					
FAO 1989[b]			4		20			0.2						
US EPA 2013[c]	PTI				0.05			0.03	0.3-1					
US FDA 1993[d]				13				1.7						

Bg=background, Bd=below detection, dry wt.=dry weight, PTI= Provisional tolerable intake.
a Background concentration by Scanes & Roach (1999).
b Standard quality guidelines for bivalve mollusks (FAO, 1989).
c USEPA (2013).
d U.S Food and Drug Administration, 1993.

The Pb concentration (2-7 mg/kg) in Port Kembla is also higher than its background site and all other standards (0.2 0.025 and 1.7 mg/kg by FAO, USEPA and USFDA respectively) (Table 5.2). The industrial complexes, including the major metal smelting operations adjoining this port are likely the major sources of Pb (Luoma and Rainbow, 2005). However, Zn concentrations (13-51 mg/kg) in the oysters at all ports also demonstrate the oysters are unsafe as food as their concentrations are considerably higher than their corresponding USEPA (provisional tolerable intake) standard (0.3-1 mg/kg). It is known that molluscs possess high affinity for accumulation of Zn (Paez-Osuna and Osuna-Martínez, 2011) and it is generally agreed that the highest concentrations of Zn in marine biota are found in the tissues of filter feeding molluscs, especially oysters (Eisler, 2000). Unlike Port Eden, the oysters in all other ports contained higher concentrations of Mn than the background values given by Scanes and Roach (1999). The results also portray remarkable Mn bioaccumulation inside Port Jackson, Port Botany, Port Kembla and Port Yamba compared to their background sites. Notable amounts of Al, Fe, Br, Si and Sr were detected in almost all ports although they do not have any standard values to compare. Significant amounts of Ti was also found in the oysters at Port Kembla. In addition, concentrations of some elements (Hg, Cd, Ag, Ni, Co, Ba, Sn) were measured but found below detection limit in all study points, therefore they were not reported further.

5.3.1 Bioconcentration ratio (BCR)

BCR values in S. *glomerata* shown in Fig. 5.2 present an order of Fe > Zn > As > Cu at Port Jackson, Cu > Zn > Fe >Mn at Port Botany and Port Newcastle, Fe > Cu >As > Pb at Port Kembla, Cu > Mn > Fe > Zn at Port Yamba and Zn > Al > As > Fe at Port Eden. BCR values of As, Cr and Pb in some of the ports are less than 1 which demonstrate almost similar concentrations of those elements in oyster and water. However, only eight metals are calculated because others are below detection limit in water. BCR values greater than 1000 indicate significant and slow accumulation (Kwok et al., 2014). High BCR values also demonstrate the uptake of free metal ions from solution more effectively via dermal organs (Jayaprakas et al., 2015). BCR values of Fe and Cu in almost all ports are >1000 with the highest values (Fe=46,470, Cu=10,588) at Port Kembla which demonstrate considerable Fe and Cu concentrations in the port environment. Except for Port Kembla and Port Yamba, significant Zn concentrations (as BCR >1000) were found in all other ports.

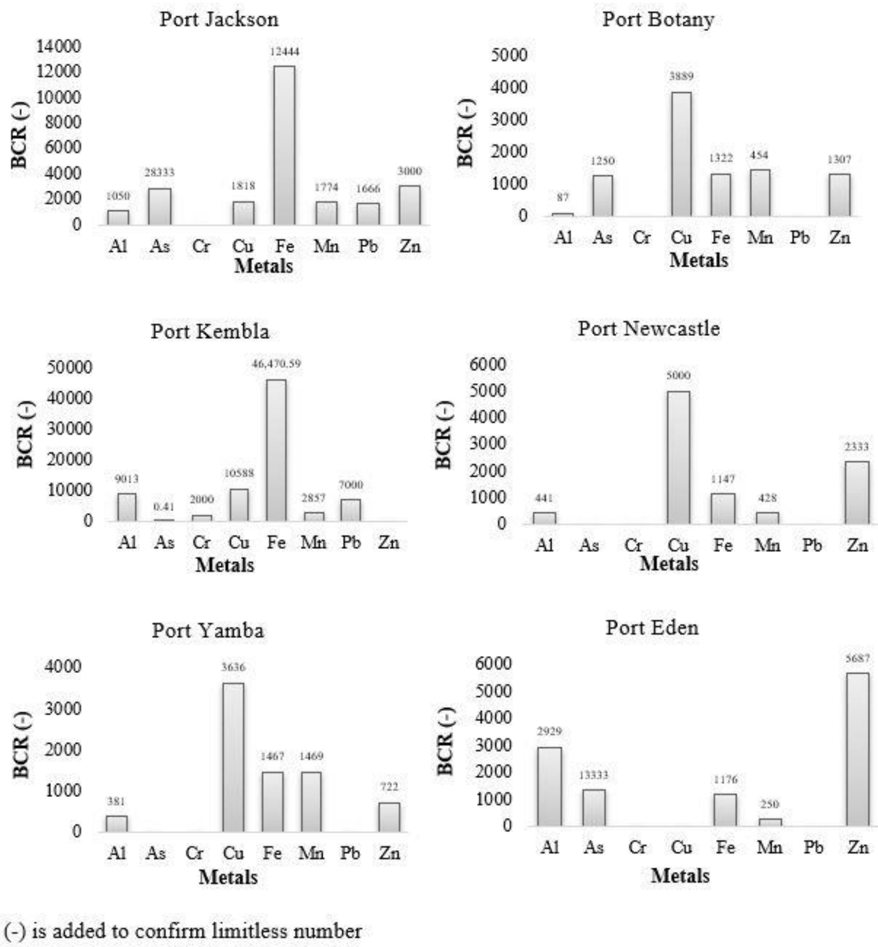

Fig. 5. 2 Bioconcentration Ratio (BCR) in oysters (*S. glomerata*) from the seaports of NSW, Australia.

5.3.2 Biota sediment accumulation factor (BSAF)

The average concentration of the trace element was applied to determine the biota sediment accumulation factor (Fig. 5.3). Significant bioaccumulation of Cu at Port Botany (7), Port Newcastle (2.63) and Port Yamba (40) and bioaccumulation of Zn (2.43 and 4.33) and Mn (4.70 and 1.33) at Port Botany and Port Yamba indicates availability of these trace metals in the port environment as well as high-level absorbing capacity in the soft tissues of the oysters. Bioaccumulation of As and Sr were observed at Port Jackson whereas Si bioaccumulation was also found in the oysters at Port Kembla.

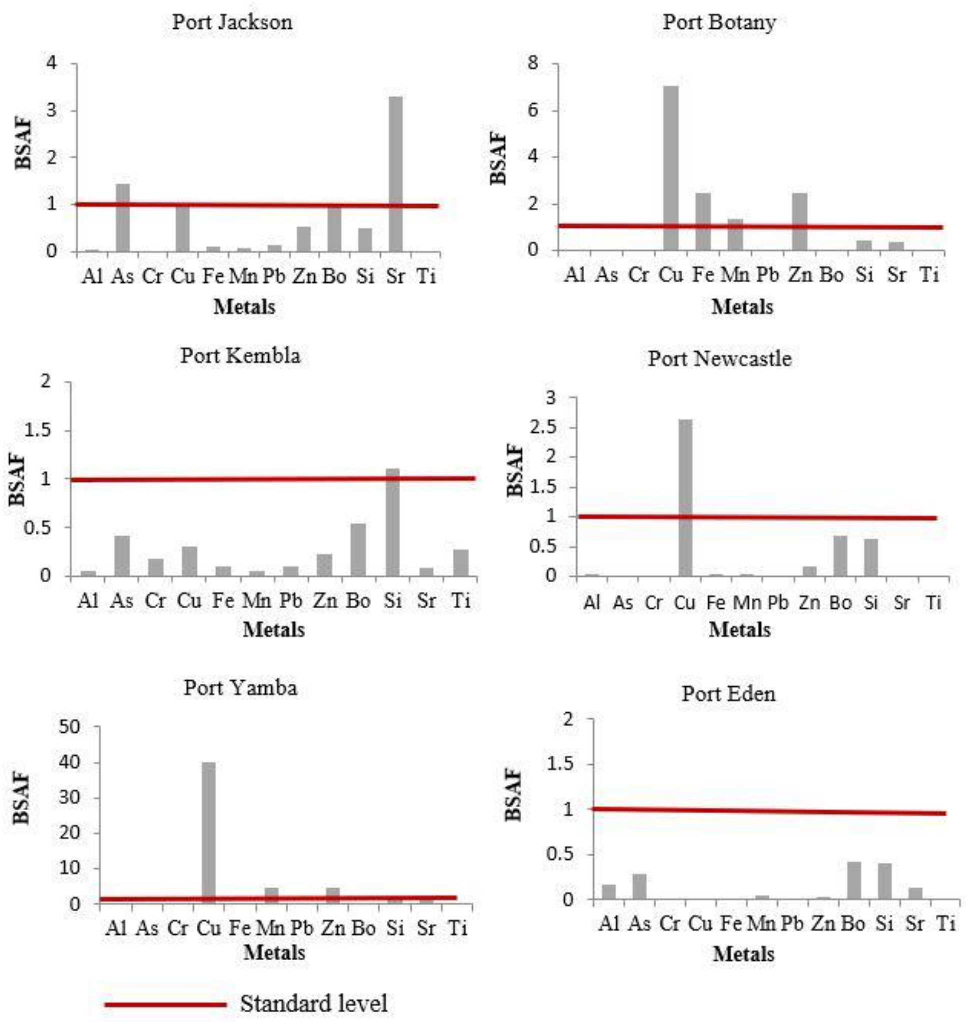

Fig. 5. 3 Biota sediment accumulation factors (BSAFs) for oysters in the study ports of NSW, Australia.

Based on the results, *S. glomerata* is considered to be strong accumulators for Cu and moderate accumulators for Zn and Mn.

5.3.3 Integrated metal concentration

The severity of metal pollution was determined by integrated metal concentration (IMC) (Table 5.2). The results suggest that the oysters at Port Eden and Port Botany are comparatively less contaminated than the oyster samples from the other port sites. The results also imply that the oysters at Port Kembla are severely contaminated followed by Port Jackson and Port Yamba with notable enrichment of Fe, Zn, Cu and Al. For calculation of IMC reference site values are required. If the reference values are affected by non-point pollution sources the IMC values may be affected because of the undue influence of one of the measurements used in the final composite values (DelValls et al., 1998). Therefore, no threshold for maximum pollution is given for this index.

Table 5-2. Integrated metal contamination (mg/kg) in the oysters of NSW seaports.

	Integrated metal concentration (mg/kg)								Total=
Port	**Al**	**As**	**Cu**	**Fe**	**Mn**	**Zn**	**Sr**	**Ti**	$\sum(C_{contaminated}-C_{clean})$
Jackson	7	1.5	-10	320	2.5	2	141	0	458
Botany	-5	0	13	-305	8	-9	-4	0	-388
Kembla	36.5	3.5	5	650	7	28	-129	13	644
Newcastle	-4	0	9.5	49	-2.5	19	18	-5	45
Yamba	29	0	40	175	13.5	2	-9	2	264
Eden	-24	-2	-10	10	0.5	33.5	-108	-1	-110

The variations of trace elements concentrations in the oysters between the background and study port areas by means of ANOVA are shown in Table 5.3. The results revealed that the variations were insignificant (P>0.05).

Table 5-3. Significance (variations were significant at P<0.05) analysis of trace elements concentrations between the background and port oysters.

Study Area	Df	P-Value
Port Jackson	24	0.45
Port Botany	24	0.46
Port Kembla	24	0.42
Port Newcastle	24	0.7
Port Yamba	24	0.29
Port Eden	24	0.76

Correlation analysis was also performed on the normalized data set to test the relationship between the environmental parameters and significant correlations among metals (Table 5.4). According to the Pearson statistical analysis (significant at $P < 0.05$) strong positive relationship exists between weight and length of oyster ($r^2 = 0.98$). Al shows strong positive correlation with Cu, Mn and Si whereas Cr shows strong positive relation with Pb and Ti. However, Cu shows strong positive correlation with Mn and Si, while Mn is strongly correlated with Si and I. Analysis results also reveal that a strong positive correlation exists between Pb and Sr.

Table 5-4. Correlation analysis of trace elements in the oyster of the seaports of NSW, Australia.

	Length	*Weight*	*Al*	*As*	*Cd*	*Cr*	*Cu*	*Fe*	*Mn*	*Ni*	*Pb*	*Zn*	*B*	*Si*	*Br*	*Sr*	*Ti*	*I*
Length	1																	
Weight	**0.987***	1.000																
Al	0.731	0.791	1.000															
As	-0.601	-0.666	-0.339	1.000														
Cd	-0.315	-0.277	0.069	0.610	1.000													
Cr	-0.125	-0.106	0.181	0.441	0.731	1.000												
Cu	0.605	0.681	**0.863***	-0.557	-0.302	-0.004	1.000											
Fe	0.044	-0.069	0.060	0.739	0.359	0.477	-0.224	1.000										
Mn	0.726	0.765	**0.931***	-0.401	-0.202	0.123	**0.947***	0.073	1.000									
Ni	0.021	0.119	0.554	-0.129	0.078	0.447	0.748	-0.121	0.655	1.000								
Pb	-0.117	-0.130	0.131	0.540	0.682	**0.980***	-0.068	0.632	0.104	0.365	1.000							
Zn	-0.241	-0.342	-0.398	0.749	0.578	0.369	-0.772	0.722	-0.538	-0.604	0.474	1.000						
B	-0.139	-0.063	0.355	0.268	0.520	-0.047	0.111	-0.047	0.083	0.106	-0.116	0.017	1.000					
Si	0.752	0.799	**0.996***	-0.315	0.032	0.183	**0.862***	0.125	**0.949***	0.544	0.149	-0.374	0.303	1.000				
Br	0.104	0.097	0.079	-0.211	-0.327	0.392	0.385	0.059	0.372	0.586	0.408	-0.349	-0.736	0.121	1.000			
Sr	0.032	-0.129	-0.384	0.475	-0.132	0.001	-0.509	0.755	-0.268	-0.574	0.191	0.690	-0.464	-0.306	0.062	1.000		
Ti	-0.138	-0.118	0.177	0.458	0.759	**0.999***	-0.022	0.478	0.105	0.432	**0.977***	0.387	-0.014	0.176	0.354	-0.007	1.000	
I	**0.900***	**0.853***	0.712	-0.368	-0.401	-0.070	0.650	0.314	**0.816***	0.156	0.000	-0.211	-0.215	0.765	0.292	0.249	-0.091	1.000

"Bold*" mark denotes strong correlation.

Principal component analysis (PCA) of the oyster data summarizes four groups of pollutants and the contamination levels of each group of pollutants in the oysters of the studied ports. Four significant principal component groups were determined by deriving the eigenvalues and eigenvectors from the correlation matrix. The percentage of the total variance of each principal component (PC) group is shown in Table 5.5. Four component groups generating about 95.8% of the total variance were obtained. The first component group consists of 37.75% of the variation with the greatest weights (>0.70) for Cu, Mn, U, Cd and Br, and moderate weights for I and Si. PC_2 accounted for 27.64% of the variation with the important components comprising of Fe, Pb, Cr and Al. PC_3 and PC_4 exhibited 21.03% and 9.37% of the variation respectively and had moderate weights for U, Br and I.

Table 5-5. Component matrix of the oysters of NSW seaports.

	PC_1	**PC_2**	**PC_3**	**PC_4**
Eigenvalues	5.66	4.15	3.16	1.40
% of variance	37.75	27.64	21.03	9.37
Cumulative %	37.75	65.39	86.42	95.80
Eigenvectors				
Cu	.94	.136	-.127	-.282
Mn	.887	.439		
U	.783		.602	-.133
Br	.769		.603	-.199
Zn	-.754	.385	.462	.232
Cd	.707	-.536	.333	.224
I	.688	.330	.114	.636
As	-.641	.457	.174	-.211
Fe	-.184	.866	.145	.36
Pb		.819	.464	-.328
Cr		.77	.301	-.509
Al	.392	.735	-.509	.147
Si	.562	.667	-.431	.203
Bo	-.27	.362	-.858	
Sr	-.507	.23	.732	.384

Extraction Method: Principal Component Analysis.

a. 4 components extracted.

The cluster analysis (HCA) results for the oysters from the sampling sites based on the trace element concentrations were presented as a dendrogram shown in Fig. 5.4. Two main different clusters were identified from the trace element enrichment dendrogram (Fig. 5.4a). The first cluster group comprising Se, Cd, U, Cr, V, Pb and Ti with two sub-groups of Se, Cd, U as one sub-group and Cr, V, Pb and Ti as the second sub-group. The second HCA cluster group also consists of two sub-cluster groups, one of which comprises of Cu, Mn and I and the other group includes Fe, Si, Zn, Al, B, Sr, Br and As.

The dendrogram can also help to explain and group the impact of port activities on trace element enrichments, as presented in Fig. 5.4b. The analysis results demonstrated that the fishing fleet activities and trade of woodchip, break and bulk machinery for the oil and gas industry at Port Eden are significantly responsible for the trace element contamination in oyster followed by the container, crude oil and bulk liquid operations (fossil fuel, chemical and bio-fuel) at Port Botany and bulk liquids, oil, fertiliser, pulp, steel products and various ores related activities at Port Kembla.

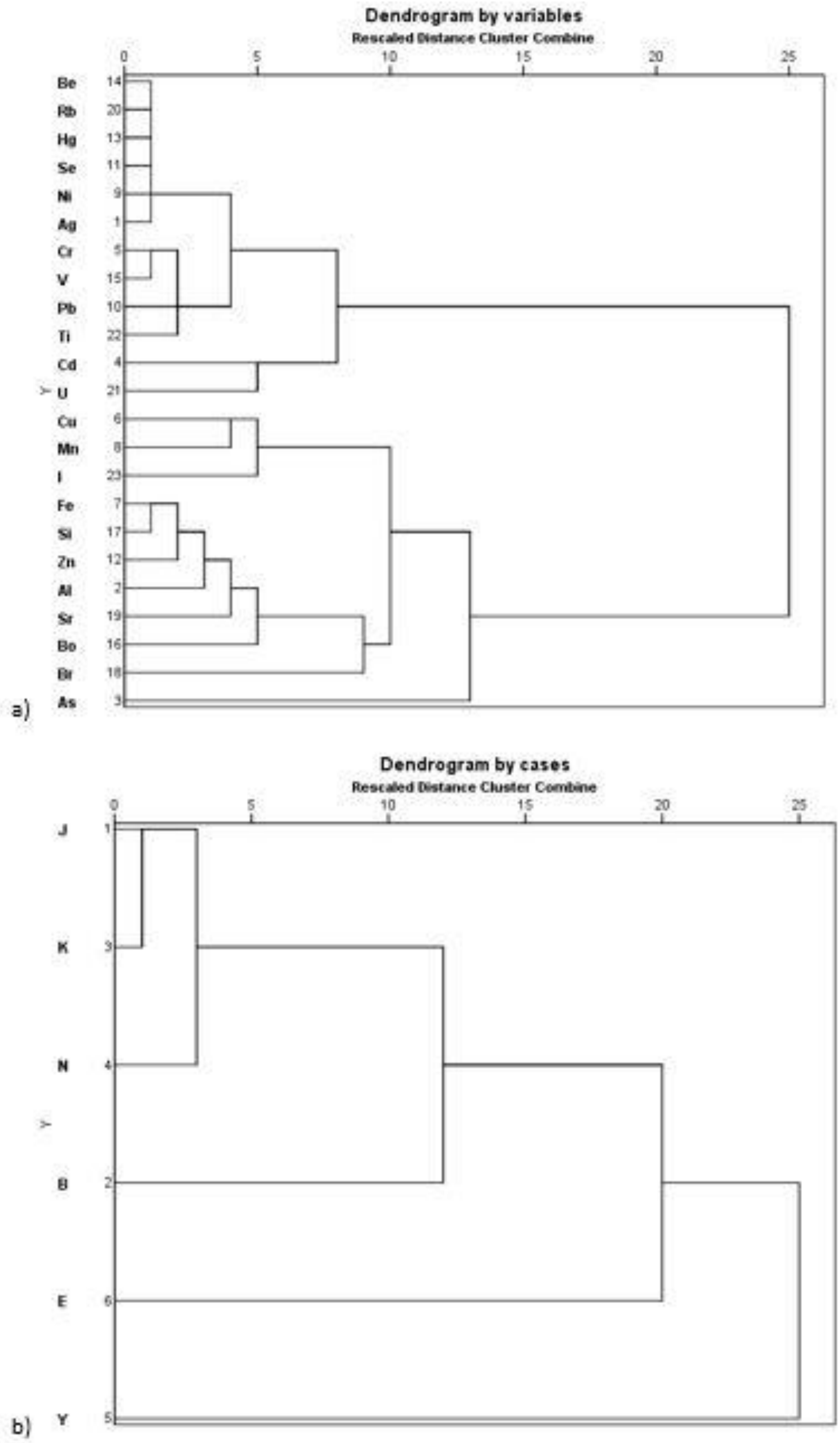

Fig. 5. 4 Hierarchical dendrogram showing the clustering of (a) trace elements and (b) study sites of the sea ports of NSW, Australia.

5.4 Conclusions

The present study showed the pattern distribution of trace elements in the sea port environments using oyster (*S. glomerata*) as a bioindicator. *S. glomerata* has been known as an effective ecological tool to trace the trace metals or toxic elements (for example, Cu, Zn, As, Pb, Fe, Mn and Sr) as it is widely grown in the Pacific Ocean areas. The results illustrate that the varying levels of trace elements in the oysters and their concentrations were highly dependent on the nature of the ports and human activities in the vicinity of the port areas. The BCR and BSAF analyses demonstrate significant accumulation of Fe, Cu, Mn, Zn, As and Sr, which reflect their availability in seawater and sediments. Likewise, the integrated metal contamination analysis determined severe contamination of Fe, Zn, Cu and Al contamination in the oysters at all port areas. Overall, *S. glomerata* is an important bioindicator to detect the distribution of contaminants in the port environment. Further measures are still required for suitable and effective management of the toxic trace elements in the NSW ports to alleviate the anthropogenic impacts on the sea environment.

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Chapter 6: Assessment of trace elements pollution in sea ports of New South Wales (NSW), Australia using macrophytobenthic plant *Ecklonia radiata* as a bio-indicator

The present chapter illustrates the accumulation of trace elements in the seaweeds (*Ecklonia radiata*) from the sea ports of Australia. The unique accumulation properties of seaweeds, such as prolific, widespread, persistent, reactive to certain natural and anthropogenic stresses make them ideal bioindicators. Moreover, *Ecklonia radiata* is a common seaweed along the coastal marine environment of Australia, therefore used as a bioindicator to assess the distribution and levels of trace elements in the port's environment compared to the background ecosystem. Different accumulation indices and statistical analysis were used to identify trace element contamination in seaweeds.

Authors Contributions

Study Conception and Design: Vladimir Strezov and Sayka Jahan

Acquisition of Data: Vladimir Strezov and Sayka Jahan

Analysis and Interpretation of Data: Vladimir Strezov and Sayka Jahan

Drafting of Manuscript: Sayka Jahan

Critical Revisions: Vladimir Strezov

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Assessment of trace elements pollution in sea ports of New South Wales (NSW), Australia using macrophytobenthic plant *Ecklonia radiata* as a bio-indicator

Abstract

In this study seaweeds (*Ecklonia radiata*) from six major sea ports of NSW, Australia were used as a bioindicator to assess the distribution and concentrations of trace elements accumulation in the ports compared to the background ecosystem. Bioconcentration ratio (BCR), biota sediment accumulation factor (BSAF), enrichment factor, multivariate statistical analysis and hierarchical cluster analysis were used to identify trace elements contamination. The results illustrate BCRs of Al, Fe, Mn, Zn, Pb, Cu, As and Ba in *E. radiata* whereas the BSAFs portray B enrichment in all sea ports along with bioaccumulation of As in Port Jackson and Pb in Port Botany. However, trace element variations between studied and background locations were found to be significant for Port Kembla and Port Newcastle. The principal component analysis result explained four principal groups with 76.25% cumulative variance. Cluster analysis was further performed to detect major groups of elements and sites to portray interconnection between the contaminants and the locations.

Key Words: Trace elements, bioaccumulation, seaweed, seaports, Australia.

6.1 Introduction

Marine and estuarine environments are facing significant adversity due to contamination with toxic trace metals from intense anthropogenic activities, such as dredging, aquaculture, industrial activities, mining activities, port operations, tourism, and recreational boating and sewage discharge, with consequent adverse effects on biodiversity and food webs (Bae et al., 2017, Bonanno and Orlando-Bonaca, 2018, Henriques et al., 2017, Lewis and Devereux, 2009, Serrano et al., 2011). Trace metals mostly persist in the environment and tend to accumulate in organisms, becoming detrimental to plants, animals and ecosystems, and can pose serious threat to human health (Bonanno and Martino, 2017, Deboudt et al., 2004, Ikem and Egiebor, 2005, Islam et al., 2007, Roca et al., 2017, Stankovic and Jovic, 2012, Wang et al., 2013).

There are a number of studies exploring the end effects of trace elements contamination on the environment with a recommendation for appropriate monitoring and control of trace element contamination (Callender, 2003, Sheppard, 1993, Stankovic and Jovic, 2012). Although a number of plants and animal species are used as bioindicators for biomonitoring studies, the macrophyto benthic plants act as a unique bioindicator for assessing the ecological status of littoral ecosystems (Bonanno and Martino, 2017, Farias et al., 2018, Sidi et al., 2018, Umetsu et al., 2018). The unique accumulation properties of macrophyto benthic plants, such as prolific, widespread, persistent, reactive to certain natural and anthropogenic stresses make them ideal bioindicators (Besada et al., 2009, Bonanno and Martino, 2016, Reizopoulou and Nicolaidou, 2004, Rubio et al., 2017, Zalewska and Danowska, 2017). For trace element concentration analysis, the macrophytes offer advantages over measurements of concentrations in seawater and sediment. Because in seawater and sediment, trace elements concentrations are often influenced by wide fluctuations, pH, oxidation–reduction potential, organic content, and grain size composition of sediment (Topcuoglu et al., 2003). The cell wall of seaweeds is rich in hydroxyl, sulphate, phosphate and carboxyl polysaccharide groups that provide binding and complexation sites for trace metals and metalloid cations (Brito et al., 2016, Bryan et al., 1985, Tropin, 1995). This property enables seaweeds to accumulate trace elements thousands of times higher than their corresponding concentrations in sea water (Conti and Cecchetti, 2003, Khaled et al., 2014).

Environmental quality monitoring of trace elements has been conducted over the years for assessment of contamination in Australian marine and estuarine environments. High to moderate contamination of the marine environment adjacent to urbanized and industrialized estuaries have been reported in these studies (Batley 1995, Bonanno and Orlando-Bonaca, 2018, Stankovic and Jovic, 2012). Monitoring of trace elements in the marine environment in Australia has been conducted using a number of different biological organisms as bioindicators, depending of the trace element of consideration. Cd concentrations in the coastal waters of North Queensland were determined by Olivier et al. (2002) using tropical oysters, concluding that the concentration of Cd in oysters increased as ambient dissolved Cd concentrations decreased. Trace metals concentrations in fish in Port Kembla, NSW were reviewed by He and Morrison (2001) who concluded that there has been a continuous improvement in the port environment over the last 20 years, but suggested further monitoring due to increased anthropogenic activities in the area. Other recent studies on trace elements concentrations in the water, sediments and oysters in six major seaports of NSW, Australia by Jahan and Strezov (2017, 2018, 2019) observed significant concentrations of Cu, Pb and Zn including enrichment of As, Cd, Al, Fe, Mn, Br and Sr in the port water, sediments and oysters.

Application of seaweeds for biomonitoring of trace elements accumulation in the sea ports in Australia has still not been conducted but may provide a feasible alternative for frequent biomonitoring of concentration of trace elements. *Ecklonia radiata* seaweed, which is commonly known as golden kelp, is evidenced to be one of the most suitable seaweeds for biomonitoring of trace element contamination in the marine environment due to its potential accumulation capacity (Cechinel, et al., 2016; Mahmood et al., 2017).

The present study investigated the levels and patterns of trace element concentration in *Ecklonia radiata* seaweed under different port activities in NSW, Australia with the aim to portray the state of trace elements contamination in the port environments. This study also represents a new perspective for biomonitoring of trace elements in aquatic ecosystem using principal component and hierarchical cluster analysis methods.

6.2 Materials and methods

6.2.1 Study site

Six major sea ports in the state of NSW, Australia (Port Jackson, Port Botany, Port Kembla, Port of Newcastle, Port Yamba and Port Eden) were selected for conducting this study which are different both by location and activities (Fig. 6.1). Port Jackson, located near the central business district of Sydney, is mainly engaged with cruise shipping, recreational boating and water sports and is a well-mixed estuary because of low freshwater discharge and tidal turbulence (Jahan and Strezov, 2017). Port Botany is the 2nd port located in Sydney with container, crude oil and bulk liquid (fossil fuel, chemical and bio-fuel) operations. Port Kembla is located in the southern part of New South Wales. It is a significant export location for coal with many facilities and berths. This port deals with imports of iron ore, dolomite, limestone, sulfphur, copper, phosphate rock and petroleum products and export of iron and steel, coal, coke, tinplate and copper cables. The Port of Newcastle is located at the mouth of Hunter River known as the world's largest coal export port, which also handles import and export of raw materials for steelworks, fertilisers, products from the aluminium industries, steel products, mineral sands, grain and woodchips. Port Yamba is Australia's easternmost sea port which is the home of the New South Wales' second largest fishing fleet and handles container liquid berth, livestock and explosive products. Port Eden is a small seaport situated in the south coast of NSW and is one of the largest fishing fleets in this state. Woodchip break bulk and machinery equipment, mainly for the oil and gas industry are the major activities in this port (Jahan and Strezov, 2017).

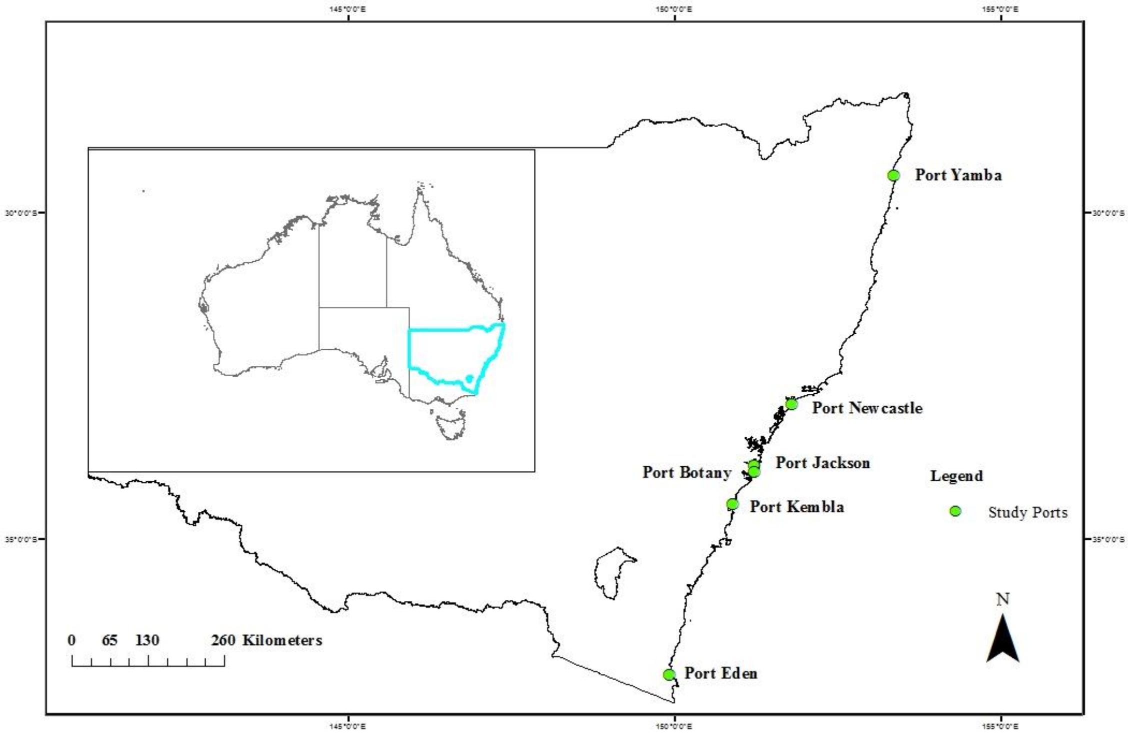

Fig. 6. 1 Map of the study area.

6.2.2 Sample collection, processing and analysis

Grab samples of benthic macroalgae (*Ecklonia radiata*) were collected from the six sea ports from April to June 2017. Three sampling points from each port were selected to collect samples. Among three points two points were selected from the port areas and one was selected from background area (same hydrogeological area but non-port area). From each point, three sub-samples were collected from at least 2 m apart, contains the entire branch with both old and new growth. The collected samples were then shipped in an icebox to the laboratory for analysis.

Prior to analysis all samples were washed several times with deionized water to remove any adhered material and dried at 100±5ºC until desiccated and then crushed to a fine powder. Individual sample (0.4-0.6 g) was added to 5 ml of HNO_3, 2 ml of H_2O_2 and

3 ml of deionized water and then digested in acid-washed microwave digestion vessels at 190ºC for 20 min for further analysis (Roberts et al., 2006).

The concentrations of trace elements in the samples were determined by inductively coupled plasma mass spectrometry (ICP-MS Agilent 7700X and Varian, vista-pro ICP-AES), while mercury was determined by cold vapour atomic absorption spectrometry (CV-AAS) to reach the practical quantitation limits (PQLs). Quality and accuracy of the experimental procedure and the equipment were ensured using duplicate analysis, laboratory control samples (LCS – sample blank spikes to determine recovery acceptance) and sample spikes. The limit of quantification (LOQ) was calculated as 10 times the standard deviation of the sample blank (Sanagi et al., 2009) which ranged from 0.389 mg/l to 0.0999 mg/l depending on elements. A standard reference material from National Measurement Institute (NMI, matrix reference AGAL-6) was also analysed continuously after every five samples and the simultaneous analysis of standard materials gave acceptable recoveries (90-125%).

6.2.3 Calculation and statistics

Prior to analysis, all data were natural log transformed (ln(1+x)) to meet the assumption of normality for the tests. One-way ANOVA (α=0.05) tests were used to compare trace elements concentrations in the algae from the six study ports. Pearson's correlation analysis was performed to investigate the existing correlations between trace elements concentrations in the sampled algae. Principal component analysis (PCA) and a multivariate statistical analysis were used to create an ordination plot to demonstrate the variance between trace elements concentrations in algae and develop groups both by cases and variables to identify links between elements and sampling sites by a dendrogram, as described by Jahan and Strezov (2018). This technique reduces the number of variables to a smaller set of factors, which are easier to explain when displayed with correlations existing between original variables (DelValls et al., 1998). For PCA, only PCs with eigenvalue >1 were retained and variables were centered as mean (Kaiser, 1960). Finally, algae to water and sediment concentration ratios (CR) were determined by dividing the concentration of trace elements in algae by the average concentration of trace elements in water and sediments taken from the same sampling points. All statistical analyses were performed using Microsoft Excel 16 and SPSS version 25.

6.2.4 Data Processing

6.2.4.1 Enrichment factor (EF)

An enrichment factor (EF) is generally conducted to determine whether trace elements in biota are from anthropogenic events or natural origin (Dickinson et al., 1996, Hornung et al., 1989, Jahan and Strezov 2018). The EF method normalizes the metals, trace elements and rare earth elements with respect to a sample reference metal, such as Fe, Sc or Al (Ashraf, 2011, Ashraf et al., 2016, Ravichandran et al., 1995). In the present study, Fe was selected as the normalization element as this element is predominant in the study area. EF was calculated according to the following equation:

$$EF= (C_x/Fe_x)_{Sample}/(C_{ref}/Fe_{ref})_{Background\ Sample} \quad \text{.........(1)}$$

where C_x is the concentration of an element in the sample, Fe_x is the concentration of Fe in the sample; C_{ref} is the concentration of an abundant and common element in the seaweed, and Fe_{ref} is the concentration of Fe in the seaweed (Turekian and Wedepohl, 1961).

EF values of each sample fall into one of the five tiers, as proposed by Sutherland (2000). The elemental ratios indicate no enrichment when EF<2 or moderate enrichment if the values fall between 2 and 5. If the EF values fall in the range between 5 and 20, 20–40, and >40, they are considered as significantly enriched, very highly enriched, and extremely enriched, respectively. Generally, if the enrichment factor is close to or less than 1, it shows that the main source of trace elements originates from crustal or marine environments. The enrichment factor value becomes significantly larger than 1 when the main source is from an anthropogenic contribution.

6.2.4.2 Bioconcentration Ratio (BCR)

Bioconcentration is a process where the biota absorbs a chemical compound through its different body parts from the ambient environment (Jonathan et al., 2017). It is a quantitative measure of the plant bioaccumulative capacity (Leal et al., 1997, Szefer, 2002, Zalewska & Saniewski, 2011, Zalewska & Suplińska, 2012). The calculated bioconcentration ratios also form the basis for risk assessment of harmful effects of the hazardous substances on specific biota (IAEA, 2014). The extent to which bioconcentration occurs is calculated by using the formula (2) (Arnot and Gobas, 2006):

$$BCR = \frac{C_{Algae}}{C_{Water}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

where C_{Algae} is the concentration of an element in the algae, which was measured in this work, while C_{Water} is the concentration of the same element in the water, which was derived from the median values from Table 3-4. of chapter three for the same sea ports, study locations and the same time of sampling. Typically, when the BCR is >1 it is considered bioaccumulation.

6.2.4.3 Biota sediment accummulation factor (BSAF)

Biota Sediment Accumulation Factor (BSAF) is used to calculate the ratio between the concentration of an element in biota to the concentration in sediments (Thomann et al., 1995). The BSAF for each biota sample was calculated with equation (3):

$$BSAF = \frac{C_{Algae}}{C_{Sediment}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

where C_{Algae} and $C_{sediment}$ are the concentrations of trace elements in the algae and in sediment (Negri et al., 2006) and bioaccumulation of trace metals is confirmed when BSAF is higher than 1. In this work, the sedimentary metal concentrations for the same sea ports, study locations and the same time of sampling were derived from Table 4-3. of chapter four.

6.3 Results and discussion

6.3.1 Trace elements concentrations in algae

The bioconcentration patterns and average concentration of trace elements in the studied seaweed (*Ecklonia radiata*) are shown in Table 6.1. Except for Port Botany, the concentrations of As (4-12.5 mg/kg) in all of the studied port areas were much higher than their background values. The enrichment factors (EF) also support significant enrichment of As (Table 6.2) in Ports Jackson and Port Eden. In Australia and New Zealand, the only regulation applied to seaweed food is related to inorganic As. This is because marine algae can contain high levels of As, but most is bound into organic molecules which are not acutely toxic like the inorganic forms (Andrewes et al., 2004). Evidence in the literature suggests that brown algae have higher As content than red or green algae. In this work, the concentration of As in the *Ecklonia radiata* collected from the six ports were above the standard values (1 mg/kg) given by the Australia and New Zealand Food Authority (2005) guidelines for permissable inorganic As concentrations in edible seaweeds.

The study further revealed high concentrations of Fe in the seaweeds in all of the studied ports with the highest concentration (1000 mg/kg) at Port Botany. With the exception to Port Jackson, Port Yamba and Port Eden, the concentrations of Mn in all other study ports were higher than their background concentrations. Zn concentrations in the seaweeds in all ports were also considerably higher than their corresponding background concentrations, which was further supported by EF (Table 6.2), as moderate to significant enrichment in the seaweeds at Port Yamba and Port Eden indicate the impact of sea port activities on the port environment. Moreover, considerable amounts of Al, Pb, B, Br, Si, Sn, Sr, Rb and Ti were also found in almost all ports among which B, Sn, Si and Br showed moderate to significant enrichment at Port Eden, Rb and Ti showed moderate to significant enrichment at Port Jackson and Port Eden and I showed moderate to very high enrichment at Port Jackson, Port Newcastle and Port Eden (Table 6.2). Some trace elements, such as Mn, Fe, Zn, in small amounts are essential coenzymes, however in high concentrations they become toxic to the living organisms. Besides, other elements, such as Al, Cd and Pb, are non-essential and become a concern for their toxicity even at low concentrations. Brown algae *Ecklonia radiata* (Golden Kelp) has potential applications in the functional food and nutraceutical industries. Moreover, it is used in food preservation, cosmetics and processed primarily into fertilisers and animal feeds that may cause successive trace elements accumulation in the food chain with possible chronic effects on biota in the trophic levels as well as animals who consume kelp as food (Almela et al., 2002, Charoensiddhi et al., 2018). However, in Australia no legislation has been set for controlling the maximum limit of the elements in seaweeds or their derived products, probably because consumption of seaweed is still limited (Rubio et al., 2017).

Table 6-1. Trace elements concentrations in *Ecklonia radiata* in the major ports in NSW, Australia.

Parameters	mg/kg	Al	As	Cu	Fe	Mn	Pb	Zn	B	Si	Br	Sr	Rb	Ti	I
Port Jackson	Bg(n=3)	290	Bd	13	480	31	7	23	36	110	180	81	1	2	46
	Study point (n=6)	106±76	12±2.9	4±1.5	645±786	12.5±10.60	2±1.5	20±11.5	37±7.07	65±7.07	106±37	160±28.3	5.5±2.12	5.5±0	1505±1125
Port Botany	Bg(n=3)	12	7	Bd	19	3	Bd	4	20	30	65	110	2	Bd	18
	Study point (n=6)	270±28.3	Bd	2±1.5	1000±1132	9±8.5	10±0	9.5±2.12	15±7.07	65±7.07	40±0	91±12.72	1±0.707	47±60.81	18.5±6.36
Port Kembla	Bg (n=3)	15	Bd	Bd	37	2	Bd	1	30	20	72	21	1	Bd	4
	Study point (n=6)	111.5± 140	6.5±2.12	7±2.90	310±368	15±18.4	3±0	23.5±0.70	26.5±9.20	60±56.6	110±99	190±0	3.5±0.70	2±0	191±239
Port Newcastle	Bg(n=3)	38	Bd	Bd	43	Bd	Bd	1	6	60	58	11	Bd	Bd	1
	Study point (n=6)	510± 42.5	4.5±0.70	2±0	685±49.5	27.5±0.70	Bd	9.5±2.2	25±7.07	95±7.07	78±5.7	130±0	2.5±0.70	21±2.9	106±34
Port Yamba	Bg(n=3)	26	12	Bd	64	6	Bd	Bd	53	40	91	230	3	Bd	54
	Study point (n=6)	34.5±36	Bd	Bd	47±44	3.5±2.2	Bd	1.5±0.70	8±2.9	35±35.4	79.5±13.5	3.5±0.70	Bd	1±0	Bd
Port Eden	Bg(n=3)	1100	4	2	2200	42	3	12	33	40	Bd	1000	1	11	Bd
	Study point (n=6)	190± 56.6	12.5±5	Bd	500±141.5	4±1.5	2.5±0.70	34.5±0.70	39.5±0.070	90±0	Bd	275±49.5	4.5±2.2	6.5±2.2	Bd

Parameters	mg/kg	Al	As	Cu	Fe	Mn	Pb	Zn	B	Si	Br	Sr	Rb	Ti	I
Port Jackson	Bg(n=3)	290	Bd	13	480	31	7	23	36	110	180	81	1	2	46
	Study point (n=6)	106±76	12±2.9	4±1.5	645±786	12.5±10.60	2±1.5	20±11.5	37±7.07	65±7.07	106±37	160±28.3	5.5±2.12	5.5±0	1505±1125
Port Botany	Bg(n=3)	12	7	Bd	19	3	Bd	4	20	30	65	110	2	Bd	18
	Study point (n=6)	270±28.3	Bd	2±1.5	1000±1132	9±8.5	10±0	9.5±2.12	15±7.07	65±7.07	40±0	91±12.72	1±0.707	47±60.81	18.5±6.36
Port Kembla	Bg (n=3)	15	Bd	Bd	37	2	Bd	1	30	20	72	21	1	Bd	4

	Study point (n=6)	111.5± 140	6.5±2.12	7±2.90	310±368	15±18.4	3±0	23.5±0.70	26.5±9.20	60±56.6	110±99	190±0	3.5±0.70	2±0	191±239
Port Newcastle	Bg(n=3)	38	Bd	Bd	43	Bd	Bd	1	6	60	58	11	Bd	Bd	1
	Study point (n=6)	510± 42.5	4.5±0.70	2±0	685±49.5	27.5±0.70	Bd	9.5±2.2	25±7.07	95±7.07	78±5.7	130±0	2.5±0.70	21±2.9	106±34
Port Yamba	Bg(n=3)	26	12	Bd	64	6	Bd	Bd	53	40	91	230	3	Bd	54
	Study point (n=6)	34.5±36	Bd	Bd	47±44	3.5±2.2	Bd	1.5±0.70	8±2.9	35±35.4	79.5±13.5	3.5±0.70	Bd	1±0	Bd
Port Eden	Bg(n=3)	1100	4	2	2200	42	3	12	33	40	Bd	1000	1	11	Bd
	Study point (n=6)	190± 56.6	12.5±5	Bd	500±141.5	4±1.5	2.5±0.70	34.5±0.70	39.5±0.070	90±0	Bd	275±49.5	4.5±2.2	6.5±2.2	Bd

Bg= Background, Bd= Below detection, Values presented as mean

Table 6-2. Enrichment factor of different trace elements in the seaweed (*Ecklonia radiata*) of the studied ports.

	As	Cu	Mn	Pb	Zn	B	Sn	Si	Br	Rb	Ti	I
Port Jackson	8.94	0.23	0.30	0.21	0.65	0.77	1.12	0.44	0.44	4.10	2.05	24.37
Port Botany	0.00	0.04	0.06	0.19	0.05	0.01	0.02	0.04	0.01	0.01	0.89	0.02
Port Kembla	0.02	0.02	0.02	0.01	0.08	0.00	0.00	0.01	0.00	0.01	0.01	0.15
Port Newcastle	0.28	0.13	1.73	0.06	0.60	0.26	0.06	0.10	0.08	0.16	1.32	6.65
Port Yamba	0.11	1.36	0.79	1.36	2.04	0.21	1.36	1.19	1.19	0.45	1.36	0.03
Port Eden	13.75	2.20	0.42	3.67	12.65	5.27	4.40	9.90	4.40	19.80	2.60	4.40

6.3.2 Algae to water concentration ratio

The bioconcentration ratios (BCR) in *Ecklonia radiata* are shown in Fig. 6.2. They are generally presented in the order of Fe >Al > Mn > Pb >Cu > Zn at Port Jackson and Port Kembla, Fe > Pb > Al > Mn > Zn at Port Botany, Al > Fe > Mn > Cu > Zn at Port Newcastle, Fe > Mn > Al > Zn at Port Yamba and Al > Zn > Fe > As > Mn > Pb at Port Eden. BCR values greater than 1000 indicate significant bioaccumulation that increase possibility for chronic effects and food chain accumulation. However, high BCR values also justify the uptake of free metal ions from solution more competently via different body parts (Kwok et al., 2014, Jayaprakas et al., 2015).

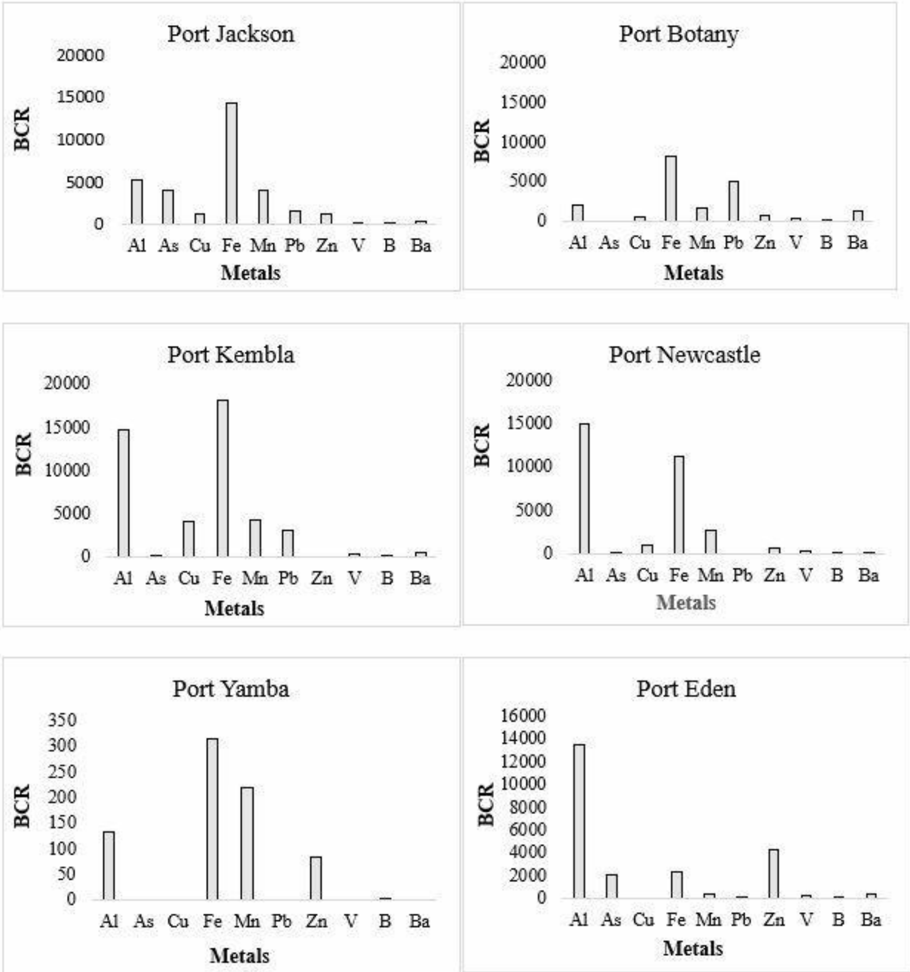

Fig. 6. 2 Bioconcentration ratio (BCR)for (*Ecklonia radiata*) in the study ports.

The bioconcentration ratio suggested that all ports have high Fe accumulation (>1000) with the highest value at Port Kembla. Significant Al (>1000) bioaccumulation was also found in all ports, except for Port Yamba. Notable amount of Mn (>1000) accumulation was found in the seaweeds at Port Jackson, Port Botany, Port Kembla and Port Newcastle, Pb (>1000) accumulation in Port Jackson, Port Botany and Port Kembla, and Zn (>1000) accumulation at Port Jackson and Port Eden. All elements bioaccumulated in this species, reflecting their availability in the water of seaports that ultimately increase the possibility of chronic effects on trophic levels (Bonanno and Martino, 2017a, Roca et al., 2017).

6.3.3 Biota sediment accumulation factor

Algae to sediment accumulation factors (BSAF) are presented in Fig. 6.3.

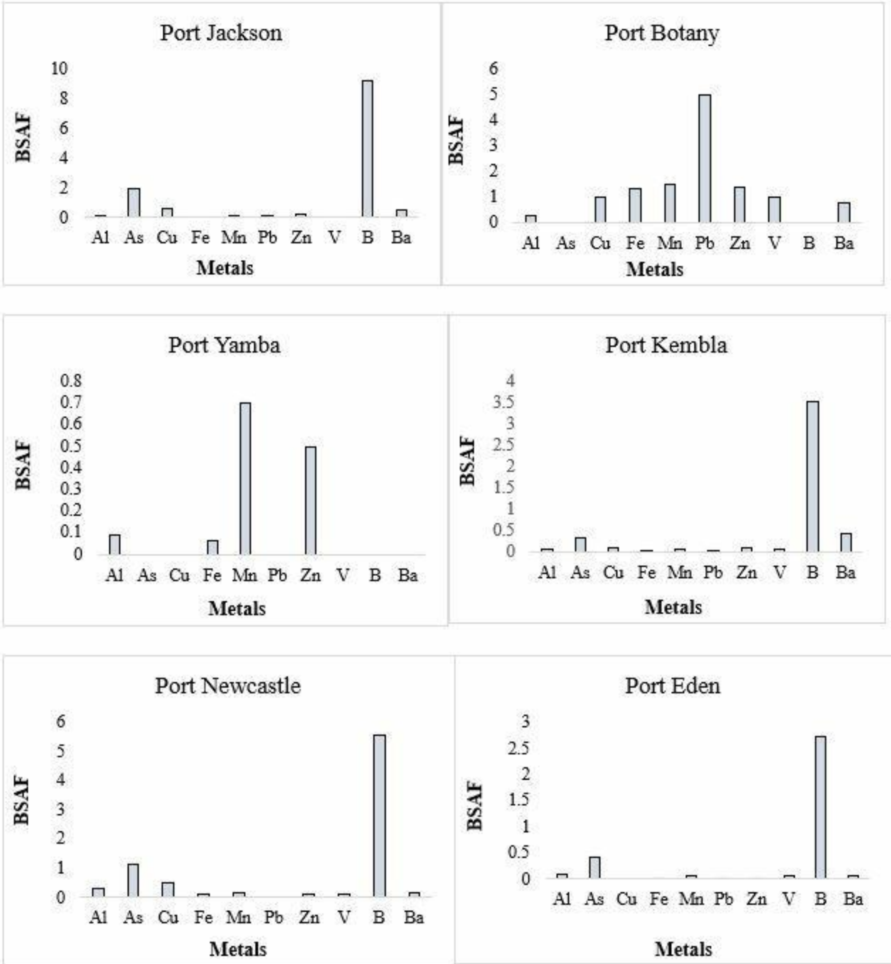

Fig. 6. 3 Biota sediment accumulation factors (BSAFs) for seaweed (*Ecklonia radiata*) in the study ports.

BSAFs were the highest for B in all the sea ports, indicating enrichment of this metal in the port environment and high absorbing capacity in the soft tissues of *E. radiata*. As B is an element found in lubricants, which is a commonly handled substance in the ports, this may be one of the important sources of B in the ports (Gubelit et al., 2016). Significant bioaccumulation of As (BSAFs=2) in Port Jackson and Pb (BSAFs=5) in Port Botany also demonstrate the availability of these metals in the respective port environments. The probable sources of Pb in Port Botany may be from combustion engines and petroleum hydrocarbons inside port area (Gubelit et al., 2016). The concentration ratios for other elements are not very significant as they are below or slightly above 1.

Analysis of variance was conducted to determine the significant differences in the calculated parameters between the seaweeds collected from the background sites and the ports. Prior to analysis, the normality and homogeneity variance assumptions were verified and, when necessary, a log(1+x) transformation data were utilised. The variation of trace elements between different locations by means of ANOVA was found significant ($P < .05$) for Port Kembla (0.015) and Port Newcastle (0.020) (Table 6.3), which demonstrates the impacts of port activities on the biotic environment in these sea ports.

Table 6-3. Significance analysis of trace elements concentrations between the background and port seaweed (*Ecklonia radiata*).

Ports	**Df**	**P-value**
Port Jackson	33	0.40
Port Botany	33	0.077
Port Kembla	33	0.015
Port Newcastle	33	0.020
Port Yamba	33	0.28
Port Eden	33	0.96

Table 6.4 outlines the correlations between trace elements accumulated in the seaweed samples. Correlation analysis elucidates general relationships that may exist between the accumulated elements in all seaweed samples. Al is significantly positively correlated with Fe (0.98), Mn (0.78), Si (0.75) and Ti (0.78) while it has negative correlation with Na and Br. As has significant positive correlation with K (0.79) and Rb (0.88) Cu is positively correlated with Zn (0.82). Fe shows strong positive correlation with Mn (0.81) and Ti (0.87), while V shows with Ca (0.76) and Pb (0.79). Sr is positively correlated with B and Ba whereas similar trend is found between K and Rb.

Table 6-4. Correlation matrix for trace elements accumulation in sea port algal samples.

	Al	*As*	*Cu*	*Fe*	*Mn*	*Pb*	*Zn*	*V*	*B*	*Ba*	*Sn*	*Si*	*Na*	*Ca*	*S*	*K*	*Br*	*Sr*	*Rb*	*Ti*	*I*
Al	1																				
As	0.08	1.00																			
Cu	0.33	0.40	1.00																		
Fe	**0.92***	0.19	0.48	1.00																	
Mn	**0.78***	0.19	0.26	**0.81***	1.00																
Pb	0.38	-0.09	0.60	0.62	0.44	1.00															
Zn	0.59	0.48	**0.82***	0.67	0.48	0.52	1.00														
V	0.54	-0.17	0.20	0.67	0.65	**0.79***	0.30	1.00													
B	0.31	0.70	0.52	0.45	0.49	0.28	0.50	0.23	1.00												
Ba	0.53	0.71	0.46	0.58	0.43	0.09	0.66	0.16	0.55	1.00											
Sn	0.15	0.31	0.20	0.34	0.36	0.20	0.34	0.21	0.20	0.44	1.00										
Si	**0.75***	0.24	0.42	0.66	0.53	0.23	0.56	0.16	0.36	0.37	0.17	1.00									
Na	-0.38	-0.24	-0.05	-0.41	-0.33	-0.12	-0.22	-0.11	-0.25	-0.43	-0.21	-0.18	1.00								
Ca	0.63	0.05	0.38	0.73	0.55	0.70	0.51	**0.76***	0.52	0.35	0.07	0.32	-0.42	1.00							
S	0.19	0.40	0.37	0.25	0.10	0.17	0.36	0.06	0.68	0.33	-0.01	0.28	-0.05	0.48	1.00						
K	0.05	**0.79***	0.35	0.14	0.16	-0.12	0.49	-0.33	0.70	0.51	0.32	0.30	-0.33	0.06	0.47	1.00					
Br	-0.33	-0.28	-0.41	-0.35	0.04	-0.18	-0.36	-0.17	-0.22	-0.49	0.22	-0.07	0.13	-0.42	-0.26	0.06	1.00				
Sr	0.53	0.69	0.51	0.62	0.51	0.36	0.69	0.37	**0.77***	**0.76***	0.18	0.40	-0.39	0.67	0.69	0.54	-0.45	1.00			
Rb	0.06	**0.88***	0.42	0.14	0.05	-0.14	0.54	-0.34	0.56	0.65	0.34	0.34	-0.28	-0.06	0.33	**0.90***	-0.10	0.54	1.00		
Ti	**0.78***	0.07	0.28	**0.87***	0.66	0.54	0.48	0.53	0.22	0.35	0.19	0.48	-0.50	0.60	0.15	0.07	-0.30	0.45	0.03	1.00	
I	0.14	0.42	0.10	0.22	0.45	0.08	0.33	0.05	0.45	0.24	0.49	0.33	-0.25	0.07	0.21	0.67	0.59	0.36	0.55	0.16	1

* Values significant at $P < 0.05$ and N=18.

6.3.4 Principal component analysis

Principal component analysis (PCA) was used to compare the level of trace elements accumulation in the seaweeds of the studied port areas. Four principal components were extracted by applying the principal component analysis (PCA) on the twenty-three elements, covering 76.25% of the cumulative variance (Table 6.5). The loading of the variables on the four principal components shows that Fe, Sr, Zn, Ca, Al, Ba, Mn, B, Ti, Cu and Si were the dominant variables on the PC1 (0.89, 0.87, 0.80, 0.77,0.77, 0.74, 0.73, 0.73, 0.72, 0.64 and 0.62 respectively), while Rb, K and As (0.83, 0.82 and 0.70) were the dominant variables on the PC2 (Table. 6.5). Lastly, Br (0.77) is the dominant component of PC3.

Table 6-5. Varimax normalization rotated loading for four factors obtained according to pollutants in the seaweed samples (*Ecklonia radiata*) of the studied sea ports.

Variables	Factor 1	Factor 2	Factor 3	Factor 4
Variance (%)	38.85	20.81	10.15	6.44
Cumulative (%)	38.85	59.66	69.81	76.25
Fe	.893	-.300	.211	.158
Sr	.873	.189	-.261	-.177
Zn	.805	.201	.007	.412
Ca	.772	-.436	-.129	-.190
Al	.771	-.296	.234	.271
Ba	.737	.334	-.150	.063
Mn	.731	-.195	.490	-.061
B	.728	.362	-.188	-.262
Ti	.718	-.384	.205	.020
Cu	.637	.159	-.227	.473
Si	.613	.111	.280	.426
Pb	.591	-.504	.063	.060
S	.504	.262	-.378	-.132
Na	-.489	-.029	-.053	.437
Rb	.443	.833	-.082	.009
K	.453	.827	.009	-.178
Cr	.406	-.774	-.105	-.286
As	.526	.695	-.255	-.132
V	.557	-.679	.192	-.137
U	-.459	.485	.433	.352
Br	-.408	.220	.765	-.265
I	.375	.516	.609	-.327
Sn	.348	.283	.517	-.024

The best results for cluster analysis were obtained using normalized data that present similar relationship between metals by using both the linkages between single and average values. The resultant dendrograms (Fig. 6.4) confirmed the results obtained with the PCA and determined four main clusters. The first cluster contains Al, Fe, Sr, Mn and Zn at distance 1-3. The second cluster contains Ca, S, K, Si, B, Na at distance 1 and both the first and second cluster form another cluster with Br at distance 6. The third cluster contains As, Rb, Ba and I while the fourth cluster comprises Cr, V, Pb, Ti, Cu, Sn and U and they both form fuse cluster at distance 8. Lastly, at a higher distance (about 25) the four clusters fused forming the final cluster. The dendrogram also assists to portray and cluster each port based on trace elements contamination, as presented in Figure 4b. The analysis results explain that the seaweed in Port Eden is significantly contaminated by trace elements, followed by Port Botany, Port Kembla, Port Jackson and Port Yamba.

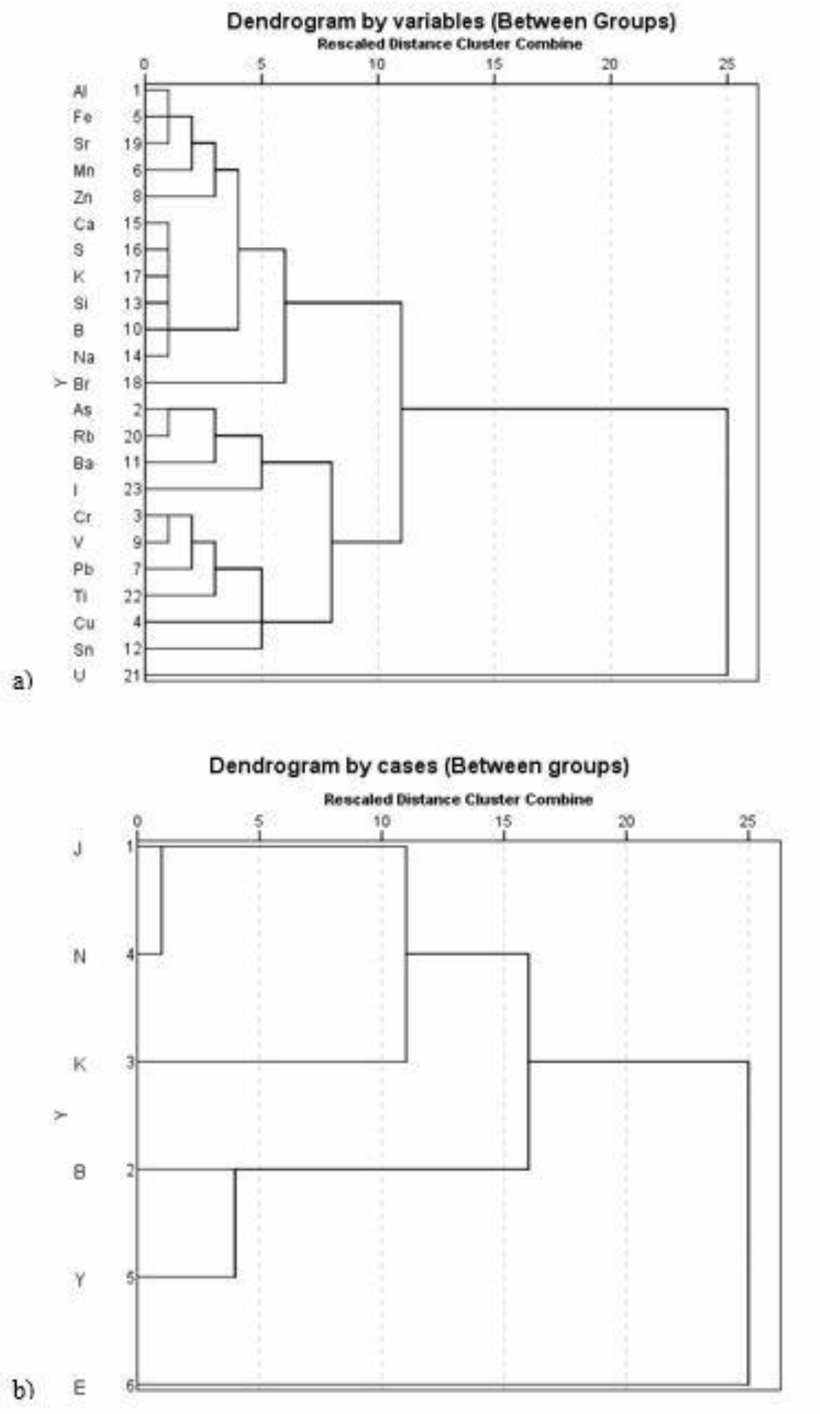

Fig. 6. 4 Hierarchical dendrogram showing the clustering of (A) trace elements and (B) sites in the seaweed of the studied ports.

6.4 Conclusions

The work presents the pattern of bioaccumulation of trace elements in seagrass-dominated ecosystems from the involved abiotic components. The seaweed (*Ecklonia radiata*), used in this is a bioindicator, is suitable biomonitor species for trace elements (As, Fe, Mn, Pb, Zn Al, B, Br, Si, Sr and Ti) in the sea ports of New South Wales. All trace elements bioaccumulated in this species, reflecting their availability in seawater and sediments. The results dictate that, along with other anthropogenic activities, port activities may have notable influences on the levels of trace elements in the port area. However, *Ecklonia radiata*, is commonly used as animal food, has application in food preservation, cosmetics and fertilisers, may cause successive trace elements accumulation in the food chain with possible chronic effects on biota. Hence, beyond biomonitoring species the results presented here also provide a scope to study the indirect effects of toxicants upon associated fauna. Moreover, in the port environment where contaminants are unlikely distributed (as in this study), there is a need for close monitoring to investigate the degree of contamination and the effects of these complex exposure scenarios for appropriate and effective management initiatives.

6.5 References

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Chapter 7: Interrelationship of microplastic pollution in sediments and oysters in a seaport environment of the eastern coast of Australia

Microplastics are one of the most concerning pollutants of this century mainly because of their non-biodegradable nature that allows them to retain for decades when disposed in the marine environment. Sea ports are recipients of large amount of discharges through storm water and other commercial activities, which may additionally add to the overall marine microplastic pollution. This section is designed to assess the interrelationship of microplastic pollution in sediments and oysters at six major seaports (Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden) of New South Wales (NSW).

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Interrelationship of microplastic pollution in sediments and oysters in a seaport environment of the eastern coast of Australia

Abstract

Since the middle of the twentieth century, microplastics have emerged as a pollutant of concern. Seaports are recipients of large amount of discharges through ballast water, ship traffic and other commercial activities, which may additionally add to the overall marine microplastic pollution. The aim of this study was to determine the interrelationship of microplastic pollution in the sediments and oysters at six major seaports (Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden) of New South Wales (NSW). The results revealed the significant abundance of microplastic particles both in sediments and oysters in all the studied seaports which were estimated to be around 83–350 particles/kg dry weight in the sediments and 0.15–0.83 particles/g wet weight in the oysters. Although, the abundance of microplastics showed similar pattern in the sediments and oysters of the studied seaports, oysters had higher number of microplastics than sediments in all sea ports. Moreover, the results showed that the shapes, size and colours in the oysters did not necessarily match the main components in the sediments, although the polymer types matched well between each other. Black fibres between 0.1 mm–0.5 mm in size were the most abundant microplastics in oysters, whereas white spherules between 0.5 mm–1 mm in size were dominant in the sediments of NSW seaports. Moreover, the analysis of variance between microplastic abundance in sediment and oysters showed a non-significant positive linear relationship. Fourier Transform Infrared analysis further indicated that both sediments and oysters contained microplastics with two main polymers, polyethylene terephthalate and nylon, which suggests that the abundance of microplastics in the study ports was highly influenced by the port activities, mainly the intensive commercial fishing and fish processing activities along with intensive anthropogenic and industrial activities inside and surroundings the port environments.

Keywords: Microplastics, Sediment, Oyster, Seaport.

7.1 Introduction

Plastics are non-biodegradable polymers made up of different groups of petrochemical materials. Certain advantages of plastics, such as high durability, resistance and low weight, increased their use in the past decades. However, their low recycling rate and poor disposability have created new challenges for waste management that has led to the accumulation of plastics either in landfills or in the environment. It has been estimated that approximately >240million tonnes of plastics are used per year around the globe, while the global manufacturing of plastics has grown over a hundred times to the current level of 320 million tonnes/year (Plastics Europe, 2016; Zhao et al., 2018). A significant amount of plastics, nearly 10% of the total annual production, ends up in the marine environment through either deliberate or accidental release (Cole et al., 2011; Vaughan et al., 2017). Currently, plastics are the most common and abundant types of marine litter (Frias et al., 2016), mainly due to terrestrial runoff, commercial and maritime activities in the marine environment (Zhao et al., 2018; Lee et al., 2013; Dekiff et al., 2014; Mathalon and Hill, 2014; Yu et al., 2016; J. Li et al., 2018, H-X. Li et al., 2018).

The degradation of plastics in the marine environment due to ultraviolet radiation or wave action may result into smaller particles. One subgroup of the smaller plastics that has raised particular concern are microplastics (MPs), commonly defined as pieces of plastics smaller than 5 mm (Cole et al., 2011; Lots et al., 2017). Microplastics could be classified as primary and secondary microplastics. Primary microplastics are generally synthesized in the industries for use in cosmetic products by industries, pre-production pellets and synthetic fibres for clothes, while the secondary microplastics are produced from the degradation of larger plastics by photo-degradation, mechanical action or biological processes (Blumenröder et al., 2017; Botterell et al., 2019; Carr et al., 2016; Napper et al., 2015; Napper and Thompson, 2016; Zhao et al., 2018). The smaller size of microplastics can be ingested by the marine biota through targeted feeding, inhalation at the water-air interface, or by trophic transfer from prey species. Therefore, microplastics are more potential direct threat to marine environment than macroplastics (Lusher et al., 2015).

Various hydrodynamic processes and marine currents help to disperse the microplastics throughout the wide range of marine environments (Ng and Obbard, 2006). Otherwise, microplastics can suspend or sink in the ocean depending on the density of the polymer, age and fouling levels. Microplastics can be deposited in the sediment and can be ingested by marine biota, such as small fish and zooplanktons (Blumenröder et al., 2017; Kolandhasamy et al., 2018; Neves et al., 2015). Once ingested, the microplastics can be stored in the cells or tissues and hence their hyper accumulation could have detrimental effect on health of the aquatic organism and may further contain toxic trace elements and organic contaminants, such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls and organochlorine pesticides (Brennecke et al., 2016). Consequently, these toxic organic contaminants could be delivered to marine organisms by direct microplastic ingestion or endocytosis (Hodson et al., 2017), which can be further biomagnified to other animals of lower or upper level of food chain. If this biomagnification continues, the microplastic pollution could also reach to the apex predators and humans. However, there is limited data on biomagnification under realistic concentrations so further work is required to verify this threat.

Most studies on microplastic assessment have been conducted on the shorelines of the northern hemisphere, while less attention has been paid for southern hemisphere or pacific region (Reisser et al., 2013; Rudduck et al., 2017; Wilson and Verlis, 2017). Earlier, Browne et al. (2011) conducted a study for microplastic pollution worldwide including Australian coastlines, which suggested presence of approximately 11–30 microplastic particles per 250 ml sediment and their concentration was found increasing in locations with higher population (Browne et al., 2011). Furthermore, Reisser et al. (2013) carried out an assessment of microplastics at 57 locations around Australian coastline. The study showed considerable contamination, demonstrating a mean sea surface plastic concentration of nearly 8966 pieces per square kilometre (Reisser et al., 2013). In a separate study, Ling et al. (2017) estimated the concentration of microplastics at 42 coastal and estuarine sites across south-eastern Australia. The results revealed that on average, 3.4 microplastic particles were present per mL sediment, whereas, the highest concentration of 12 per ml sediment was found in Bicheno, a small town in Tasmania, which is occupied by a large number of fishing fleet (Ling et al., 2017).

Seaports are the major marine active sites for commercial, trade and recreational activities, which are exposed to a large quantity of discharge water. The level of input of port activities on the overall microplastic pollution load is largely unknown. As a nation dependent on maritime trade, Australian sea ports play an important role in the national economy by commodity exports and imports, tourism and fisheries and therefore urge proper attention for sustainable sea port management. Moreover, most of the previous studies demonstrated pollution of microplastics either on the surface water/beach sediment or its impact on megafauna, whereas less attention has been paid on the bioaccumulation of microplastics in bivalve mollusks, such as oysters. In this study, sediment and oysters were selected, rather than water samples because the water is transient and only reflects what is there at that point in time. Oysters and sediments provide better reflection of long-term loads in the area, which is also supported by a number of previous studies (Li et al., 2015; Van Cauwenberghe and Janssen, 2014; Peng et al., 2017; Claessens et al., 2011). In addition, a significant amount of water needs to be sampled for an accurate reflection of loads. The sediments, which are sinks for plastics in the environment, are a better surrogate particularly in semi-enclosed port areas for the relative microplastic loads in waterways. However, oysters are commonly used to biomonitor accumulation of pollutants in local biota and are suitable to monitor long term loads in the area which is also supported by many studies (Goldberg, 1986; Kolandhasamy et al., 2018; Yin and Wang, 2017). Oysters being sessile are more reflective of local microplastic loads in water than migratory or transient seabirds and fish. As filter feeders, oysters have been shown to accumulate plastics (Goldberg, 1986; Yin and Wang, 2017). Oysters are also common across the sample locations in the study area making them a suitable indicator for bioavailability of microplastics. As a common food source, it is also important to investigate the impact of marine activities on microplastic pollution in shellfish. Therefore, the present study aimed to investigate the interrelationship in the distribution, loads and properties of microplastic pollution (e.g., polymer type, colour, size) in the sediments and oysters (Saccostrea glomerata) of the six major seaports along the NSW coastline of Australia. This study also aimed to illustrate microplastic distribution in the port environment compared to a background (non-port area) to determine whether these facilities are a potential source of microplastics to the environment.

7.2 Methods

7.2.1 Sampling locations

In the present study six seaports of NSW (Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden) were selected as study sites, as shown in Fig. 7.1. The six seaports are in diverse geographical and hydrological conditions and are engaged in various activities. Port Jackson estuary is one of the highly urbanized (77%) and populated areas (4.6 million) in Australia located in Sydney, which is also well known as a tourist location with about 10 million tourist visitor per year (ABS, 2011; Jahan and Strezov, 2017; Sydney Tourism Statistics, 2018). The catchment is a complex hydrological system adjoining the main channel with large, shallow and polluted bays (polluted with sewage, toxic chemicals and microplastics) which are a significant reservoir for tidal waters (Hatje et al., 2003; Montoya, 2015). Port Botany is an important import and export port in Sydney located in a semi-enclosed estuary. This bay is connected and influenced by two major river systems, namely the Georges and Cooks Rivers, with catchments extending into the Sydney Metropolitan area and characterized by broad inflows of stormwater from urban and industrial areas (Spooner et al., 2003; Jahan and Strezov, 2018). Port Kembla is one of four major ports in NSW surrounded by a number of large industries e.g. Australia's largest steelworks, copper smelter, fertiliser manufacturing plant, cement industry and galvanizing plant. Allans Creek and Illawarra stormwater from urban areas are the major drainage systems to the port area (He and Morrison, 2001; Jahan and Strezov, 2019a). Port Newcastle is another major port in Australia, with coal as the main shipped commodity, located in the mouth of the Hunter River estuary (Jahan and Strezov, 2019b). Port Yamba is located on the Clarence River estuary which is the major agricultural catchment zone on the NSW Tasman Seashore and has a large fishing fleet. Port Eden is the largest fishing port in NSW located at the head of Twofold Bay, which also handles woodchip break bulk and machinery equipment, mainly for the oil and gas industry (Jahan and Strezov, 2017).

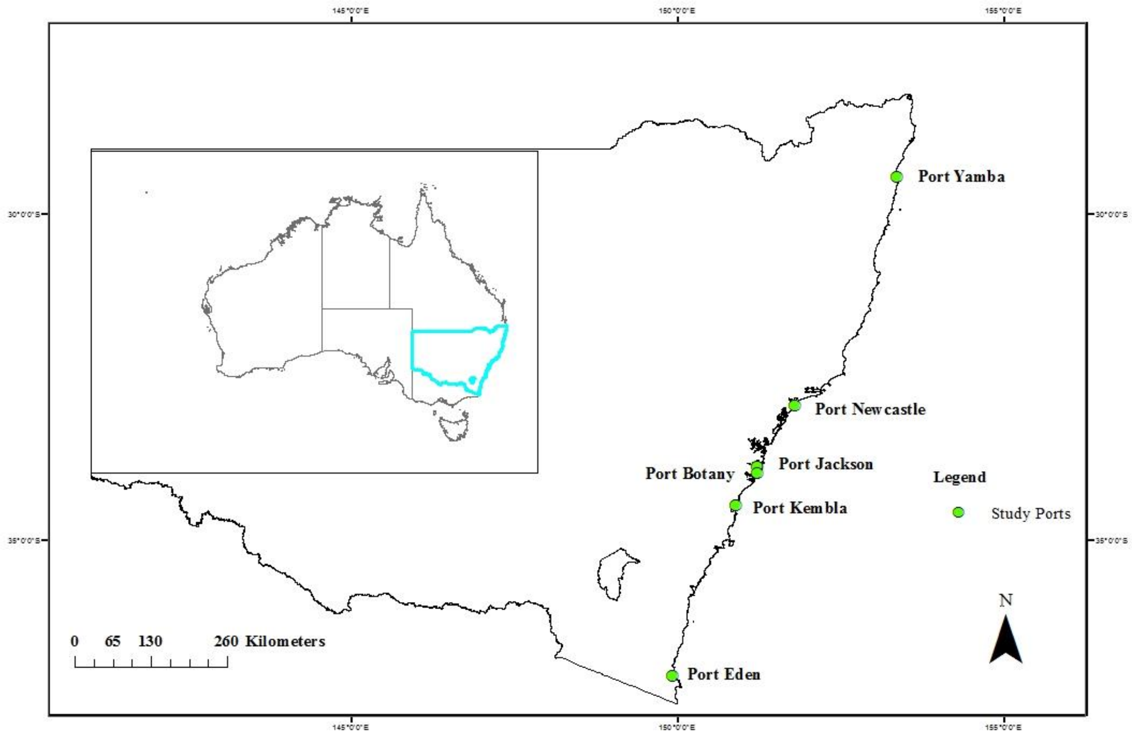

Fig. 7. 1 Map of the study area

7.2.2 Sediment sampling, microplastic extraction and polymer identification

7.2.2.1 Sample collection

Samples were collected during March–July 2017 which covers two seasons (autumn and early winter) in Australia with temperature ranges from 9 °C to 23 °C. A total of 18 sediment samples were collected at water depths ranging from 1 to 10 m (depending on the hydro bathymetry of the sampling location) from the six seaports of NSW. A stainless steel Ekman grab sampler with $6 * 6 * 6$ in. sample area was used to collect the samples, during which the sampling depth was measured with a marked string. The coordinates of the sampling location points are listed as supplementary information in Table S7.1 in Appendix E. From each port, three composite samples were collected from the top 5 cm of the sediment, of which one was background sample selected from similar hydrogeological area but far from the effects of port and other industrial activities. From each sampling point, two replicate sediment samples were collected approximately 1 m apart to make one composite sample. Composite samples were taken to reduce sampling error as often, one sample is not enough to present real conditions. The sediment samples were then stored in a glass bottle and carried to the laboratory for microplastic isolation.

At the same time of sediment sampling within the port 20-30 oysters were collected from the nearby rocky shoreline by hand using a stainless-steel shucking knife at each sampling point. Different size (3 cm - 7 cm) oysters were collected and immediately stored in an ice box and transferred to the laboratory for further analysis.

7.2.2.2 Microplastics Extraction

In this study, microplastic extraction from sediments was performed based on density separation technique in accordance with Thompson et al. (2004) and subsequently used in a number of studies (Blumenröder, et al., 2017; Yu et al., 201; Zhao et al., 2018). All the sediment samples were oven dried at 60°C for 48 hours to a constant weight. Three sub-samples from each replicate were analysed. In each glass beaker, 50 g of dried sample was mixed with 200 ml of saturated sodium iodide (NaI) solution (NaI with ρ = 1.20 g/ml) and agitated for 1 min using a magnetic stirrer and left to stand for 5 mins to settle the sediment. The top half of the solution was then carefully transferred to another glass beaker. This procedure was repeated three times to increase the recovery rate. Then, 5 ml of hydrogen peroxide (H_2O_2 35%) was added to the sample solutions to achieve a final concentration of 0.73% to degrade the organic matter (Zhao et al., 2018). After 24 hours of sedimentation the clean supernatant was decanted into a clean 500 ml glass beaker and then filtered through filter paper (Whatman GF/B glass microfiber pore size 1.0 μm) under vacuum filtration (Peng et al., 2017). The glass beaker and all the equipment used were washed with Milli-Q water and were filtered through the same filter paper to reduce sample loss. The filter paper was then placed into a covered petri dish and kept for microscopic (Olympus, SZ40) inspection. In order to prevent potential contamination during the microplastic extraction process, all apparatus openings were covered with aluminium foil. To validate the method, blank experiments were conducted on deionised water and magnetic stirrer solution prior to working with the collected samples (Zhao et al., 2018). In addition, three positive blank experiments with sediment were conducted with polyethylene terephthalate, PVC, polystyrene and nylon polymers which gave 98–100% microplastic recovery.

Prior to analysis, all the oyster samples were rinsed with Milli-Q water to remove the outer particles of the oyster. The shell length of the sample oyster was measured in the laboratory using Vernier callipers with 0.02mm precision. Then the soft tissue of the oysters was separated and weighted with a microbalance. The soft tissues from five individual oysters were added together as a replicate sample and from each individual sampling site, four replicates were prepared. The separation, digestion and collection of microplastics from oysters were performed by a revised procedure (Li et al., 2015; Li et al., 2018). The individual replicate sample was then added to 200 ml of 10% potassium hydroxide (KOH) solution for digestion of the tissues. All the digestion beakers were covered with aluminium foil and digested at 60-65ºC in an oscillating incubator at 70 rpm for 24 h and then kept another 24 h at room temperature. After complete digestion, 200 ml of saturated NaI solution was added to each beaker to float the microplastics and the overlying water was vacuum filtered through filter paper (Whatman GF/B glass microfiber pore size 1.0 µm). The filter paper was then placed into a covered glass petri dish for further observation under a stereo microscope (Olympus, SZ40) of 20×*20× magnification.

7.2.2.3 Polymer identification

To quantify the number of microplastics, the filter papers with the samples were stained with Nile red solution (0.1 µg/L, deionized water as solvent) used and validated by a number of studies (Erni-Cassola et al., 2017; Jessop et al., 2017; Maes et al., 2017; Shim et al., 2016) also suggested that not all polymers will be stained due to different hydrophobic properties with polymers such as PET and PVC not successfully stained. Staining does make identification easier but as not everything is potentially stained, we used both visual and staining techniques to provide a more comprehensive assessment of microplastic loads. The stained filter paper then was observed under the stereoscopic microscope (Olympus, SZ40) with fibre optic halogen lamp (Olympus LG-PS2). Another fluorescence blue lamp (SPECTROLINE EA- 160/F, 365 nm wavelength) was also used to detect glowing plastic particles that could not be seen under a halogen lamp. Moreover, fluorescencing microplastic fibres were not found in all the studied sea ports, hence, in this study, we present them separately to determine their availability. From the microscopic examination the shapes, colours, sizes and number of microplastics on filters were detected where microplastic shapes were defined as fibres, spherules, fragments and sheets. Colours were recorded as dominant visual property and the sizes were measured with the inbuilt scale inside the microscope and were categorised into five groups: 0.05–0.1 mm, 0.1–0.5 mm, 0.5–1 mm, 1–3 mm and 3–5 mm. From all sites, 352 (195 items from sediment and 157 items from oyster) suspected items of microplastics were randomly selected and tested by FTIR spectroscope (NICOLET 6700, FT-IR), of which

290 (161 items from sediment and 129 items from oyster) samples were recognized as microplastics. The spectra were collected in a reflectance mode, with 3 s of collection time and 4000–400 cm^{-1} of spectral ranges. The larger suspected samples were removed from the filter paper and tested directly by FTIR, whereas the suspected smaller particles were tested by cutting the specific part of the filter paper and using a clean filter paper as a background sample. The individual sample was tested twice by FTIR to reduce error. The resultant spectra were identified using OMNIC software and used to evaluate the polymer types with spectral assemblages (Peng et al., 2017). The abundance of microplastics in sediments were recorded as number of plastic particles per kilogram sediment (dry weight) while in the oysters microplastics were recorded as the number of plastic particles per gram (wet weight).

7.2.2.4 Contamination

For contamination prevention during laboratory analyses, strict control measures were taken. All used equipment was carefully washed with Milli-Q water and dried in oven before use to prevent airborne microplastics. The samples were also covered by aluminium foil during analysis and polymer-free gloves were used to prevent contamination.

7.2.3 Grain size analysis

To examine the correlation between grain size and microplastic abundance (Thompson et al., 2004; Vianello et al., 2013; Mohamed Nor and Obbard, 2014), the grain size distributions of sediments from each study areas were tested by using laser detection on a Malvern Mastersizer 2000 with a 300RF lens. The grain size of all sediment samples was analysed by first drying in an oven at 120 °C for 24 h and then sieving to particle size of <2000 µm (i.e. gravel-free). The samples were dispersed in water and, to break up agglomerated particles, 30 s of ultrasonication was used. From each sample a total of four measurements were made and averaged to determine the final value. The distribution abundances of grain size ranges (0.2–2000 µm) were calculated by the Malvern built-in software.

7.2.4 Statistical processing

All the statistical data were analysed with Origin 2018. To examine the linear relationship between microplastics abundance in sediment and oyster, the study adopted analysis of variance (ANOVA) for statistical inferences based on the linear regression model. ANOVA is founded on least squares and capable of modelling both balanced and unbalanced model designs (Fisher, 1925).

The model estimates for the study followed a simplified linear regression expressed as (Bowerman and T O'Connell, 1997):

$$y = \beta_0 + \beta_1 x + \varepsilon \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7.1)$$

Where y is the response variable, x represents the regressors and ε is the error term assumed to be independent and normally distributed.

7.3 Results

7.3.1 Microplastic abundance

The distribution and abundance of microplastics in the surface sediment of the study ports is shown in Fig. 7.2A. The results reveal the highest abundance of microplastics at Port Eden (350 particles/kg) followed by Port Yamba (224 particles/kg) and Port Kembla (205 particles/kg). Port Eden, Port Jackson and Port Newcastle had higher number of microplastics than their background environment. The other three ports, Port Botany, Port Kembla and Port Yamba, had the opposite trends. These differences of microplastic abundance in background and port environments were proven statistically significant ($P < .05$) as shown in Table 7.1.

Microplastics were found in oyster samples collected from the six study ports. The abundance of microplastics in the sampled oyster ranged from 0.15 to 0.83 (particles/g) of wet weight tissue inside the port areas and 0.06 to 0.44 (particles/g) of wet weight tissue in the background area (Fig. 7. 2B). Port Jackson had the highest number (0.83 particles/g) of microplastics, followed by Port Eden (0.63 particles/g), Port Yamba (0.60 particles/g), Port Newcastle (0.32 particles/g), Port Botany (0.22 particles/g) and Port Kembla (0.15 particles/g). However, at Port Kembla, the abundance of background microplastics (0.44 particles/g) was higher than the port area (0.15 particles/g). These variations of microplastic abundance are also statistically significant ($P < .05$), which is shown in Table 7.1.

Correlation analysis was also performed to test the relationship between microplastics abundance and sediment properties. According to the Pearson statistical analysis ($P < .05$) sedimentary microplastics abundance showed strong positive relationship with fine sediment particle (0.721) and total organic carbon (0.944) while they showed negative correlation with medium sand, coarse and very coarse sediment as shown in Table 7. 2.

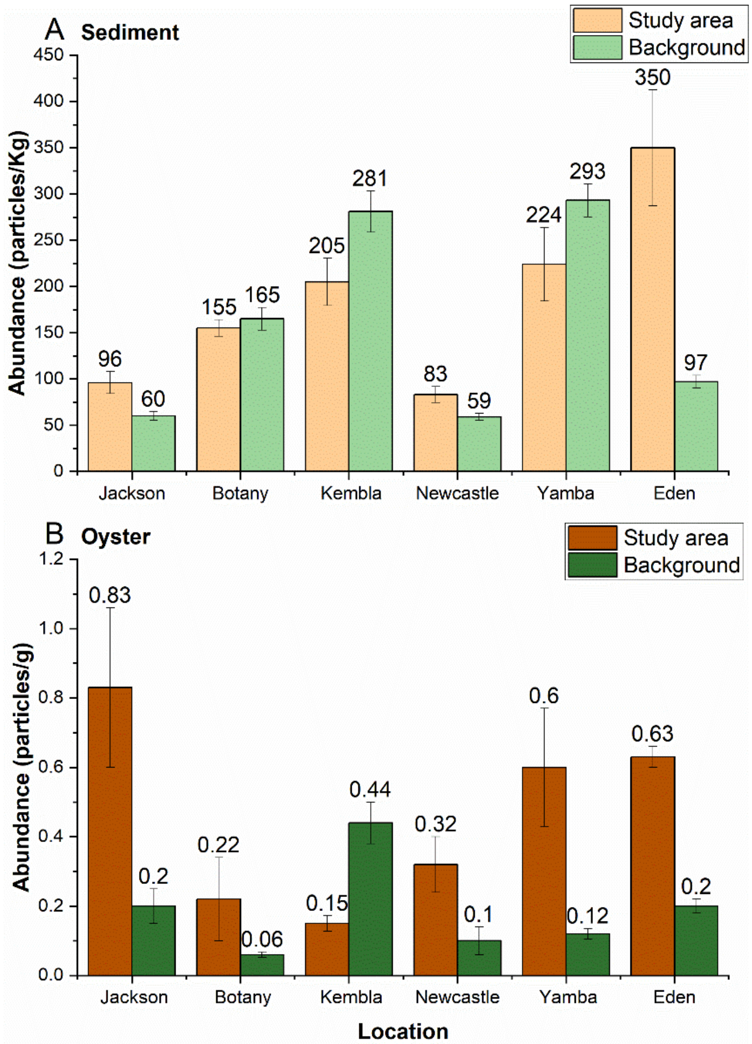

Fig. 7. 2 Abundance of microplastics in the (A) sediment and (B) oyster of the study seaports.

Table 7-1. Significance analysis of microplastic contamination between background sites and study ports.

Location	Sediment		Oyster	
	df	P	df	P
Port Jackson	9	0.012	9	0.032
Port Botany	9	0.0065	9	0.017
Port Kembla	9	0.003	9	0.0009
Port Newcastle	9	0.030	9	0.0697
Port Yamba	9	0.002	9	0.0008
Port Eden	9	0.0005	9	0.0015

Table 7-2. Correlation analysis of sediment properties with microplastics abundance in sediment and oysters of the seaports of NSW, Australia.

	Sedi MPs	*Oyster MPs*	*Moisture*	*F sand*	*M sand*	*C sand*	*VC sand*	*TOC*
Sedi MPs	1							
Oyster MPs	0.183	1						
Moisture	0.125	-0.030	1					
F sand	**0.721***	0.588	-0.047	1				
M sand	-0.353	-0.223	-0.402	-0.504	1			
C sand	-0.562	-0.545	0.195	-0.795	-0.103	1		
VC sand	-0.433	0.173	-0.191	-0.219	0.809	-0.366	1	
TOC	**0.944***	0.110	0.179	0.490	-0.150	-0.442	-0.336	1

Bold* denotes significant correlation, Sedi MPs= Sediment microplastics, Oyster MPs= Oyster microplastics, F sand= Fine sand, M sand= Medium sand, C sand= Coarse sand, VC sand= Very Coarse sand, TOC= Total Organic Carbon.

The linear relationship between microplastics abundance in sediment and oyster was calculated using ANOVA, with corresponding results presented in Fig. 7.3. While the overall linear regression estimate is significant at 5% level, a statistically insignificant positive relationship with 41% goodness of fit estimate ($R^2 = 0.41$) is found between the data series.

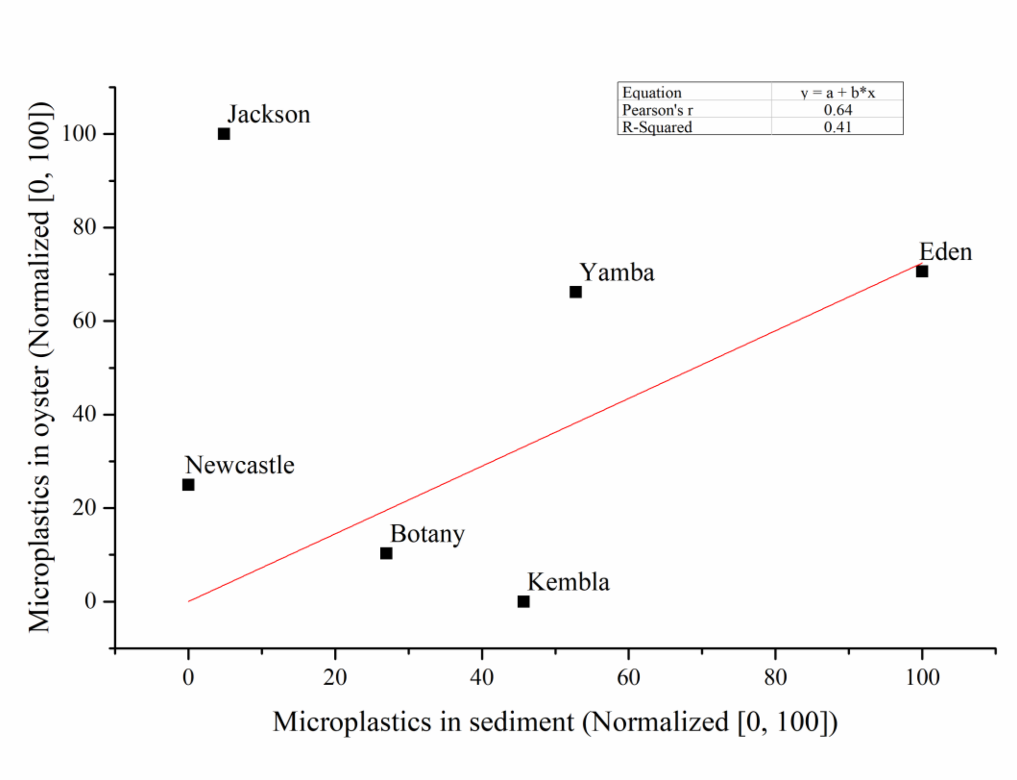

Fig. 7. 3 Correlation between microplastic abundance in the sediment and oysters of the seaports of NSW, Australia.

7.3.2 Microplastic characteristics

7.3.2.1 Microplastic colour

Multiple colours (transparent, white, black, blue, red and brown) of microplastic particles were identified from the sediments of the study ports. White was the dominant colour in all ports followed by transparent, black, red, blue and brown (Fig. 7.4. and Fig. 7.5.A).

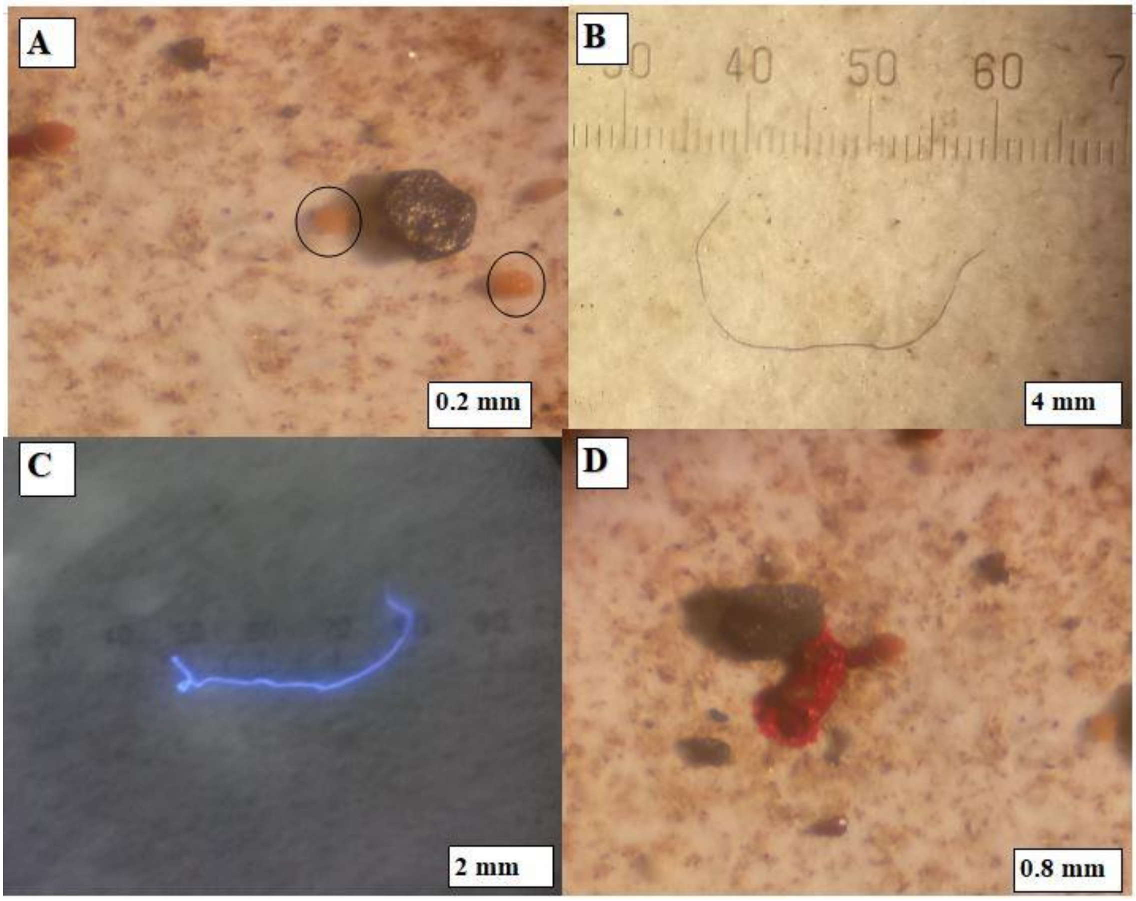

Fig. 7. 4 Photographs of (A) spherule, (B) fibre, (C) fluorescent fibre and (D) fragment microplastics identified in sediments and oysters of the seaports.

Five different colours (white, transparent, black, blue and red) of microplastics were detected in the oysters at the studied ports (Fig. 7. 6.A). The black coloured particles were dominant (about 51%) among all identified particles.

7.3.2.2 Microplastic shape

The identified microplastics were sorted into three shapes, namely fibre, fragments and spherules which were classified under two categories (normal microplastics and glowing microplastics) (Fig. 7. 4 and Fig. 7. 5.B). Among the different shapes, spherules were most abundant in all studied ports accounting for 24%–86% of the total microplastics, followed by fibres (5%–37%) and fragments (3%–13%). Spherules and fibres accounted for 61%–91% of the total microplastics at different sites with the highest percentage (91%) at Port Yamba followed by Port Eden (88%).

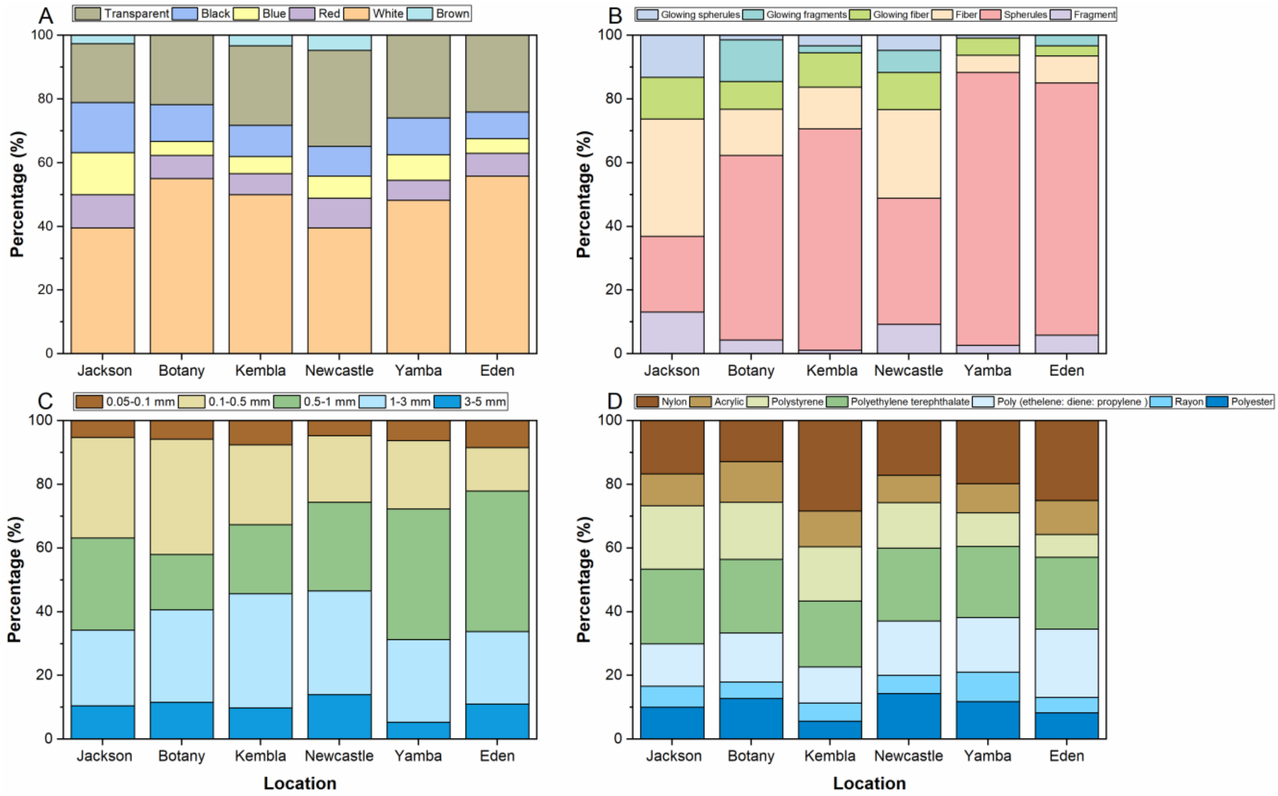

Fig. 7. 5 (A) Colours (B) shapes, (C) sizes, and (D) polymer types of microplastics in the surface sediments of six seaports of NSW, Australia.

Five types of microplastic shapes including fibre, fragments, spherules, glowing fibre and glowing spherules were detected in the soft tissues of the examined oysters (Fig. 7. 6.B). Fibre (43%-80%) was the dominant microplastic particles in the oysters at all study ports, followed by fragments (14%-43%). Fibres and fragments accounted for 52%-100% of the total microplastics at different sites with the highest percentage (100%) at Port Kembla, Port Newcastle and Port Eden (Fig. 7. 6.B).

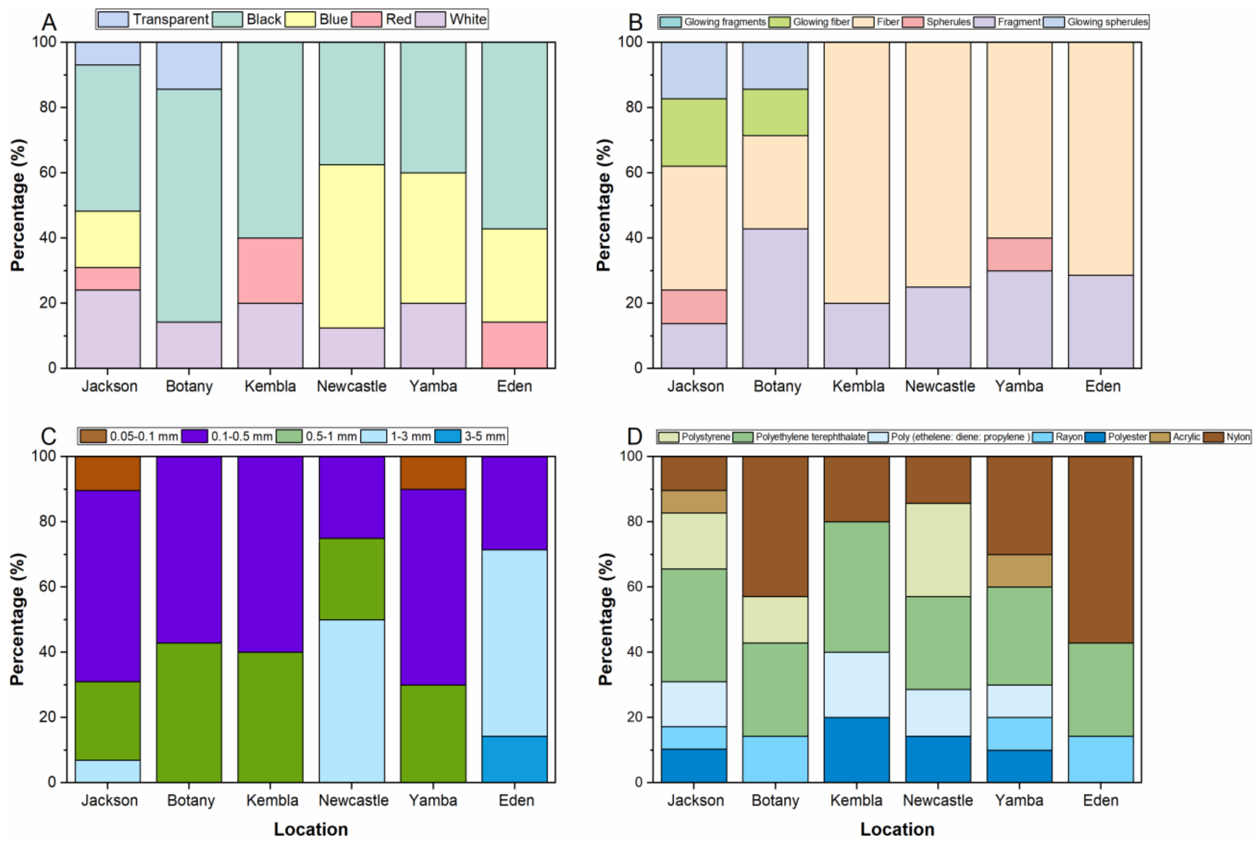

Fig. 7. 6 (A) Colours (B) shapes, (C) sizes and (D) polymer types of microplastics in the oysters of six seaports of NSW, Australia.

7.3.2.3 Microplastic size

The sizes of the sedimentary microplastic particles in the studied ports ranged between 0.1 mm to 4.9 mm, among which in Port Jackson (32%) and Port Botany (36%) size range of 0.1 mm - 0.5mm was the dominant size fraction (Fig. 7.5.C). However, in Port Kembla and Port Newcastle, the sizes from 1 mm-3 mm were the greatest size fractions (36% and 33% respectively). Similarly, at Port Yamba and Port Eden, the highest percentage (41% and 44%) of the total particles was in the 0.5 mm -1 mm size class.

Different sizes of microplastic particles were also detected in the oysters of the studied ports, of which 48% of the total plastic particles were in the sizes of 0.1 mm - 0.5 mm followed by 0.5 mm-1 mm size ranges (27%) in all ports. At Port Jackson, Port Botany, Port Kembla and Port Yamba, around 60% of all plastics were between 0.1 mm-0.5 mm size group (Fig. 7.6.C). However, at Port Eden and Port Newcastle 57% and 50% of the plastic particles were in 1 mm-3 mm size group respectively.

7.3.2.4 Microplastic composition

The study examined 195 suspected microplastics from the sediments of the study ports using FTIR analysis in which 161 items (82.56%) were confirmed as plastic polymers. The identified polymers included polyester, rayon, poly (ethylene: diene: propylene), polyethylene terephthalate, polystyrene, acrylic and nylon (Fig. 7.5.D). Nylon accounted for 28% and 25% of microplastics at Port Kembla and Port Eden followed by polyethylene terephthalate 21% and 23% respectively. All other ports were dominated by polyethylene terephthalate (21%–23%), followed by poly (ethylene: diene: propylene) (8%–21%), polystyrene (7%–20%), polyester (8%–15%), rayon (5%–9%) and acrylic (6%–11%).

In total, 157 suspected microplastics from sampled oysters were analysed with the FTIR in which 129 items (82.3%) were confirmed as plastic polymers. Among all the identified microplastic particles polyethylene terephthalate comprised 32% followed by nylon 29% in all ports. An exception was Port Eden and Port Botany where 57% and 43% of the microplastics were nylon (Fig. 7.6.D). The others comprise polyester (0%–20%), rayon (0%–14%), poly (ethylene: diene: propylene) (0%–20%), polystyrene (0%–31%) and acrylic (0%–11%) out of the total identified polymers.

7.4 Discussion

7.4.1 Abundance comparison between sediment and oyster of study area and other ecosystems

This study presents the inter-relationships between microplastic abundance in the sediments and oysters of seaports in NSW, Australia. The results demonstrated significant abundance of microplastics in the sediments and oysters in most ports. The ports with the highest microplastic concentrations in the sediments (Port Eden, Port Yamba and Port Kembla) also had oysters with the largest abundance of microplastics (Port Jackson, Port Eden and Port Yamba). The fishing activities at Port Eden and Port Yamba, intensive shipping and industrial activities at Port Kembla and excessive tourism, recreational boating and urban activities at and near Port Jackson were the probable reasons for microplastic abundance in these ports. Although, the abundance of microplastics showed similar pattern in the sediments and oysters of the studied seaports, oysters had higher number of microplastics than sediments in all sea ports, which demonstrates that the mobility and filter-feeding behaviour of oysters influences the accumulation of microplastics in their body. Moreover, the results showed that the type, size and colours in the oysters did not necessarily match the main components in the sediment, although the polymer composition matched well between each other. Black fibres with 0.1 mm–0.5 mm in size were the most abundant microplastics in the oysters, whereas white spherules of 0.5mm–1mm size were dominant in the sediments. The probable reasons may be that smaller fibres are more available for uptake by oysters than the longer fibres and retain them for longer in the oysters than the spherules. Fibres are likely to have a slower throughput in the filter-feeders once ingested as they get entangled and clogged. The dominance of black coloured microplastics in oysters may be a result of irritation and digestion processes or maybe a reflection of these being less dense plastics e.g. nylon only being consumed by the oysters which are indiscriminantly feeding closer to the surface layer. Similar results were also confirmed in studies conducted by Cauwenberghe et al. (2015), Cauwenberghe and Janssen (2014) and Leslie et al. (2013), where they stated that different invertebrates in polluted coastal ecosystems are more likely to ingest particles of smaller dimensions (0.01 mm–1 mm) because of their availability and easy uptake (Thushari et al., 2017). The density differences may also be the reason that spherules were the dominant microplastic in the sediments. Cheung and Fok (2017) found that microbead spherules were a range of densities and so the denser forms would directly settle from the discharge points into the surrounding sediments and unlikely be available to oysters.

7.4.2 Abundance comparison between sediment and oyster of study area and ecosystems around the world

The obtained dataset from this work was further compared with other published data which used similar methods and quantification units (particles per kg of dry weight sediment and particles per gram of wet weight oyster), which are summarized in Table 7.3. Comparing to other studies across the global marine coastal sediments, the abundance of microplastics (83–350 particles/kg) in the sediments of the studied Australian seaports in this work was higher than the microplastic abundance in the sediment (21.1 particles/kg) of New Zealand (Clunies-Ross et al., 2016), Singapore (37 particles/kg) (Mohamed Nor and Obbard, 2014), Russia (1.3–36.2 particles/kg) (Esiukova, 2017) and France (0.97 particles/kg) (Frere et al., 2017), whereas, the amount of microplastics was lower than those in the sediments of Japan (1845 particles/kg) (Matsuguma et al., 2017), China (6912 particles/kg) (Qiu et al., 2015), South Africa (1750 particles/kg) (Matsuguma et al., 2017) and Italy (1512 particles/kg) (Vianello et al., 2013). Comparable results were found in the sediment of South Korea (199.7 particles/kg) (Eo et al., 2018), Malaysia (300 particles/kg) (Matsuguma et al., 2017), Germany (88.1 particles/kg) (Hengstmann et al., 2018), Tunisia (316 particles/kg) (Abidli et al., 2018) and Bohai sea beach in China (127 particles/kg) (Yu et al., 2016; Mu et al., 2019).

The abundance of microplastics in the oyster (0.15–0.83 particles/g) from the studied ports in this work was comparable with other similar international studies [Belgium (0.26–0.51 particles/g) (De Witte et al., 2014), Germany (0.36 particles/g) (Cauwenberghe et al., 2015), France (0.47 particles/g)] (Van Cauwenberghe and Janssen, 2014), with the exception to the oysters in China (1.5–7.2 particles/g) (Li et al., 2015, J. Li et al., 2018; H-X. Li et al., 2018) which are considerably higher. Fibres were the dominant microplastic types in the oysters of the studied ports. Fibres were recorded as the most common type of microplastics in the aquatic environment and are documented as widely ingested by various aquatic biota (oyster, snail, starfish, sand-shrimp, mussels, and fish) (Li et al., 2016; Rochman et al., 2015; Salvador Cesa et al., 2017; Setala et al., 2016; Watts et al., 2015; Wang et al., 2019). The major sources of fibrous microplastics might be associated with the domestic stormwater, particularly water from sewage, industrial effluents or from plastic fishing nets and ropes used in the seaport areas (Napper and Thompson, 2016; Wang et al., 2019). Other notable source of fibrous microplastics could be the effluent from treatment plants which is usually effective in removing larger fibres, but smaller fibres could escape and contribute to the disposal of fibres to the marine environment (Murphy et al., 2016). Additionally, extensive fishing activities at some ports might result in fibrous pollution from lost or spared fishing gear, ropes, nets and lines (Wang et al., 2019). Although the possible effects of fibrous microplastics on crustaceans and fish were discussed in previous studies, their impacts on oysters is not known and hence further study is required (Watts et al., 2015; Jemec et al., 2016; Salvador Cesa et al., 2017). In the present study, smaller plastic particles were the most abundant microplastics (size ranges 0.1 mm –3mm) in the oysters collected at the studied seaports which is comparable to those in the oysters from China (0.02 mm – 5 mm) (J. Li et al., 2018, H-X. Li et al., 2018). However, small particles might harm oyster health as they could be easily ingested and accumulated in their soft tissue and may act as additives and adsorbed pollutants from the surrounding environment (J. Li et al., 2018, H-X. Li et al., 2018). Polyethylene terephthalate and nylon were the dominant polymers in the oyster at all ports, which is similar finding to the oysters (*Saccostrea cucullata*) from China shown in Table 3 (J. Li et al., 2018, H-X. Li et al., 2018).

Table 7-3. Distributions, major types, sizes and compositions of microplastics in the sediments and mollusc around the world.

Location	Substrate	Items (particles/Kg dry weight)	Major types	Major size(mm)	Major composition	Lower size limit (mm)	References
Sediment							
Australia	Marine sediment	83-350	Spherules and fibres	0.1-3	Nylon and PET	0.05	This study
New Zealand	Greater Canterbury region	21.2	Fragments	2-5	PS	<1	Clunies-Ross et al. (2016)
Japan	Tokyo Bay Canal sediment	1845	Fragments	0.3-5	PE and PEP	0.3	Matsuguma et al. (2017)
Chile	Continental coast sediment	1-805	Fragments	1-4.75	-	1	Hidalgo-Ruz and Thiel (2013)
South Korea	Sand beach	199.7	Foam	0.1-5	PS	0.02	Eo et al. (2018)
China	Bohai Sea Beach	127	Fragments	0.01-5	PEVA	0.01	Yu et al. (2016)
China	Beibu Gulf beach	6912	Fibres	0.1-5	PET	<1	Qiu et al. (2015)
Singapore	Coastal sediment	37	Fibres	0.02-5	PE and PP	<0.02	Mohamed Nor and Obbard (2014)
Malaysia	Straight of Johor coastal sediment	300	Fragments	0.315-5	PS and PP	0.3	Matsuguma et al. (2017)
Germany	Isle of Rügen, Beach sediment	88.1	Fibres	0.2-5	-	0.063	Hengstmann et al. (2018)
South Africa	Durban bay sediment	1750	Fragments	0.31-5	PE and PEP	0.3	Matsuguma et al. (2017)
Canada	Nova Scotia, sediment	150-800	Fibres	1.0-5	-	3	Mathalon and Hill (2014)
Tunisia	Coastal sediment	316	Fibres	0.1-5	PP	0.1	Abidli et al. (2018)
Russia	Kaliningrad, beach	1.3-36.2	Foam	0.5-5	PS	0.5	Esiukova (2017)

France	Brest Bay sediment	0.97	Fragments	0.3-5	PE	0.33	Frere et al. (2017)
Italy	Lido Di Dante sediment	1512	Fragments	0.007-1	PE and PP	0.015	Vianello et al. (2013)
Mollusc		**Items (particles/g wet weight)**					
Australia	Oyster (*Saccostrea glomerata*)	0.15-0.83	Fibres	0.1-3	Nylon, PET	0.05	This study
Belgium	Blue mussel *(Mytilus edulis)*	0.26-0.51	Fibres	1-1.5	PCB	0.2	De Witte et al., 2014
Germany	Blue mussel *(Mytilus edulis)*	0.36	Particles without observed fibres	0.02-0.09	PS	0.015	Van Cauwenberghe et al., 2015
China	Bivalves	2.1-10.5	Fibres, fragments and pellets	<0.25	PE	0.005	Li et al., 2015
China	Oysters (*Saccostrea cucullata*)	1.5-7.2	Fibres	0.02-5	PET	0.02	Li et al., 2018
France	Oyster (*Crassostrea gigas*)	0.47	Particles	0.005-0.01	-	0.005	Van Cauwenberghe and Janssen, 2014

All values are mean abundance, "-" means not reported in the article. PE: polyethylene; PEP: polyethylene-polypropylene; PS: Polystyrene; PEVA: Polyethylene vinyl acetate; PET: polyethylene terephthalate.

At Port Eden, Port Yamba and Port Botany, nylon was the dominant polymer in oysters, the major source of which for the two former sites is likely to be from fishing activities, such as from fishing ropes and nets, which dominate these seaports (Fig. 7.6.D). The Port Botany is a major cargo shipping terminal and the microplastic is likely from mooring lines and cargo netting. The diversity of microplastic type and polymer composition found in Port Jackson stands as an outlier to that of the other NSW ports and indicates that a diversity of sources (e.g. stormwater, shipping and recreational boating) are influencing this location.

7.4.3 Statistical significance of microplastic abundance between sediment and oyster

Sediment and oyster demonstrated a statistically insignificant positive linear relationship, as shown in Fig. 7.3. Oysters were collected from intertidal and shallow subtidal areas of the respective ports and as such microplastic loads represent what is available in the water column to these species. The sediment samples represent the loads present in benthic environments. The limited similarities in the microplastic findings between sediments and oyster suggests there to be different factors at play between these two compartments (e.g. currents, deposition). Thus, biota confined to these habitats may be exposed to differential microplastic loads and therefore sampling from just one compartment in these semi-enclosed waterways may not be representative of all exposure pathways.

7.4.4 Correlation analysis of microplastic abundance

The microplastic abundances in sediments showed strong relationship with grain size and total organic carbon content of the sediment, although microplastic abundances in oysters were not influenced by these factors, as shown in Table 7. 2. Dominance of fine grain sediment and high organic carbon in the sediment of the studied areas showed strong positive correlation with microplastic abundance in sediments, whereas coarser sediments showed negative correlation with microplastic. Smaller grain size and total organic carbon provide larger surface area to volume ratios than lager grain sizes, which helps retention of the microplastic particles (Wu et al., 2014). The mechanism of higher retention of microplastics on smaller sediment grain size is likely through sorption, co-precipitation and complexing of the microplastics on particle surfaces, which has been also shown to be the driving mechanism for higher accumulation of metal pollutants on smaller sediment grain sizes (Pourang et al., 2005).

7.4.5 Significance analysis of microplastic abundance between study port and background area

The abundance of microplastics varied among the seaports compared with their background environment which was tested by analysis of variance (ANOVA) and found statistically significant ($P < .05$) for all study ports, as presented in Table 7.1. This variation mostly depends on the type of human activities along with seaport activities. Some ports, such as Port Kembla and Port Yamba, where the port catchment is small, and Port Botany, which is a restricted area, there are other sources of microplastics from anthropogenic activities. Thus, the microplastics abundance in background environment in these locations was higher than in the port environment. The major sources of microplastics in the background marine environments are municipal waste from urban areas, sewerage, atmospheric deposition and industrial effluents. The ports with larger number of microplastics than their background areas, such as Port Eden, Port Jackson and Port Newcastle in this study, are influenced by higher anthropogenic activities in and near the ports which are further influenced by surrounding urban activities. Spherules (microbeads) and fibres accounted for 77% of the total microplastics in the sediments and oysters at the seaports of NSW, Australia, whereas fibres and fragments are the most common types of microplastics in the global marine environment (Mu et al., 2019). The ports with the largest fishing and fish processing activities, such as Port Eden, Port Botany and Port Yamba, had the highest number of microplastics with the largest proportion of spherules and fibres. This study confirms the impact of commercial fishing and the use of plastic nets and ropes as some of the most important activities for deposition of microplastics in the marine environment. Stormwater from residential areas and effluents from industries along with port activities are additional sources of the spherules and fibrous microplastic particles. In this study, the size distribution of most microplastics ranged from 0.1 mm to 3 mm which comprises 83% of the total microplastics and comparable to those identified in sediments of the global coastlines, as shown in Table 7. 3. Polyethylene terephthalate, polyethylene, polystyrene and nylon were the major polymer types in the studied ports which were also similar to other global studies (Table 7. 3). All these polymers are widely used in agriculture, food package, garments, construction materials, fishing ropes and nets.

7.5 Conclusions

Microplastic pollution in the sediments and oysters at the seaports in NSW, Australia are reported in this work for the first time. The results demonstrated a high level of microplastics at concentrations similar to other more populous regions of the world both in the sediments and oysters of the studied seaports. However, the abundance of microplastics in oysters is greater than that in sediments although their distribution shows similar pattern. A statistically insignificant positive relationship was found between the microplastic abundance in the sediments and oysters of the studied ports. The microplastic abundance in the seaport environments was higher compared to their background environment with some exceptions. Small sizes (<1mm) and spherules, fibres and fragments were the dominant types of microplastics in the studied ports, most of which were identified as polyethylene terephthalate and nylon polymers. This study demonstrates that ports are a potential source and a sink for microplastic and are highly influenced by the port activities along with intensive anthropogenic activities inside and surroundings the port environments. Further, ports with intensive commercial fishing and fish processing activities, such as Port Eden and Port Yamba, had the highest abundance of microplastics in both sediments and oysters, which identified fishing nets and ropes as some of the most important sources of microplastics in the port environment. Future management strategies therefore also need to include fishing activities in port as potential sources of impacts to these coastal environments.

7.6 References

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Chapter 8: Conclusions and Recommendations

This study was carried out at six major sea ports, namely Port Jackson, Port Botany, Port Kembla, Port Newcastle, Port Yamba and Port Eden, of NSW, Australia. The aim of this thesis was to explore the effects of diverse and extensive seaport activities on the surrounding environment. The study results demonstrate environmental deterioration from different commercial and recreational activities in and around the seaport areas along with other regular urban activities. The results further revealed that the major threats to the seaport environment are interconnected and the key sources of the threats lie in the water as well as in the inland catchments. Therefore, integrated strategic planning for seaport environment management are of the utmost importance along with integrated catchment management which is equally important for the sea and land. A comprehensive assessment of different pollutants in the seaport environment were examined and compared with their background environment and with different national and international standards (ANZECC, USEPA, FAO) which highlights the importance of implementing monitoring and successful and meaningful management initiatives at the seaports in Australia.

The key research outcomes achieved through this PhD research project are summarized as follows:

Water quality analysis of the port environment concluded a substantial level of chemical and biological contaminants and highlighted an average of good water quality with an exception at Port Botany, Port Yamba and Port Eden. Lower DO levels, higher turbidity, fecal coliforms reduced the water quality of Port Botany and Port Eden. The high concentrations of Cu, Mn, Pb and Zn in the ports water suggests that regular monitoring and management of port activities to account for both biological and chemical toxicological profiles of the discharging activities.

The concentrations and distribution of contaminants at the surface sediments of the seaports demonstrated significant concentrations of metals at Port Eden followed by Port Kembla, Port Jackson and Port Newcastle. The study further reported significant levels of As, Cu, Fe, Pb, Ni, Co and Zn in the sediment of all ports which were higher than the background concentrations and the standards given by ANZECC/ARMCANZ (2000) and other international guidelines. Substantial enrichment of some other trace elements e.g. Al, Bo, Co, Mo, Ba, Sn, Sr and Ti were also higher than the background surface sediments, although currently no guidelines exist for the concentration of these elements in sediments and therefore, needs appropriate attention.

Oyster and seaweed were used as bioindicators to assess the concentration of trace elements in the biota of the studied sea ports. The results illustrate varying levels of elements in oyster and seaweed and show that their concentrations were highly dependent on the nature of the ports and human activities in the vicinity of the port areas. The bioconcentration ratio and biota sediment accumulation factor analyses demonstrate significant accumulation of Fe, Cu, Mn, Zn, As, Al, Cr, Pb and Sr in oyster and Al, Mn, Pb, Fe, Zn, Br, As, Si, Sn and B in seaweed which reflect their availability in seawater and sediments.

Investigation of interrelationship between microplastic contamination in the sediments and oysters at the studied sea ports revealed considerable abundance of microplastic particles at 83-350 particles/kg dry weight in the sediments and 0.15-0.83 particles/g wet weight in the oysters at the seaports. However, the abundance of microplastics in oysters is greater than that in sediments although their distribution shows similar pattern. A statistically insignificant positive relationship was found between the microplastic abundance in the sediments and oysters of the studied ports. The microplastic abundance was also higher than their background areas in most ports except the background sediments of Port Botany, Port Kembla and Port Yamba and the background oyster at Port Kembla. Spherules, fibres and fragments of small sizes (<1 mm) and white and transparent colour were the dominant categories of microplastics most of which were identified as polyethylene terephthalate (23% and 35% respectively) and nylon (20% and 29% respectively) polymers by FTIR. This study demonstrates that ports are a potential source and a sink for microplastics and are highly influenced by the port activities along with intensive anthropogenic activities inside and surroundings the port environment. Furthermore, ports with intensive commercial fishing and fish processing activities, such as Port Eden and Port Yamba, had the highest abundance of microplastics in both sediments and oysters, which identified fishing nets and ropes as some of the most important sources of microplastics in the port environment.

Recommendations

This study accomplished a comprehensive study on the trace elements and microplastic contamination at the major sea ports of NSW, which provide important baseline information for future scientists, researchers, managers, government and nongovernment organizations. However, to attain sustainable management of sea port environment there is still a need for further research. The followings are thus recommendations to further enrich the study.

- In the port environment where contaminants are unevenly distributed (as in this study), an effective and independent monitoring plan is recommended for long-term spatial and temporal distribution of pollutants and the effects of these complex exposure scenarios for appropriate and effective management initiatives.

- Source identification of trace elements is an important requirement, as currently little knowledge exists with regards to the pollutant generation capacity specific to land uses in seaport. The unique nature and activities of individual port and the different land uses, such as cargo handling, container loading, storage of hazardous substances near port area and vehicle marshalling, may often contribute to emission of pollutants to the surrounding environment.
- Focus should be given on the short term and long term ecological risk assessment of trace elements and establish the trend in tolerance limit or trigger value to ascertain the impact trends for some commonly found trace elements, such as Fe, Al, Bo, Co, Mo, Ba, Sn, Sr and Ti, which do not have any trigger values or standard limits.
- To avoid regulatory intervention discrepancies in the water and sediment quality indices in terms of their ecological and toxicological impacts, focus should be given on building more comprehensive indices which cover wholistic pollutant groups e.g. physical, chemical and biological pollutants.
- Also need to highlight the unknown impacts of multiple stressors.
- Focus should be given on the impacts of metals and other contaminants on community structure and organism survival.

Appendix A

Table S2.1 The methods used to determine the contaminants, the types of studied samples, types of data, timeframe of sampling and predictive modelling

References	Location and Sampling Period	Materials studied	Analytical Methods	Types of data Quan.	Qual.	Time frame	Predictive modelling
Water Pollution							
Hatje et.al. (2003)	Sydney harbour, Australia, 1999	Metals	GFAAS (Perkin Elmer 4100ZL) and ICP-AES (Spectro Flame-EOP)	√		Medium term	×
Lee et.al. (2016)	Sydney estuary, Australia, 2015	Metals	ICP-OES	√		Short term	Biokinetic and equilibrium model
Taylor (2003)	Port Botany, Australia, 1992-1999	Metals, organochlorine, nutrients	×	√		×	×
Beavington (1975)	Port Kembla, Australia, 1974	Metals	×	√		Short term	×
Bowen (1979)	Port Kembla, Australia, 1977-78	Metals	×	√		Long term	×
He and Morrison (2001)	Port Kembla, Australia, 1970s-1990s	Metals, nutrients	×	√		Long term	×
Angel et al. (2010)	Port Curtis, Australia, 2003-2004	Trace metals	ICP-AES (Spectroflame EOP, Spectro Analytical Instruments, GmbH, Kleve, Germany)	√		Long term	×
Angel et al. (2012)	Port Curtis, Australia, 2003-2004	Trace metals	ICP-AES (Varian730 ES)	√		Medium Term	×
Farias et al. (2018)	Derwent Estuary, Tasmania, 2013	Metals	ICP-AES	√		Short term	×

References	Location and Sampling Period	Materials studied	Analytical Methods	Types of data Quan.	Qual.	Time frame	Predictive modelling
Sediment Pollution							
Birch and Taylor (1999)	Port Jackson, Australia, 1999	Heavy metals	Flame Atomic Absorption Spec-trometer (FAAS)	√		×	×
Montoya (2015)	Sydney Harbour, Australia, 2008	Dioxin, metals, microplastics	×	√	√	Long term	×
Birch (2017)	Sydney Harbour, Australia, 2016	Metals, PAHS, Organochlorine, PCBS	×	√	√	×	×
Birch et al. (1996b)	Sydney estuaries, Australia, 1996	Metals	Perken Elmer 3000 atomic absorption spectrometer	√		Short term	×
Dafforn et al. (2012)	NSW coast, Australia, 2010	Metals and PAHs	ICP-AES (Perkin Elmer, Optima7300DV, USA)	√	√	Short term	×
Birch et al. (1998a)	Hawkesbury River, Australia, 1998	Heavy metals, organochlorine, nutrients	×	√	√	Short term	×
Birch (2017a)	Sydney estuary, Australia, 1980-2017	Metals	×	√		Review	×
Birch et al. (1997)	Port Hunter, Australia, 1996	Metals and organics	Flame Atomic Absorption Spectrometer	√		Short term	×
Birch and Taylor (2004)	Sydney Harbour, Australia, NA	Metals, PCBs	×	√		Long term	×
Bately and low (1985)	Port Kembla, Australia, 1985	Heavy metals, tributyltin	×	√		Long term	×
He and Morrison (2001)	Port Kembla, Australia, 1970s-1990s	Metals, nutrients	×	√		Long term	×
Kachenko and Singh (2006)	NSW, Australia, 2004	Heavy metals	ICP-AES	√		Short term	×

Jafari (2009)	Port Kembla, Australia, 2008	Trace metals	X-Ray Fluorescence Spectrometry	√	Short term	×
Dafforn et al. (2012)	NSW coast, Australia, 2010	Metals and PAHs	ICP-AES (Perkin Elmer, Optima7300DV, USA)	√ √	Short term	×
Birch and Taylor (2000a, 2000b)	Sydney Harbour, Australia, NA	Heavy metals, organochlorine, PAHs	Atomic Absorption Spectrometer (model 3000)	√	Short term	×
Fabris (1999)	Port Philip Bay, Australia, 1993	Heavy metals	Furnace- or flame- atomization atomic-absorption spectrometry	√ √	Short term	×
Birch and Taylor (2004)	Sydney Harbour, Australia, NA	Metals, PCBs	×	√	Long term	×
Talbot and Chegwidden (1983)	Western Australia, 1983	Heavy metals	Perkin-Elmer 503 AAS flame	√	Short term	×
Birch and Olmos (2008)	NSW estuaries, Australia, NA	Heavy metals	Flame Atomic Absorption Spectrometer (FAAS)	√	Short term	×
Reichelt and Jones (1994)	Cleveland Bay, Australia, 1991	Heavy metals	Flame Atomic Absorption Spectrometer (FAAS) and graphite furnace AAS	√	Short term	×
Ward and Young (1981)	South Australia, 1979	Trace metals	Atomic Absorption Spectrometer	√	Short term	×
Tiller (1989)	South Australia, NA	Heavy metals	×	√	Short term	×
Jones et al. (2005)	Port Curtis, Australia, 2001-2002	Metals, PAHs	Solvent-extraction graphite furnace atomic adsorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, atomic fluorescence spectrometry	√ √	Medium term	×
Angel et al. (2012)	Port Curtis, Australia, 2003-2004	Trace metals	ICP-AES (Varian730 ES)	√	Short term	×
Jones et al. (2003)		Trace elements	X-ray fluorescence and neutron activation analyses	√	Long term	×

Townsend and Seen (2012)	Derwent estuary, Australia, 1996-1997	Metals	ICP-AES	√	Short term	×
Farias et al. (2018)	Tasmania, Australia, 2004	Metals	ICP-AES	√	Short term	×
	Derwent Estuary, Tasmania, 2013					
Biotic Pollution						
Birch et al. (2014)	Sydney estuary, Australia, 2005-2008	Metals	ICP-AES	√	Long term	×
Spooner et al. (2003)	Botany Bay, Australia, 1999	Trace metals	Perkin-Elmer SCIEX Elan 6000 ICP-MS	√	Medium term	×
Dafforn et al. (2012)	NSW coast, Australia, 2010	Metals and PAHs	X-Ray Fluorescence Spectrometry	√ √	Short term	×
Chakraborty and Owens (2014)	South Australia, 2010	Metals	Inductively coupled plasma mass spectrometer (ICP-MS)	√	Short term	×
Gall et al. (2012)	Port Kembla, Australia, 2008-2009	Metals	Inductively coupled plasma mass spectrometry (ICP-MS)	√ √	Short term	×
Maher et al. (2016)	NSW, Australia, 2009-2013	Metals	Inductively coupled plasma mass spectrometry (ICP-MS)	√	Short term	×
Jones et al. (2005)	Port Curtis, Australia, 2001-2002	Metals, PAHs	Solvent-extraction graphite furnace atomic adsorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, atomic fluorescence spectrometry	√ √	Medium term	×
Scanes and Roach (1999)	NSW, Australia, 1993	Trace metals	Inductively coupled plasma mass spectrometry (ICP-MS)	√	Medium term	×

NA= Not available, x = Undefined, Short term=1 to 6 months, Medium term= 6 to 12 months, Long term=More than 12 months.

Appendix B

Table S3.1 Australian and international standards and /or guidelines for Marine water ecosystem.

Parameter (mg/l)	ANZECC, 2000 (Marine water trigger value)	USEPA, 2009 (MCL)	UK, 2014 (MAC)
pH	8.4		
DO %	90		
Fecal Coliform (MPN)		9.9	
Silver	0.0008	-	-
Aluminum	-		
Arsenic	-	0.036	0.025
Cadmium	0.0007	0.0093	
Chromium	0.0077	-	0.015
Copper	0.0003	0.0031	0.00376
Iron	-		0.001
Manganese	-		-
Nickel	0.007	0.0082	0.03
Lead	0.0022	0.0081	0.025
Selenium	-	0.071	-
Zinc	0.007	0.081	0.04
Mercury	0.0001	0.00094	
Beryllium	-	-	-
Vanadium	0.05		0.1
Boron	-	-	7
Cobalt	0.000005	-	-

Table S3.2 Descriptions of study ports

Study ports	Major Activities	Reference
Port Jackson	Port Jackson (Sydney Harbour) is the premier port of Australia. Passenger shipping, recreational boating and water sports are the major activities at this port.	Harris and O'Brien, 1998
Port Botany	Port Botany is located at the mouth of the George River. Principal imports to the port are crude oil, bulk liquids and containers and exports are petroleum products and containers.	
Port Kembla	Port Kembla is a commercial port for importing iron ore, dolomite, limestone, sulphur, copper, phosphate rock and petroleum products and exporting iron and steel, coal, coke, tinplate and copper cables.	
Port Newcastle	The Port of Newcastle is located on the Hunter River estuary. Its main use is (inbound) raw materials for steelworks, fertiliser and aluminium industries and (outbound) coal, grain, steel products, mineral sands and woodchips.	
Port Yamba	Port Yamba is located on the Clarence River estuary, on the NSW coast. It is the home of the second largest fishing fleet of NSW and handles a range of imports and exports, such as container liquid berth-livestock and explosive products.	
Port Eden	Port Eden is located at the head of Twofold Bay. It is one of the largest fishing fleets in New South Wales, Australia. Woodchip export is currently the major trade for the port, while the principal imports are break bulk and machinery and equipment, mainly for the oil and gas industry.	

Table S3.3 Environmental Water Quality Index (EWQI) calculation

Location	**ATSDR Total Points**	**Jackson**										**Botany**									
Parameters		1 Bg High	1 Bg Low	2 High	2 Low	3 High	3 Low	4 High	4 Low	5 High	5 Low	1 High	1 Low	2 High	2 Low	3 High	3 Low	4 High	4 Low	5 Bg High	5 Bg Low
Silver	605	bd	bd	bd	bd	bd	0.61	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	0.61	bd	0.61
Aluminum	686	13.03	11.66	15.8	15.8	14.4	19.2	10.29	11.7	9.6	9.6	43.2	53.5	21.95	120	103.6	342	20.6	48	12.35	15.8
Arsenic	1672	5.016	6.688	5.02	6.69	5.02	6.69	5.016	5.02	5.02	5.02	5.02	3.34	5.016	11.7	6.688	8.36	6.69	6.69	5.016	13.4
Cadmium	1319	bd	bd	bd	bd	bd	1.32	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Chromium	896	0.896	bd	0.9	0.9	0.9	0.9	0.896	bd	bd	bd	bd	bd	bd	bd	0.896	1.79	bd	bd	bd	bd
Copper	806	3.224	2.418	3.22	2.42	3.22	2.42	2.418	2.42	3.22	2.42	2.42	1.61	0.806	2.42	2.418	7.25	3.22	3.22	1.612	2.42
Iron	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Manganese	798	3.192	2.394	2.39	3.19	3.19	2.39	1.596	1.6	1.6	2.39	2.39	3.99	4.788	4.79	3.192	9.58	2.39	3.99	1.596	2.39
Nickel	996	0.996	bd	1	1	1	bd	bd	1	1	bd	1	bd	0.996	1	bd	1	bd	1	bd	1
Lead	1529	1.529	1.529	3.06	3.06	1.53	1.53	1.529	1.53	1.53	1.53	1.53	1.53	1.529	3.06	3.058	10.7	1.53	3.06	1.529	1.53
Selenium	776	bd	15.52	15.5	15.5	15.5	15.5	15.52	15.5	15.5	15.5	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Zinc	915	34.77	8.235	20.1	8.24	15.6	8.24	14.64	6.41	11	9.15	14.6	3.66	4.575	13.7	10.07	16.5	22.9	10.1	7.32	6.41
Mercury	1459	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Beryllium	1031	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Vanadium	650	2.6	2.6	1.95	1.95	1.95	1.95	1.95	1.95	2.6	2.6	4.55	5.2	2.6	4.55	3.9	6.5	3.25	4.55	3.25	3.25
Boron	438	1946	1962	1918	1848	1949	2002	1932	1958	1870	1914	1866	1949	1936	1923	1949	2024	1885	1825	1879	2018
Cobalt	1012	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Molybdenum	442	3.536	3.978	3.98	3.98	3.98	3.98	3.978	4.42	3.98	3.54	4.42	4.86	4.862	4.86	5.304	5.3	4.86	4.86	4.862	5.75
Antimony	601	0.307	0.391	bd	0.32	0.31	bd	bd	bd	bd	bd	0.6	0.6	0.601	bd	0.601	0.6	0.6	0.6	bd	bd
Barium	802	6.376	6.496	5.74	5.8	5.58	6.09	5.389	6.4	5.72	6.1	8.02	10.4	8.822	11.2	7.218	9.62	9.62	12	6.416	7.22
Bismuth		bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Tin	487	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd

Total of ATSDR	2021	2024	1997	1917	2021	2072	1995	2016	1931	1972	1953	2038	1993	2100	2096	2443	1961	1924	1923	2078
EWQI	0.041	0.034	0.04	0.04	0.04	0.04	0.038	0.04	0.04	0.04	0.03	0.03	0.035	0.03	0.034	0.03	0.04	0.03	0.036	0.03

Continued...

Location	**ATSDR**					**Kembla**										**Newcastle**					
Parameters	**Total Points**	1 Bg High	1 Bg Low	2 High	2 Low	3 High	3 Low	4 High	4 Low	5 High	5 Low	1 High	1 Low	2 High	2 Low	3 High	3 Low	4 High	4 Low	5 Bg High	5 Bg Low
Silver	605	2.42	1.82	1.82	1.21	1.82	1.21	1.82	1.21	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Aluminum	686	25.38	2.74	0.69	5.49	3.43	2.06	11.66	1.37	2.06	15.09	9.14	13.03	9.14	6.86	2.59	42.53	17.85	85.75	3.40	2.06
Arsenic	1672	5.02	5.02	3.34	5.02	5.02	5.02	8.36	6.69	5.02	6.69	5.40	6.69	6.07	5.02	6.32	5.02	3.34	6.69	5.02	5.02
Cadmium	1319	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Chromium	896	0.90	bd	bd	bd	0.90	bd	bd	bd	0.90	bd	bd	bd	0.90	bd	0.90	0.90	bd	bd	bd	bd
Copper	806	0.81	bd	bd	0.81	3.22	1.61	0.81	0.81	1.43	0.81	bd	4.03	bd	0.81	0.81	2.42	0.81	1.61	bd	bd
Iron	0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Manganese	798	29.53	1.60	0.80	0.80	7.18	3.99	3.19	3.19	0.80	2.39	4.29	3.99	6.38	5.59	4.29	11.17	4.66	27.13	0.80	1.60
Nickel	996	2.99	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Lead	1529	bd	bd	bd	bd	1.53	1.53	1.53	1.53	bd	bd	bd	bd	bd	bd	bd	bd	bd	1.53	bd	bd
Selenium	776	0.78	bd	bd	bd	bd	bd	bd	bd	1.55	bd	2.21	1.68	2.21	2.33	bd	0.54	bd	3.88	bd	1.55
Zinc	915	0.92	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	18.30	bd	bd	bd	9.15	bd	bd	bd	bd
Mercury	1459	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Beryllium	1031	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Vanadium	650	1.95	2.60	1.95	2.60	2.60	2.60	2.60	2.60	2.60	2.60	2.55	2.55	2.55	2.55	2.55	2.55	3.13	3.13	2.55	2.55

Boron	438	2010.42	1991.59	2002.10	1991.59	1969.25	1940.78	1935.52	2013.49	1987.21	2013.49	1997.46	1987.03	2073.14	2005.50	2016.09	1937.42	1970.67	2022.58	2128.70	1975.73
Cobalt	1012	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Molybdenum	442	3.98	4.86	4.86	5.30	5.75	5.30	5.75	5.30	3.98	3.98	2.85	3.60	3.52	3.60	3.52	3.92	3.86	3.92	4.29	3.67
Antimony	601	0.60	0.60	0.60	0.60	0.60	0.60	0.60	bd	bd	bd	0.33	0.33	0.33	0.33	0.33	bd	0.33	bd	0.33	bd
Barium	802	4.81	4.81	4.81	4.81	6.42	5.61	6.42	5.61	5.61	4.81	7.40	10.65	7.77	8.23	7.41	8.23	7.41	8.72	4.18	3.90
Bismuth		bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd	bd
Tin	487	bd	bd	bd	bd	0.49	bd	0.49	bd	0.49	0.49	bd	0.36	bd	0.36	0.31	0.36	bd	0.36	0.26	0.36
Total of ATSDR		2090.49	2015.63	2020.97	2018.22	2008.19	1970.31	1978.74	2041.80	2011.64	2050.34	2031.63	2052.23	2112.00	2041.15	2045.11	2024.18	2012.07	2165.29	2149.53	1996.42
EWQI		0.035	0.037	0.036	0.039	0.036	0.039	0.04	0.04	0.037	0.038	0.036	0.036	0.035	0.038	0.036	0.036	0.039	0.04	0.035	0.036

Continued….

Location	**ATSDR**	**Yamba**										**Eden**									
Parameters	**Total Points**	1 Bg High	1 Bg Low	2 High	2 Low	3 High	3 Low	4 High	4 Low	5 High	5 Low	1 High	1 Low	2 High	2 Low	3 High	3 Low	4 High	4 Low	5 Bg High	5 Bg Low
Silver	605	0.15	0.1	0.14	0.1	0.14	0.07	0.13	0.07	0.09	0.35	0.33	0.07	0.09	-0	0.07	-0.04	0.05	-0.02	0.01	-0.02
Aluminum	686	15	28.6	78.87	155	70.17	802	28.8	172	26.35	94.3	bd	bd	Bd	10.7	bd	bd	bd	8.88	bd	bd
Arsenic	1672	4.05	4.08	5.35	5.2	4.93	7.89	2.63	5.4	4.89	4.42	3.56	48.4	2.52	9.45	5.75	10.5	3.73	2.56	4.93	6.87
Cadmium	1319	0.03	0.14	0.13	0.03	0.16	0.07	0.11	0.06	0.06	0.04	0.07	9.88	0.01	1.25	0.08	1	0.05	0.11	0.3	1.11
Chromium	896	0.39	0.56	0.60	0.77	0.51	1.61	0.7	0.51	0.67	0.78	0.68	0.15	0.37	0.39	0.22	0.3	0.24	0.04	0.44	0.1
Copper	806	0.34	0.15	5.52	2.88	7.80	12.7	0.64	3.51	5.26	33.2	bd	bd	Bd	bd	bd	bd	bd	bd	bd	bd

Iron	0	0	0	0	0	0	0	0	0	0	0	bd	0	Bd	0	bd	0	bd	bd	bd	0
Manganese	798	8.91	7.58	10.1	14.5	11.01	35	7.27	7.37	7.46	10.1	1.22	40.6	0.55	10.8	0.8	7.25	0.94	1	1.77	5.49
Nickel	996	bd	bd	bd	bd			bd	bd	bd	bd	0.32	8.86	0.35	1.5	0.29	1.63	0.28	0.25	0.31	1.55
Lead	1529	0.19	0.02	0.30	0.77	0.59	6.89	0.19	0.9	0.25	1.56	0.27	0.96	0.19	0.17	0.23	0.78	0.17	0.06	0.06	0.15
Selenium	776	bd	bd	bd	bd			bd	bd	bd	bd	bd	bd	Bd	bd	bd	bd	bd	bd	bd	bd
Zinc	915	bd	bd	12.91	bd	10	32.4	bd	bd	bd	11.6	2.80	26.3	1.93	6.96	2.08	8.34	1.36	5.25	1.03	2.42
Mercury	1459	-0.09	-0.2	-0.15	0.01	-0.06	0.16	-0.13	-0.1	-0.03	-0.06	0.04	-0.32	-0.34	-0.6	-0.39	-0.47	-0.32	-0.29	-0.4	-0.34
Beryllium	1031	-0.01	0.13	0.09	0.08	0.11	0.13	0.09	-0	0.04	-0.09	-0.07	0.85	-0.02	0.62	-0.04	0.41	-0.02	-0.04	0	0.47
Vanadium	650	1.63	2.46	2.37	2.81	2.98	5.51	2.64	3.11	2.79	2.7	2.66	2.33	2.50	2.66	2.84	2.4	2.98	2.66	2.46	2.72
Boron	438	1994	2077	2103	2042	2033	2082	2074	2083	2082	2056	1912	1747	2002	1950	1920	1903	1946	1935	1894	1866
Cobalt	1012	0.2	0.14	0.43	0.22	0.36	0.85	0.28	0.24	0.20	0.15	0.02	1.58	0.02	0.32	0.03	0.23	0.04	0.05	0.11	0.3
Molybdenum	442	3.66	4.24	4.27	4.23	3.96	3.87	3.51	4.07	3.98	4.32	3.41	3.57	3.90	3.7	3.75	4.17	4.4	3.81	4.14	3.7
Antimony	601	0.14	0.17	0.24	0.13	0.24	0.26	0.28	0.23	0.13	0.19	bd	bd	Bd	bd	bd	bd	bd	bd	bd	bd
Barium	802	8.61	8.56	9.16	9.1	8.88	8.78	8.31	8.09	8.45	7.64	4.50	23.4	4.52	7.37	4.45	6.79	4.23	4.64	4.59	6.07
Bismuth		0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Tin	487	2.92	1.46	2.43	0.97	1.46	1.46	1.46	0.97	1.46	0.97	0.48	0.49	0.48	0.49	0.49	0.49	0.49	0.49	0.49	0.49
Total of ATSDR		2041	2135	2236	2239	2157	3002	2131	2289	2144	2229	1932	1914	2019	2006	1941	1947	1965	1965	1914	1897
EWQI		0.04	0.04	0.034	0.03	0.033	0.02	0.03	0.03	0.035	0.03	0.038	0.02	0.037	0.03	0.04	0.03	0.04	0.04	0.04	0.04

Bd=below detection, EWQI= Environmental Water Quality Index.

Appendix C

Table S4.1 Study area and global metal concentrations in total surficial sediment (mg/kg dry wt.)

	Cd	Co	Cr	Cu	Ni	Pb	Zn	References
Port Jackson	Bd	1	4	6.00-7	2.0-3	18	80-90	This work
	Bd	1	4	7	3	18	85	
Port Botany	Bd	Bd	1.00-2	0-2	Bd	2	4.0-9	This work
	Bd	Bd	1	2	Bd	2	7	
Port Kembla	Bd-0.6	2	9.00-13	41-76	6.0 -34	27-120	180-290	This work
	0.6	2	11	59	20	74	235	
Port Newcastle	Bd	2	3.00-4	4	3	24	76-80	This work
	Bd	2	4	4	3	24	78	
Port Yamba	Bd	Bd	Bd-1	1	Bd	1	3	This work
	Bd	Bd	1	1	Bd	1	3	
Port Eden	Bd-0.6	4.0-20	19-43	190-2200	9.0-15	120-410	890-3800	This work
	0.6	12	31	1195	12	165	2345	
Hong Kong, China	0.1 - 5.3		5-560	1.0-4000	5.0-220	9-260	17.0-790	Zhou et al., 2007
	0.33		49	119	25	54	148	
Quanzhou Bay, China	0.3-0.9		51-122	25-120	16.0-46	32-101	106-242	Yu et al.,2008
	0.59		82	71	33	68	180	
Tamaki Estuary	0.1-1			21-47		51-122	138-272	Abrahim and Parker,2008
Auckland, New Zealand	0.28			35		73	207	
Qua Iboe Estuary			0.01-0.02	43-45	21	43-46	102-104	Udofia et al.,2009
Niger Delta, Nigeria			0.014	44	21	45	102	
Lima Estuary			24-84	16-406	1.0-46	19-64	59-398	Cardosa et al.,2008
Viana do Castelo, Portugal			57	45	14	37	111	
Port of Barcelona	0.4-2.8		39-110	71-531	18-34	86-89	183-1133	Guevara-Ribaetal., 2004
Barcelona, Spain	1.22		68	183	25	189	391	
Gulf of Gemlik		13-24	71-181	23-58	35-165	0.1-67	88-185	Ünlü et al., 2008
Sea of Marmara, Turkey		19	117	41	110	29	128	
San Pablo Bay	0.1-0.4		15-39	25-49	27-45	15-27	48-79	Lu et al., 2005
San Francisco, USA	0.21		21	39	37	22	65	
Montevideo Harbour			79-253	59-13	26-34	44-128	174-491	Muniz et al.,2004
Uruguay			161	89	30	85	312	
Gulf of Paria			10.0-40	5.0-22	5.0-24	1.0-37	48-158	Rojas de Astudillo et al., 2005
Southeast coast of India	87±10	211±8.5	131±13	123±10	272±11	343±15	519±26	Jha et al., 2019
Persian Gulf, Iran	0.2-0.49	8.5-13	41.19-59.9	13.4-571	59.8-97.6	5-19.8	36.2-302	Lahijanzadeh, et al., 2019

Bd= below detection

Table S4.2. Comparisons of the results from different indices used in this study.

Sediment quality indices	Outcome	Port area
EF index	Cu, Zn	Port Eden
Igeo index	Cu, Zn, As, Cr, Pb	Port Eden
PER index	Cu, As, Zn, Pb	Port Eden
SPI index	Cu, Zn	Port Eden

Appendix D

Table S5.1. Recovery (%) and practical quantification limit (mg/kg dry wt.) of analyzed trace elements

Trace elements	Recovery (%)	Detection limit (mg/kg dry wt.)
Al	96.3	1
As	102	4
Cr	105	1
Cu	103	1
Fe	108	1
Mn	102	1
Pb	95.6	1
Zn	101	1
Hg	98.3	0.1
Cd	106	0.4
Br	104	5
Si	99.8	10
Sr	109	1
Ti	106	1

Appendix E

Table S7.1. Coordinates of sampling locations in NSW seaports.

Study Area	Site Id	Coordinates	Study Area	Site Id	Coordinates
Port Jackson	1Bg	33◦51'00.6"S 151◦16'01.6"E	**Port Newcastle**	1	32◦55'31.6"S 151◦46'44.9"E
	2	33◦ 51' 37.1"S 151◦12' 34.7"E		2	32◦55'24.4"S 151◦47'24"E
	3	33◦51' 28.6"S 151◦12' 56.6"E		3Bg	32◦55'29.3"S 151◦47'34.8"E
Port Botany	1	33◦58'55.6"S 151◦12'32.1"E	**Port Yamba**	1Bg	29◦25'14.1"S 153◦20'20"E
	2	33◦57'27.5"S 151◦11'54.8"E		2	29◦26'7.2"S 153◦20'42.9"E
	3Bg	33◦59'15.1"S 151◦13'52.9"E		3	29◦26'0,8"S 153◦20'43.9"E
Port Kembla	1Bg	34◦25'27.3"S 150◦54'23.1"E	**Port Eden**	1	37◦04'19.8"S 149◦54'32.3E"
	2	34◦28'30.7"S 150◦54'39.9"E		2	37◦04'17.4"S 149◦54'27.8"E
	3	34◦28'05.8"S 150◦54'02.7"E		3Bg	37◦04'14.7"S 149◦54'38.4"E

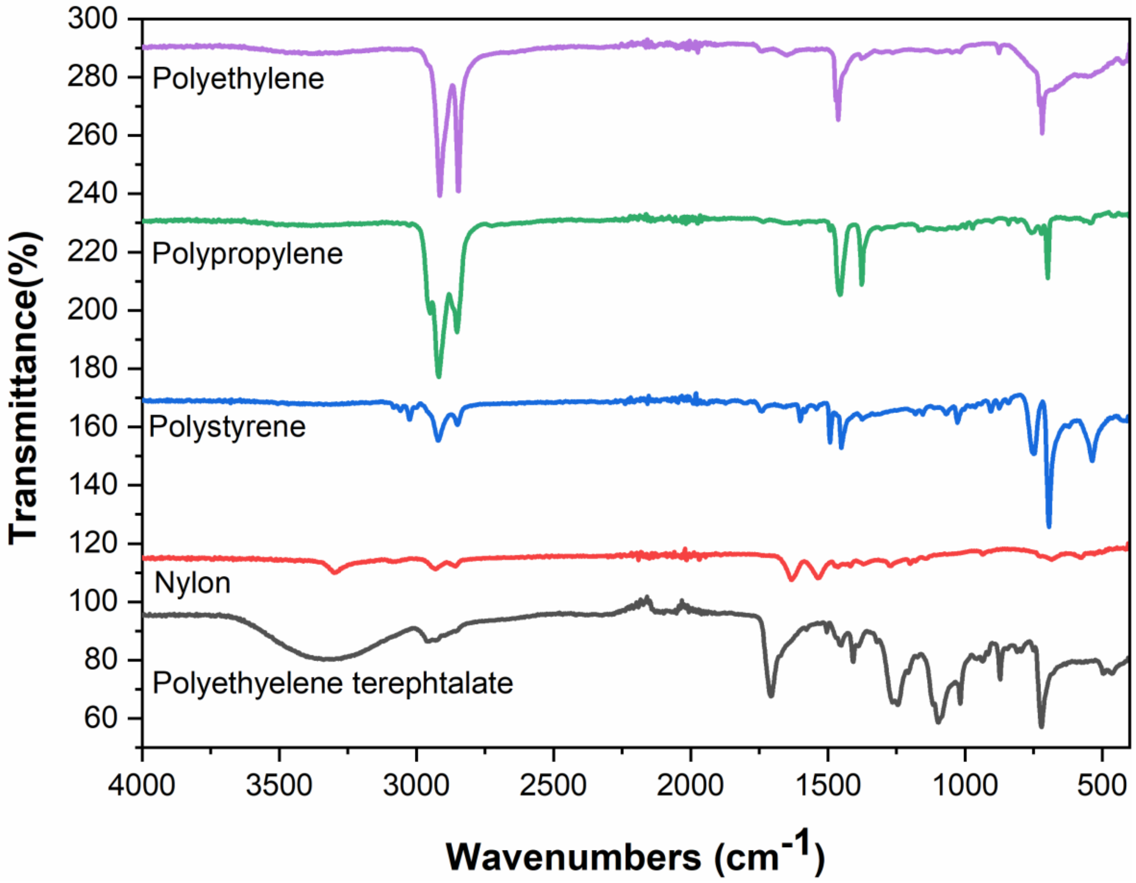

Fig. S7.1. Examples of Fourier transform infrared spectra of identified microplastic polymers