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Graphical Abstract

Highlights

Ten global harbours were assessed for anthropogenic change (AC) and ecological risk (ER)

AC was high for Derwent River, Santander and Sydney estuaries

AC was moderate for Rio de Janeiro and Dublin Port, slight for Hong Kong, minimal for Darwin.

Derwent River sediment was rated at high ER, Sydney and Santander estuaries with moderate risk.

An improved technical framework for sediment quality assessment is provided.

Sediment metal enrichment and ecological risk assessment of ten ports and estuaries in the World Harbours Project

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ABSTRACT

Ten global harbours were assessed for sediment quality by quantifying the magnitude of anthropogenic change and ecological risk. Anthropogenic change (enrichment) was high for Derwent River and Sydney estuary, moderate for Santander Harbour, Rio de Janeiro and Dublin Port, slight for Hong Kong, minimal for Darwin. All 10 enrichment indices used showed similar results. Derwent River sediment was rated at high ecological risk, followed by Sydney and Santander estuaries with moderate risk. Auckland and Darwin sediments exhibited minimal ecological risk and sediment in the remaining harbours (Dublin, Hong Kong, Ravenna, Ria de Vigo and Rio de Janeiro) were assessed at slight ecological risk.

The extraordinary variety of environments and types/quantities/qualities of data investigated resulted in as much a critique and development of methodology, as an assessment of human impact, including unique techniques for elemental normalisation and contaminant classification. Recommendations for an improved technical framework for sediment quality assessment are provided.

Keywords: Sediment Quality Guidelines, Environmental Indices, Anthropogenic Change, normalisation, Classification scheme

1. INTRODUCTION

Substantial anthropogenic stress on coastal marine environments has reduced sediment and water quality in many global harbours and estuaries resulting in threatened benthic and pelagic populations (Costanza et al., 1997; Chapman and Wang, 2001; Costanza et al., 2014). It is important that the extent of contamination of an estuarine environment is assessed as accurately as possible and that the level of threat to the health of these sensitive environments is determined with care. Choosing an appropriate methodology to assess environmental condition is complex and requires an integrated strategy (Rees et al., 2008). Ecosystem indicators used to assess anthropogenic stress are commonly compromised by natural spatial and temporal variability. This confounding of natural and anthropogenic-induced stress results in inappropriate and often erroneous assessment (Hogg and Norris, 1991). Increasingly, sediments are being used to assess the status of aquatic environments due to the advantage sediments have in faithfully recording and time integrating environmental events, both temporally and spatially (Rodrigues et al., 2006; Birch et al., 2008). Moreover, sediments greatly influence the quality of overlying and interstitial water and are an extensive habitat to a large number of faunal and floral species (Simpson et al., 2015).

The condition of estuarine environments may be described using a wide range of approaches, e. g. ecological risk indicators (Singh et al., 2005), concentration factors/indicators (Guo et al., 2010) and enrichment factors/indicators (Caeiro et al., 2005). However, from a management perspective, it is important to know by how much the system has deviated from the pristine condition, i. e. the magnitude of anthropogenic change, and the degree of risk of potential harm posed by sedimentary contaminants to biological communities (Birch, 2016). These two types of information differ fundamentally and are based on different types of data. A full and comprehensive assessment of sediment health is complex and requires a raft of chemical, sedimentological and ecological approaches (Ponti et al., 2009; Birch, 2016; Birch, 2018), however information on the degree of anthropogenic change and level of ecological risk posed by sedimentary chemicals provides a useful initial screening assessment of environmental quality in marine environments.

The objectives of the present work are to determine the magnitude of anthropogenic change and the risk posed by sedimentary contaminants to the biotic ecosystem for the ten harbour estuaries involved in the World Harbour Project (WHP) from a wide range of environments in multiple locations across the globe (Fig. 1) in an effective and regionally consistent manner using traditional, as well as innovative methodologies.

1.1 The WHP Concept

The WHP was initiated by the Sydney Institute of Marine Science (SIMS) and aims to develop resilient urban harbours through a global network of collaborating researchers (Steinberg et al., 2016). The project brings together international research institutions and agencies concerned with the health of these heavily urbanised waterways and the increasing challenges these environments face. Like Sydney, many of the great cities of the world, such as Auckland, Rio de Janeiro and Hong Kong, are located on the coast. These working harbours are part of the fundamental fabric of those communities and the relationship between the residential, industrial and marine environments require ongoing study and management. The WHP tackles issues surrounding the multiple uses of harbours through global collaborative projects and targeted workshops. The Project works to facilitate and link programs across major international harbours, with a proactive focus on investigating and restoring ecosystem functioning and the consequent development of management best-practices that can be applied by all partner cities

1.2 Harbours of the WHP

The morphodynamic characteristics of estuaries influence benthic contaminant distributions and concentrations through tidal patterns, flushing and structural control (Roy et al., 2001; Birch et al., 2016). Numerous classification schemes have been developed in an attempt to combine diverse physical, biological and ecological characteristics of coastal waterways (Dalrymple et al., 1992; Edgar et al., 2000; Roy et al., 2001). The ten harbour estuaries assessed in the current work (Fig. 1) have been loosely separated into five morphodynamic groups, namely (1) funnel-shaped, wave-dominated, drowned-valley estuaries: Derwent River (Tasmania, Australia), Sydney estuary (New South Wales, Australia), Ría de Vigo (Spain) and Auckland Harbour (Waitemata Bay, New Zealand); (2) tide-dominated, drowned-valley estuaries: Darwin Harbour (Australia) and Santander Harbour (Spain); (3) open ocean embayments: Hong Kong; (4) partially enclosed embayments: Rio de Janeiro, Guanabara Bay, (Brazil); and (5) river mouths/canals: Dublin Harbour (Ireland) and Ravenna Harbour (Italy).

Auckland Harbour, Waitemata Bay, New Zealand

The Waitemata Harbour (80 km^2) is the largest east coast estuary in the Auckland region and is comprised of tidal creeks, embayments and a central basin (Aguirre et al., 2016). Sediment studies have been mainly confined to urban and rural tidal creeks, local harbours and embayments, which receive the major contaminant loads, leaving the central basin largely un-surveyed. These peripheral environments are predominantly muddy and fringed by mangrove mudflats. The catchment (185 km^2) comprises mainly urban (21%), rural (25%), forest (21%) and minor industrial landuses. Urbanised catchments have been identified as major sources of fine sediment and metals to the harbour (Aherns, 2008; Mills et al., 2012; Mills and Williamson, 2014). Henderson Creek, which drains the largest urban subcatchment, as well as a substantial area of rural land, contributes the largest loads of sediment and metals to Central Waitemata Harbour. Present-day surface sediments show spatially-variable concentrations of metals with maximum concentrations occurring on intertidal flats near tidal creek outlets and stormwater drains in the south western embayment of Central Waitemata Harbour and upper Shoal Bay. Marked increases of metal discharge was initiated around 1950 coinciding with the beginning of rapid urbanisation and reached a maximum more than 20 years ago, while declining slightly to the present time.

Darwin Harbour, Northern Territory, Australia

Darwin Harbour (~1220 km^2) is approximately 35 km long and 5 km wide at the mouth. The waterway is macro-tidal (range up to 8m) and comprises extensive mudflats (containing substantial calcium carbonate from shell material) fringed by large stands of mangroves separated by deep tidal channels. Parts of the Harbour are relatively poorly flushed, especially in the dry season when the residence time in the upper arms is ~20 days. Most (85%) of the catchment (~2010 km^2) is open space, while urban and light industry occupy 7% (no heavy industry), horticulture makes up about 1-2 % of the area and rural/residential comprises 6 %. Although sedimentary metal concentrations are generally low, moderate environmental concern is for elevated metals along the developed eastern side of Darwin Harbour and in the vicinity of the sewage treatment plant outfall north of the city (Munksgaard et al., 2012; 2013; 2015; 2018). Metal loads have declined as a consequence of treatment system improvements, however emerging sources of metals are from removal of marine sediments associated with coastal development and dredging activities.

Derwent River, Tasmania, Australia

The Derwent River is approximately 45 km long, occupies 200 km^2 and is relatively deep (av. 25 m) (Whitehead et al., 2010), The waterbody is stratified in the narrow upper reaches and well mixed in the lower, broad seaward area. The tidal range is 1 m and average flushing time is 12 days. The catchment (8,900 km^2) is mainly agriculture and forest (76%) and urban/industry (8%) and supports 40% of the state population. The main environmental issues are metal contamination of water and sediment from a zinc smelter and nutrients from a paper mill and waste water treatment plants. Nutrient loads have declined, but Zn, mainly from groundwater, remains elevated.

Dublin Harbour, Ireland

Dublin Bay hosts Dublin, the capital city of Ireland (population >1m) (Brooks et al., 2016) and Dublin Port, busiest shipping port in Ireland, which accounts for half of the nation’s annual imports and exports (DPC, 2014). Dublin Port (3.267 km^2) has developed on both sides of the Liffey channel, but most of the shipping docks are on the northern side, while the southern port encompasses major infrastructure. Technical development and regulation backed by environmental monitoring has considerably reduced most adverse effects of deliberate contamination. Despite such controls, input of contaminants to the port from discharge of sewage and industrial waste, spillage of cargo, or ship lubricants, stormwater runoff and warm water from power stations still occurs. Riverine inputs (mainly from the Liffey River), which drain the highly urbanized and rural areas around Dublin city, are a major source of contaminants into Dublin Bay (EPA, 2006; 2015; Brooks et al., 2016; Murphy et al., 2016; Cunningham, 2018).

Resuspension of contaminated sediments may occur due to strong tidal forces, storm surges, or increased water movement from boats (Davoren et al., 2005; Macken et al., 2008; Bedri et al., 2011; Briciu-Burghina et al., 2014).

Hong Kong Harbours

Hong Kong is situated in the Pearl River Estuary (PRE), and covers about 8000 km^2 (Chen et al., 2013). The estuary (1649 km^2) is up to 30 m deep (av. <15 m) and is microtidal with a <2 m average tidal range (Mao et al., 2004). Bottom sediment is mainly mud with subordinate sand and gravel (Tanner et al., 1993). Sedimentary metals are significantly higher in harbours, e. g. Tolo Harbour and Victoria Harbour, than in offshore areas (Chan et al., 2016; Blackmore, 1998; Zhou et al., 2007a, b; Tang et al., 2008; Chen and Jiao, 2010; Liu et al., 2015; Chen et al., 2013). The territory (1108 km^2) supports >7.4 million people and comprises Hong Kong Island, Lantau Island, Kowloon Peninsula, the New Territories and 261 islands with a complex and long coastline (1200 km) (EPD, 2017; SMO, 2018). Hong Kong is a highly urbanized (81 %), coastal city receiving substantial metal loads from industrial and municipal waste waters, especially during the 1950s-1980s (Morton, 1989). Metal contamination of marine sediment is mainly attributed to: (1) historical discharge of untreated industrial wastewater and partially treated sewage (e. g., Victoria Harbour and Tolo Harbor); (2) surface runoff from Pearl River and local rivers (e. g. Deep Bay), and (3) other sources, including infiltration from septic tanks and leachate of antifouling compounds from shipping (Chen and Jiao, 2010; Liu et al., 2015). Improved conditions since the late 1980s are due to industry moving to the New Territories, Southern China and other areas of Asia (Morton, 1996; Blackmore, 1998) and improved treatment of domestic sewage (Lai et al., 2016). However, metal contamination persists due to release from legacy contaminated sediments.

Ravenna Harbour, Italy

Ravenna is the largest harbour (3.62 km^2) in the western Adriatic and is one of the most extensive commercial seaports in Italy. The harbour was established in lagoonal systems surrounding the city and is structured as a major ‘canal’ port extending for 11 km from the centre of Ravenna to the tourist seacoast. The canal is directly connected to surrounding lagoons (Pialassa Baiona and Pialassa Piomboni), which are included in the southern part of the Po River Delta Park, inscribed in the World Heritage List. Construction of two large converging jetties (2400 m long each) to protect the harbour from siltation has altered sediment transport and has re-shaped nearby tourist beaches. Environmental concerns include degradation of natural habitats, contamination of sediments and management of highly urbanised areas (Airoldi et al., 2016). Ravenna Harbour and coastal lagoons receive civil and industrial wastewater carrying nutrients, pollutants and cooling water from two power stations and industrial plants. Although discharges now comply with current laws, lax legal constraints between 1958 and 1976 resulted in sediment of Pialassa Baiona being heavily impacted by industrial metals, including Hg (Fabbri et al., 1998; 2000; 2001; McRae et al., 2000; Guerra, 2012; Guerra et al., 2014). However, sediment resuspension due to frequent maintenance dredging and to deepen the port have had minimal effects on macrobenthic assemblages inhabiting the lagoons (Guerra et al., 2007; 2009; Ponti et al., 2009; 2011).

Ría de Vigo, Spain

Ría de Vigo (156 km^2) is the most populated (411,363 inhabitants) and developed (approximately 7% industrial, 12% construction) ria in Galicia and is home to Vigo city (population 292,986) (Galician Institute of Statistics, 2017; http://www.ige.eu). The ria is approximately 30 km long and 12 km wide at the mouth. The waterway is relatively deep (av. 16 m, max. 45 m) and the water column is well mixed with a tidal range of 4 m and an average flushing time of 3-4 days (Barton et al., 2015). Sediments are predominantly organic-rich and fine grained. The catchment (578.2 km^2) is heavily urbanised and industrialised (>21%) (Fernández et al., 2016) and activities include shipbuilding, canning, automobile and steel manufacturing. Metal pollution is restricted to the inner estuary as a result of urban and industrial discharges and to intense activity of the Port of Vigo with chronic Pb pollution due to discharge from a ceramic factory located at the head of the estuary (Rubio et al., 2000; Prego and Cobelo-García, 2003; Alvarez Iglesias et al., 2006; 2007; Quelle et al., 2011). Other sources are natural, related to catchment and upwelling processes (Quelle et al., 2011). Mariculture rafts in the northern estuary have influenced the distribution of metals by increasing the carbon content and decreasing grain size producing metal sinks. Tidal currents act to redistribute metals from accumulation zones.

Rio de Janeiro, Guanabara Bay, Brazil

Guanabara Bay (449 km^2) is located in the southeastern Brazil Marine Ecoregion in the most economically developed region of the country. The bay comprises a large, shallow (av. 5.1 m) inner semi-circular water body with a maximum length of 48.2 km and a narrow inlet with a main central channel depth of 58 m. Mean spring tidal range is 1.05 m. The catchment is the largest of this ecoregion (~3700 km^2) (Kjerfve et al., 1997; Kjerfeve et al., 2001) and supports Rio de Janeiro, the second largest Brazilian city (6.5 million people). The drainage basin of the Guanabara Bay (4180 km^2) is drained by approximately 45 rivers (JICA, 1994) and the main rivers are the Macacu, Iguaçu, Estrela and Sarapui. The Guanabara Bay catchment includes, partially or totally, 12 municipalities with a population of almost 10 million inhabitants, equivalent to 80% of the population of the State of Rio de Janeiro**.** As a consequence of urban, agricultural, and industrial development, the bay is one of the most altered and polluted in the country (Carreira et al., 2002; Xavier de Brito et al., 2002; Silva et al., 2013; Camargo et al., 2017, Cordeiro et al., 2015; Baptista Neto et al., 2017). Anthropogenic metal sources to the bay include direct discharges of untreated and treated industrial waste, domestic sewage, inputs from rivers, atmospheric fallout, dockyards and agricultural activities, landfill and road runoff (Rebello et al., 1986; Abuchacra et al., 2015; Aguiar et al., 2018). Metal loads to the bay have increased substantially over the last 70 years caused by population growth in the metropolitan region (from ~2.5 to 12 million) accompanied by extensive urbanization, deforestation and industrial and agricultural growth (Moraes, 2012; Covelli et al., 2012; Figueiredo Jr. et al., 2014). Higher concentrations of metals located in the inner bay from river discharge and in sediments adjacent to harbours (Baptista Neto et al., 2006; Cordeiro et al., 2015; Aguiar et al., 2018) exhibit significant ecotoxicological effects on aquatic organisms (Moraes et al., 2000; Maranho et al., 2009; 2010; Campos et al., 2019).

Santander Bay, Spain

Santander Bay (22.5 km^2) is one of the most important and largest estuaries in northern Spain (Biscay Gulf) and includes a Special Protection Area (SPA) (Gómez et al., 2014). The bay is a natural harbour and hosts a major commercial port. The bay is characterized by a semidiurnal tidal regime with a medium tidal range of 2.9 m and interacts with freshwater discharges from the Cubas River (Puente et al., 2002). The estuary is dominated by extensive, shallow water (max. depths 10–12 m) intertidal areas (67%), which have been greatly modified by urban development and port activity (Ondiviela et al., 2013). Anthropogenic activities began in Roman times (Vigurí et al., 2007) reaching a maximum impact during the 1970s (Vigurí et al., 2007). Since marsh reclamation in 1903, the inner bay has undergone intensive industrial expansion of mainly metallurgical and chemical industries. During the last 150 years between 37% and 50% of the original intertidal zone has been reclaimed (Vigurí et al., 2007; Remoundou et al., 2015; Calleja et al., 2017) and used as grasslands, to expand the Port, and to create new industrial and residential areas, including the city of Santander. Continuous, untreated industrial discharges ceased in 2001 when a new sewer system came into operation (López et al., 2013; Echávarri et al., 2007) and all direct discharges to the bay were eliminated in 2010 when a new wastewater treatment plant was commissioned. Industrial contaminant sources are mainly located in the inner bay and on the western shore, where the port is located. Maximum metal concentrations occur in the subtidal and inner estuary related to industrial sources and are minimal in the intertidal flats (Puente et al., 2002).

Sydney estuary, New South Wales (NSW), Australia

Sydney estuary is approximately 30 km long and up to 3 km wide with an area of 50 km^2, while the catchment (500 km^2) is highly industrialized and urbanized (76%) (Birch et al., 2015; 2016; Birch, 2016) and supports the City of Sydney (population 5.5m). Estuarine water is generally well-mixed marine, but becomes stratified after prolonged heavy rain (Lee et al., 2011; Birch and McCready, 2009). Typical flushing times are 5 to 10 days, however in the upper reaches of the waterway it may be up to 130 days. Sediments in the estuary are mainly muddy in the upper reaches and sandy in the mid- and lower estuary. Sediments are significantly contaminated by metals and organic compounds (Birch et al., 2000a; 2008; 2013; McCready et al., 2004; 2006; Birch, 2017) and the waterway is classified as “severely modified” (NLWRA, 2002; Birch and Taylor, 2000a). Until recently, the harbour was a busy commercial and naval port and the shoreline was lined by factories, however, industries have moved away from Sydney and the area has converted into a mainly tourist and recreational hub (Birch and Taylor, 2000b, c).

2. METHODS AND MATERIALS

2.1 Analytical Methods

Auckland Harbour

Total recoverable metals were determined on the <500 µm fraction by hot acid digestion (HNO_3/HCl) (USEPA Method 200.2) (Table 1).

Darwin Harbour

Sediment samples were wet sieved to <2 mm grain size and digested with in a strong HNO_3/$HClO_4$ (perchloric acid) mix using open digestion tubes in a heating block. Elemental analysis was by inductively coupled plasma mass spectrometry (ICP-MS) using a marine sediment Certified Reference Material (CRM) MESS-3.

Derwent River

Shallow cores were taken using a triplicate multi-corer, with the upper 5 cm extruded and mixed to provide a total sediment integrated surface sample. Subsamples were also size normalised to 62.5 µm and analysed using inductively coupled plasma atomic adsorption spectrometry (ICP-AES).

Dublin Harbour

Samples were dried at <30^{o}C, crushed and sieved at 2mm. Samples were digested in HNO_3 using open digestion tubes in a heating block. Analysis was via inductively coupled plasma optical emission spectrometry (ICP-OES).

Hong Kong

Marine sediments were collected using a Van Veen grab sampler and samples were digested by microwave-assisted acid extraction (HNO_3) (ISO, 1995) and analysed by ICP-MS (USEPA, 1994).

Ravenna Harbour

Samples were digested in closed Teflon vessels by a mixture of HNO_3 + HCl (3:1) in a microwave system and measured by graphite furnace atomic adsorption spectroscopy (GFAAS) using a Certified Reference Material PACS-2 (Marine Sediment, NCR-CNRC, Canada).

TABLE 1

Ría de Vigo

Total sediment was digested with a strong acid mix of HNO_3/HCl/HF in Teflon digestion bombs using a microwave oven and analysed by spectrophotometer. Quality assurance systems using Certified Reference Materials (BCSS-1 and BEST-1, National Research Council of Canada).

Rio de Janeiro

Sediments were digested using a microwave-assisted procedure with concentrated HNO_3 solution (USEPA, 2007a) and analysed by ICP-OES. Analytical quality control was assessed by analysing a certified reference material (NIST 2782 Industrial Mud).

Santander Harbour

Sediment samples were collected with a Van Veen grab and grain size was determined by dry sieving. Metals analysis was for the <63 μm fraction and followed the U.S. Standard method (US EPA 6020, 2007b) using a HNO_3/HCl/HF mix and analysed by ICP-MS and a Certified Reference Material (Loamy Clay, CRM 052, Resource Technology Corporation, US).

Sydney estuary

The fine (<63 μm) fraction and total sediment were analysed by aqua regia digestion (HCl/HNO_3) (modified US EPA 200.8 Rev 4.4 method) (US EPA 1994) and analysed by ICP-OES using a reference material (AGAL-10), procedural blanks and blind replicates (Siaka et al., 1998; Birch and Taylor, 2000b).

2.2 Data availability and sample distribution

Data used for Auckland Harbour assessment were for five metals (no Al, Fe, Ni) for 41 sites sampled in 2008 (Table 2). Sampling (Cu, Pb and Zn n=1221 and for As, Cd, Cr n=37) targeted areas of interest located primarily within embayments, tributaries and coastal zones. The 298 samples collected from Darwin Harbour in 2012 were distributed on inter-tidal flats and were absent in strong-flowing tidal channels. Metals data (n=123) sampled in 2000 in the Derwent River provided an excellent coverage for contaminant mapping. Sampling (n=42) undertaken in Dublin Port in 2006 in the main channel of the docks and in two berthing basins provided sufficient coverage to map the distribution of contaminants.

TABLE 2

Duplicate samples from 45 sites for the years 1995 to 2015 (n=2676) were available for the Hong Kong coastal region, however only the most recent vintage (2015/16) of samples (n=9) confined to the harbour areas (63.0 km^2) were used for mapping in the present assessment. Several of the canals of Ravenna Harbour have been sampled, but lacked Al, Fe, or size data and only sediments (n=52) of Canale Candiano (3.52 km^2) have been assessed. The 39 samples taken in 2011 in Ria de Vigo estuary were well distributed and provided a good spatial spread of data throughout the embayment. Although sampling was undertaken for multiple years between 2005 and 2015 in Santander Harbour, sites were sparsely distributed and the data for 2015 (n=10) mapped in the present study were located close to the shoreline with an absence of samples in the central harbour (22.5 km^2). Approximately decadal sampling has been undertaken in Sydney Harbour between the years 1975 to 2015. The 2000-2015 dataset (n=1175) used in the current assessment was well distributed throughout the estuary and provided an excellent spatial platform for mapping and assessing contaminants.

As an adequate sampling density is required for GIS mapping, metal distributions of only six harbours (Darwin, Derwent, Hong Kong, Ria de Vigo, Rio de Janeiro and Sydney) could be plotted as filled contour maps (Figs. 2-8), while contaminant distributions of the remaining four harbours (Auckland, Dublin, Ravenna and Santander) were depicted as points in the Supplementary Material file (Figs, S1-S7). The amount of data available was not consistent across all 10 harbours and thus assessment could not be completed for all techniques for all harbours.

2.3 Differentiation between ‘anthropogenic enrichment’ and ‘sediment quality’

In a management perspective, two important attributes define the ‘environmental health’ of sediment in an aquatic ecosystem. Anthropogenic ‘enrichment’ is the magnitude of human-induced change in the aquatic environment and measures the departure of the system from the pristine condition. ‘Sediment quality’ is the ability of sediment to maintain a healthy benthic community and is measured by ecological risk assessment. Enrichment does not imply ecological effect, or toxicity. These two metrics are based on different methodologies and criteria, require different types of data and are entirely unrelated, however these attributes are frequently confounded and often aggregated into a single value, or index (Caeiro et al., 2005; Wilson and Jeffery, 1987; Kabir et al., 2011). To measure human-induced change requires pre-anthropogenic contaminant concentrations (commonly referred to as ‘background’) to be known and that data are normalised (either size-, or elemental normalisation) to reduce the confounding of variable grain size, while ecological risk is based on total sediment using sediment quality guidelines (SQGs). In the present work, only sedimentary metals (Cd, Cr, Cu, Ni, Pb and Zn) were considered, as a full suite of organic and inorganic pollutants were not available for all harbours.

2.4 Techniques to measure anthropogenic change (enrichment) in the WHP

Two complications with the WHP dataset, i. e. that background concentrations for metals were not available for all locations and that size-normalised data were accessible for only three locations (Derwent River, Ria de Vigo and Sydney) and Post-Extraction Normalisation (PEN) was undertaken for Sydney and Darwin. In the PEN technique, the >63 µm fraction is removed by sieving after digestion thereby capturing metals associated with the total sediment, providing an advantage over the usual size-normalisation procedure, which only measures contaminants in the <63 µm fraction (Birch and Taylor, 2000; Birch, 2003). The lack of these data restricted the ability to determine the magnitude of anthropogenic change, i. e. sedimentary metals enrichment.

Early researchers used global average upper crust and marine shale metal concentrations as 'standard reference materials' (SRMs), (Taylor, 1964; Bowen, 1979; Turekian and Wedepohl 1961; Wedepohl, 1995). SRM values are not site, or material, specific and the preferred methods of determining background are identification of a nearby 'pristine environment', or the use of sedimentary cores to obtain sediment from below the level of anthropogenic influence. Nevertheless, SRMs are still being used extensively and are entrenched in the literature (Pekey, 2006; Karbassi et al., 2008; Kabir et al., 2011).

The European Union has been concerned with the problem of establishing background metal values for their community for some time and the OSPAR Coordinated Environmental Monitoring Programme (CEMP) working group on monitoring (MON) have declared that core data will form the basis by which background is determined for the OSPAR region using only fine-grained and/or sieved samples (size normalised) to reduce the confounding of variable grain size and, if possible, samples should be taken from sediment older than 1850 AD (OSPAR, 2008). Using data from multiple studies, OSPAR (2005; 2008) established a single background metals dataset for the entire northeast Atlantic region. An investigation of background metal concentrations for 52 harbours and estuaries globally showed a remarkedly narrow range of concentrations (Birch, 2016) with means of 27 µg/g, 33 µg/g and 97 µg/g for Cu, Pb and Zn, respectively. A similar study conducted as part of the current work, but exclusively for <63 µm data, gave values of 17 µg/g, 26 µg/g and 79 µg/g, respectively, which compared closely with the OSPAR concentrations of 20 µg/g, 25 µg/g and 90 µg/g, respectively for fine sediment. Background metal concentrations are strongly influenced by geology, climate and soil processes (Birch, 2018) and will be different for each of the WHP harbours. However, in the absence of local information on background concentrations, the OSPAR pre-anthropogenic values have been adopted in the present study in order that results be consistent between the 10 harbours being assessed and that WHP outcomes can be related to other global studies.

The second difficulty in assessing the magnitude of human-induced change in ports of the WHP, i. e. the absence of normalised metals data, was addressed using a unique elemental-normalisation procedure. Aluminium has been used as a normalising element (denominator) for some time (Rubia et al., 2000; Caeiro et al., 2005; Brady et al., 2015), however an increasing number of studies are using an assumption that sediment containing 100% clay mineral material has an Al concentration of 50,000 µg/g Al and that total metal concentrations can be normalised to this concentration of Al (OSPAR, 2005; 2008; Munksgaard et al., 2012; 2013; 2015; 2018). Further assumptions are that all metals are associated with the clay mineral phase and that the Al concentration used for normalisation (50,000 µg/g Al) was the same for all locations. These assumptions were tested by comparing normalisation and enrichment determined by size-normalised core data with that determined using 50 000 µg/g Al for the Sydney estuary dataset. Pearson (product moment) correlation was used to determine the linear association between size-fractionated metals and metals normalized to various concentrations of Al. The relationship between Al and sediment size for the Sydney estuary dataset showed that a considerably lower concentration of Al corresponded to the composition of 100% clay mineral phase, i. e. 35,000 µg/g Al (and 35,000 µg/g for Fe, another normalising element). A unique opportunity to comprehensively study the relationship between Al (and Fe) and sediment size was made available by a large body of data obtained from 41 central NSW estuaries, which included sediment size, total sediment and size-normalised metals (Birch et al., 2016). Results from this study showed that the relationship between Al (and Fe) concentrations in total sediment and the fine fraction content was unique for each estuary. The procedure of choosing the appropriate Al concentration for normalisation is described in detail in Birch (2020). This understanding has led to a break-through in an ability to normalise metals data using unique Al normalising concentrations for each individual WHP harbour (the Canale Candiano of Ravenna and Auckland had neither Al and/or Fe) The use of Al and Fe in normalisation procedures should be used cautiously as Al enrichment in glacial sediments (Loring, 1991) and elevation of Fe by diagenetic processes, is well documented (Grant and Middleton, 1990; Whalley et al.,1999).

2.5 Indicators used to estimate the magnitude of anthropogenic change (MAC) (sedimentary metal enrichment)

A raft of environmental indicators is being used to assess human influence on marine ecosystems. However, terms, e. g. 'contamination factor', 'concentration factor' and 'enrichment factor' used synonymously in the literature need first to be defined for clarity. The terminology used in the present work combines terms promulgated by Caeiro et al. (2005) and Brady et al. (2015). 'Concentration factors' do not employ background, or normalisation procedures, 'contamination factors' involve pre-anthropogenic values, but do not incorporate normalised data, whereas 'enrichment factors' apply both background and some form of normalisation. Also important is whether enrichment indices are for multiple elements and whether the index is linked to a classification scheme. Assessment schemes used in the present study have been ranked based on these attributes in Table 3 and the formulae used to calculate the indices are presented in Supplementary Material.

TABLE 3

2.6 Ecological Risk Assessment (*ERA*) Risk of adverse effects to benthic populations posed by anthropogenic sedimentary chemicals

Chemical concentrations *per se* do not provide an effective means for determining potential adverse effects on benthic resources. To assess the ecological significance of contaminants bound to sediments information on toxicity, bioaccumulation and effect on the structure of biological communities are needed. These measurements require a high degree of expertise, are time consuming and expensive and, as in the case of the WHP, are frequently not available. Instead, sediment quality guidelines (SQG) are commonly used to make preliminary assessments of sediment toxicity when direct biological effects information is unavailable. Empirical methods, employing matching sediment chemistry and biological effects data, have been used in development of SQGs for determining adverse outcomes of contaminants on ecological populations using total sediment chemistry. Numerical-effects based SQGs are now in common use globally as a screening management tool to identify and prioritise contaminants and regions of concern.

There are several sediment quality effects-based guidelines commonly in use, e. g. the apparent-effects threshold (AET) scheme and screening level concentrations (SLC) (Birch, 2018). However, the most commonly used SQG for estuarine and marine environments is the US National Oceanic and Atmospheric Administration (NOAA) scheme based on concurrent sediment chemical and ecological data from the laboratory and field for a variety of techniques and benthic end points (Long and Morgan, 1990; Long et al., 1995; MacDonald et al., 1996). The scheme comprises two observed ecological effects concentrations, i. e. the effects range low (ERL) and the effects range median (ERM). The former level identifies the concentration below which adverse ecological effects are seldom observed and the latter level distinguishes concentrations above which adverse ecological effects occur frequently. Concentrations between the two levels exhibit irregular ecological response. A wide range of chemicals, including organic and metallic contaminants, has been incorporated into these SQGs and the approach is now well established in North America and in many countries in Europe, Asia, South America and Africa.

Contaminants do not occur as single chemicals within marine sediments and a number of schemes have been developed to assess the effects of chemical mixtures for aquatic sediments. The mean ERM quotient (MERMQ) scheme has been used to estimate adverse ecological effects of chemical mixtures in this WHP (Long and MacDonald, 1998). The MERMQ method requires normalising the concentration of each chemical with respect to its ERM value, summing the quotients for each substance and dividing by the number of chemicals for which guidelines are being used. MERMQ ranges of >1.5; 1.5-0.5; 0.5-0.1 and <0.1 have been related to the probability of toxicity (76%, 49%, 21% and 9%, respectively) in amphipod assemblages. The number of ERL and ERM exceedances has also been related to toxicity through whole sediment bioassays. However, these toxicity relationships should be used with caution due to area-specific nature of benthic populations and sedimentary chemicals and instead the MERMQ is considered in the current assessment as a level of risk of adverse effects to sediment-dwelling animals, rather than as a probability of toxicity.

3. RESULTS

For harbours with adequate sample density (Darwin, Derwent, Hong Kong, Ria de Vigo, Rio de Janeiro and Sydney) figures are presented as filled contour maps (Figs. 2-8) and for the remaining locations (Auckland, Dublin, Ravenna and Santander) distributions are given as points in Supplementary Material (Figs. S1-S7). Because distributions of most elements being considered in this work co-occur, only Zn is depicted in figures to limit the number of diagrams. Total metal concentrations (Table 4, Fig. S8), enrichment (Table 5, Fig. S9), contamination and enrichment indices/factors (Table 6) and ecological risk (Tables 7 and 8, Fig. 9) are described for each of the WHP locations below.

Auckland Harbour

Mean and maximum total sediment metal concentrations were low and were highest in tributaries in the south-west and west.

Concentration (CF) and contamination factors were low indicating no to slight contamination, however metal enrichment could not be estimated as no sediment size data, or total Al/Fe data were available.

No sampled areas exceeded ERL concentrations for Cu and Pb, while samples only exceeded this guideline for Zn in the upper reaches of tributaries in a small part of the southern estuary. Ecological risk is minimal (MERMQ=0.09).

TABLE 4

Darwin Harbour

Total mean and maximum metal concentrations were low for sediments mantling Darwin Harbour and were greatest in tributaries of Palmerston and Darwin, as well as along the coastal fringe towards the southeast. Copper total sediment concentrations were particularly low with mean and maximum levels of 5.4 µg/g and 23 µg/g, respectively.

Post-extraction normalised (PEN) data for Darwin Harbour showed low mean concentrations for Cu, Pb and Zn (16 µg/g, 29 µg/g and 79 µg/g, respectively) and a large number of samples were at, or close to background levels. Low PEN metal concentrations may be due to high and variable carbonate content in surficial sediments (Munksgaard et al., 3012).

Concentration and contamination factors were low, suggesting no to slight contamination. Enrichment values indicated sediments were generally uncontaminated with mean values of 0.9, 1.4 and 1.0 for Cu, Pb and Zn, respectively, except for the tidal flat sediment near Darwin City and port where enrichment was generally >2.5.

Maximum total sediment concentrations of Cr (95 µg/g), Cu (23 µg/g), Ni (27 µg/g), Pb (50 µg/g) and Zn (190 µg/g) exceeded ERL values by small margins. Metals showed a similar spatial distribution and no metals in any area of the harbour exceeded ERM concentrations. Overall ecological risk (MERMQ=0.06) was minimal.

TABLE 5

Derwent River

Mean and maximum total sediment Cd (14 µg/g and 128 µg/g, respectively), Pb (450 µg/g and 1880 µg/g, respectively) and Zn (2130 µg/g and 14600 µg/g, respectively) concentrations were extremely high and the maximum concentration for Zn is possibly the highest recorded. Total sediment, mean and maximum Cu concentrations were moderately high and Cr and Ni concentrations were slightly elevated. A very strong down-stream gradient was apparent for Cd, Cu, Pb and Zn with maximum concentrations centered on the Glenorchy area.

In the absence of total Al, normalisation was accomplished using 40K Fe as a normalising agent. Normalised metal concentrations were only moderately higher (~25%) than total concentrations due to the mainly muddy nature of bottom sediments. All environmental indictors were highest for Derwent River sediments in the WHP, indicating extreme to severe enrichment. Mean enrichment quotient, especially for Cd (77), Pb (19) and Zn (23) was also extremely high, resulting in a MEQ of 21.

Sediment in most of the estuary exceeded ERL concentrations for Pb and Zn and for large areas for Cu. Sediment in the Glenorchy area exceeded ERM concentrations for Cu and over large parts of the estuary sediment exceeded ERM values for Cd, Pb and Zn. Similar distributions of risk were presented by Pb and Zn distributions, except that Zn ERM concentrations extended further seawards than did Pb. High risk for Cd (1.40), Pb (2.04) and Zn (5.2) were moderated by low risk levels for Cr (0.10) and Ni (0.32) to give an overall risk of MERMQ=1.58.

Dublin Port

The total sediment metal concentrations reported for three vintages (2006, 2008 and 2013) of data for Dublin Port varied greatly. Vintages 2006 and 2008 had similar spatial distributions covering most of the harbour area, while 2013 data were mainly confined to the Alexandra Basin loading dock. Metal total sediment concentrations in 2006 (Cu, Pb and Zn concentrations were 49 µg/g, 81 µg/g and 217 µg/g, respectively) were substantially higher than in 2008 (mean 27 µg/g, 44 µg/g and 152 µg/g, respectively), but lower than in Alexandra dock in 2013 (mean 60 µg/g, 138 µg/g and 663 µg/g, respectively). In particular, the 2006 vintage data were normalised using 25K Al (mean Al 15,900) resulting in increased enrichment and a MEQ of 4.6. However, for the 2008 survey which covered the majority of the harbour, sediment metal concentrations exceeded ERL values only in a minor part of the inner harbour, while one site exceeded ERM values for Pb and Zn. As a result, the overall risk for this vintage was low and the MERMQ was 0.31. Concentrations of Cu, Pb and Zn displayed similar distribution patterns, i. e. increasing towards the inner harbour with a moderate elevation in a dock in the central harbour area (based on 2008 data).

These apparent high temporal fluctuations in contaminant levels for the 2006 and 2008 data from the same harbour area may have been due to changes in sediment size (ship turbulence, fluvial- or tidal-derived currents) as indicated by different mean Al concentrations. Or may be due in part to more stricter controls on inputs both within the Port/Harbour environ and upstream along the River Liffey catchment area (Brooks et al., 2016). Substantial spatial variance and high concentrations in the 2013 data may have been related to small-scale variability (debris from loading vessels), or the variance may have been analytical. The Alexandra basin has a long history of ship-building and vessel cleaning and maintenance and it is deemed the most likely source for the high concentrations found in sediments within this area (Brooks et al., 2016). Indeed, due to proposed developmental plans within the Port (most of which is to occur within the basin area – DP, 2014), it may be that this sample was selected to ascertain how contaminated sediments were so that appropriate precautions for handling could be developed prior to commencement of Port developments (DPC, 2014).

Hong Kong Harbour

Total sediment metal concentrations for Hong Kong coastline and Hong Kong Harbours were low, while maximum concentrations were also moderately low. Copper, Pb and Zn displayed similar spatial distributions and were more elevated in the harbour than for the adjacent coastline. Metal concentrations decreased rapidly seawards and were very low in blue water regions.

Normalisation was conducted using 35K Al, which increased total concentrations moderately. Total metal/total Al plots suggested some sites were slightly contaminated and total Al and total Fe were closely related (r=0.865). Environmental indicators showed Hong Kong Harbour sediments to be slightly enriched. Mean enrichment quotient, especially for Cu was moderate for coastal samples (mean 5.1 and maximum 8.8) and mean enrichment for Pb and Zn in the harbour and coastal region was <3.0.

Ecological risk in all areas was low and only in the Hong Kong Harbour area do any metal exceed ERL values, while no ERM concentrations were exceeded. Overall ecological risk is low MERMQ=0.20) and most elevated for Zn (0.36) followed by Cu (0.25).

Ravenna

Sediments in the Canale Candiano were moderately rich in total mean Cd and Pb concentrations (1.6 µg/g and 49 µg/g, respectively) and metal concentrations increased towards the city of Ravenna. Concentration and contamination indicators were slightly elevated, however no enrichment factors could be determined due to an absence of sediment size data and normalising elements for the Canale Candiano. Ecological risk was low (MERMQ=0.26) with Zn posing the highest concern (MERM=0.43).

Rio de Janeiro

Rio de Janeiro Bay was almost entirely mantled in muddy sediments (>80%) and total sediment metals were moderately high for Cu and Pb (means 62 µg/g and 66 µg/g, respectively) and high for Zn (mean 318 µg/g). All metals increased towards the SW and were greatest adjacent to Rio de Janeiro city and the Rio Pauvna and lowest in the sandy sediment off San Francisco Beach in the SE. Maximum concentration for Zn was third highest (2039 µg/g) for the 10 harbours studied.

Total sediment was normalised to 20K Al increasing total concentrations by approximately 30% for all metals. Total Al/total metal plots indicated a substantial number of contaminated samples. Environmental factors suggested slight to moderate enrichment. Mean enrichment was moderate for Cu, Pb and Zn, i. e. 4.0, 3.1 and 4.6, respectively resulting in a MEQ of 3.5 (moderate enrichment).

Sediments in the NE and SE of Rio de Janeiro Bay posed no risk to benthic resources with total metal concentrations <ERL. For Cu and Pb sediments mantling the remainder of the bay had an intermediate risk of adverse effects with total concentrations >ERL<ERM. Sediments posed a high risk due to total Zn concentrations (>ERM) adjacent to the city and off Rio Pavuna. Overall ecological risk was slight (MERMQ=0.33).

Ria de Vigo estuary

Mean Cr (70 µg/g), Cu (82 µg/g) and Ni (29 µg/g) concentrations were moderate, while maximum concentrations (198 µg/g, 479 µg/g and 43 µg/g, respectively) for these metals were reasonably high. Chromium and Zn outliers increased maximum concentrations for these metals. Sedimentary Zn concentrations displayed a distinctive decreasing gradient away from the main harbour. Copper showed a similar pattern to Zn, but trends were less strong, nevertheless concentrations were clearly elevated at the harbour, while Pb concentrations increased regularly up estuary due to discharges from a ceramic factory located at the head of the estuary (in operation since the late 1960s and closed in 2001). Secondary Pb inputs are attributed to industrial and port activities. The harbour was a significant source of Zn and Cu, and possibly Pb to the estuary.

Normalised metal concentrations were only marginally higher than total values due to a consistent muddy substrate. Contamination factors showed slight to moderate elevation and enrichment was highest for Cu (mean 4.9) and Pb (mean 5.2) with a MEQ of 4.1.

Mean sediment Cu, Ni and Pb concentrations were greater than ERL values and maximum Cu, and Zn concentrations exceeded ERM values. Ecological risk for sediments was high for Zn in the vicinity of the harbour (concentrations >ERM), while risk was moderate for Cu and Pb for most of the estuary with samples exceeding ERL values. Overall ecological risk was slight (MERMQ=0.38).

Santander Harbour

Sediments in Santander Harbour contained the second highest total Cr (83 µg/g) and Ni (48 µg/g) concentrations in the WHP. Lead and Zn sediment metal concentrations were high in the dockland area west of the harbour and Pb and Cu concentrations were also elevated in the embayment to the south. An apparent decreasing metals gradient from the upper embayment in the south towards the harbor mouth in the northeast requires verification with additional sampling.

Normalisation was undertaken using 27K Al. Although almost all samples in the 2015 vintage database were enriched (>2.5), contamination was not apparent in the total metals/total Al plots due probably the lack of uncontaminated samples. Environmental factors suggested moderate to high modification and enrichment was greatest for Cd and Zn (means 9.9 and 9.5, respectively), high for Pb (mean 5.2) and moderate for Cu (mean 2.5) and mean enrichment was MEQ>5.

Mean total Cr, Ni and Pb concentrations exceeded ERL values and mean Zn concentrations were >ERM. With a spatially limited dataset it was difficult to determine accurately the areas exposed to ecological risk by sediments, however it appeared that large parts of the port may be at risk for Cu, Pb and Zn. Overall ecological risk was moderate (MERMQ=0.51). Additional sampling and mapping is required to verify the risk distribution.

Sydney estuary

Total sediment mean (133 µg/g) and maximum (1060 µg/g) Cu concentrations were the highest recorded in the current study and maximum concentrations were highest for Pb (1932 µg/g) and second highest for Cr (298 µg/g) and Zn (11300 µg/g), while minimum values were commonly below detection due to sandy substrate in parts of the harbour. Sedimentary metal concentrations declined markedly from the upper reaches of the estuary towards the mouth and with distance from stormwater discharge points at the headwaters of offchannel embayments and tributaries. Sediments of the four south, central embayments of Blackwattle/Rozelle Bay, Iron Cove, Hen and Chicken Bay and Homebush Bay consistently contained the highest concentration of metals. Moderate metal concentrations were located in the western embayments of Middle Harbour.

Individual embayments had distinctive metal distributions in Sydney estuary (Birch et al., 2015a, b). Sediments in Homebush Bay generally had high Pb levels related to paint manufacturing, whereas surficial sediments in Hen and Chicken Bay had high Cu concentrations originating from a bronze processing plant. Sediments of Iron Cove were elevated in Pb and Cd due to historical industrial discharge and Blackwattle/Rozelle Bay sediments were highly enriched in Cu, Pb and Zn from shoreline heavy industry. Chromium was anomalously high in sediments of some bays in northwest Middle Harbour and Lane Cove related to tanning industries.

Size-normalised data were available for Sydney estuary, which allowed enrichment to be determined directly using surficial sediment concentrations and size-normalised OSPAR background metal concentrations without the use of elemental normalisation. Enrichment factors indicated moderate to high modification and enrichment was highest in the WHP for Cu (9.1) and third highest for Cd (5.1), however MEQs (8.6) were reduced by low enrichment for Cr (2.0) and Ni (0.7), especially when six elements are considered (5.7).

Copper, Pb and Zn are the contaminants of most concern in sediments of Sydney estuary and areas of the waterway with sediment exceeding ERM concentrations for these metals represented approximately 2%, 50%, and 36% of the estuary, respectively (Birch and Taylor, 2002a, b, c). Sediment in the entire estuary, except a small area near the entrance, exceeded ERL concentrations for at least one metal. Overall ecological risk was moderate (MERMQ=0.53).

4. Discussion

4.1 Sampling and Analytical methods

Sediment samples used by WHP institutions were recovered by grab (van Veen), corer or box corer. When using these different sampling devices, it is important to remove only the uppermost sediment layer so as to sample only the most recently deposited material and not to mix this surficial material with underlying, pre-anthropogenic substrate. Sampling design, density and distribution needs to be consistent. However, sampling was frequently focused on perceived source locations and points of interest with low density cover over the remaining (sometimes majority) waterway preventing a full spatial assessment. Sample density should be relative to small-scale spatial variance and proximity to discharge locations to provide optimal coverage for source identification and dispersion tracking. Sample density, which provided satisfactory regional coverage for reasonably consistent abundances was approximately 0.5-1.0 samples/km^2, but increased to 5-10 samples/km^2 in areas of interest, or in places of high variability based on data provided in the current study.

Metals in the sedimentary environment are present in the matrix of minerals and as the absorb phase of mainly fine-grained particles. The method chosen for chemical analysis of anthropogenic chemicals requires that metals from the mineral matrix be excluded from the analysis, especially as some sedimentary minerals contain high concentrations of metals incorporated in the structure. This is especially important in the coastal environment where marine and terrestrial sediments are immature and commonly contain metal-rich matrix minerals. Analytical schemes that result in assessment of both the absorbed and matrix phases confound interpretation and identification of anthropogenic contribution to the sediment. The approach used to analyse metals in sediments is therefore fundamentally important in assessment of sediment condition (Table 1). Weak acids have the advantage of providing an estimate of the trace metal bioavailable fraction (1M HCl) (Ying et al., 1982) and may be used in assessing potential toxicity (6 mol/L HCl solution for acid-volatile sulphides - simultaneously extracted metals, AVS-SEM analysis) (Di Toro et al., 1990; 1992). Strong acid digestions (HF) break down minerals and releases both matrix and adsorbed components resulting in a 4- to 9-fold elevation of metal concentrations compared to the more frequently used aqua regia (Katz and Kaplan, 1981), whereas the dilute HCl solutions only recover approximately 60% of metals relative to aqua regia. Digestion procedures used in the WHP varied from week to strong acids, which may have resulted in a mixed proportion of matrix and adsorbed metals in the analyses.

Most analyses undertaken in the WHP were by ICP, either OES, or MS, which would result in a high level of accuracy and precision, especially as most laboratories used International Reference Materials and appropriate QA/QA procedures. Not all studies incorporated sediment size, Al and Fe in the analytical stream, limiting an ability to normalise data needed for enrichment determinations.

Preferably, unconsolidated sediments should be chemically characterised using a wide variety of analytes, including metals and a range of organic contaminants, including organochlorine pesticides (OCs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). However, inconsistent organic chemical data and gaps in metal analyses across the WHP dataset prohibited such a holistic approach in the current investigation. Instead, metals that were ubiquitous in the WHP dataset were used to determine the magnitude of human induced change and possible ecological stress resulting from contamination. Although the absence of organic contaminant data in the present work is a disadvantage, the extent to which metals reflect the distribution of other priority contaminants of concern (OCs, PAHs, PCBs) in estuarine environments is also surprisingly consistent. The correlation between three metals (Cu, Pb and Zn) and OCs, PCBs and PAHs in Sydney estuary was significant (r=0.793, $p<0.05$) and with the same metals and nine OCs and hexachlorobenzene from Hawkesbury River (NSW) r=0.866 ($p<0.05$) and the same metals with PCBs from New York Harbour r=0.878 ($p<0.05$) and with sediments from San Diego Bay r=0.655 ($p<0.05$) (Birch et al., 2008). In the current study, Cu, Pb and Zn correlated with each other and with six metals (Cd, Cr, Cu, Ni. Pb and Zn) (r=0.997, $p<0.05$) and with PAHs in sediments of the Ria de Vigo Harbour (r=0.769, $p<0.05$). Estuarine sedimentary contaminants will more likely to covary in regions dominated by stormwater discharge because the chemical mix of urban stormwater is reasonably consistent (NURP, 1983: US EPA, 1983; Fletcher et al, 2004), however in areas receiving point-source, chemical-specific industrial discharge, contamination may be less likely to covary spatially.

4.2 Magnitude of anthropogenic change

The magnitude of anthropogenic change followed total metal concentrations with Derwent River having the highest Cd, Pb and Zn enrichment and Sydney the highest Cu enrichment, while Santander sediments were most enriched by Cr and Ni. The overall magnitude of anthropogenic change (MEQ) was high for Derwent River, Santander and Sydney estuary (>5.0), moderate for Rio de Janeiro (3.0-5.0), slight for Dublin, Hong Kong and Ria de Vigo (1.5-3.0) and minimal for Darwin (<1.5) (no data were available for Canale Candiano in Ravenna and Auckland) (Table 5). This enrichment appeared to be more related to location and magnitude of source than the morphodynamic characteristics of the WHP harbour estuaries.

Enrichment (MEQ) was calculated for six metals (MEQ/6=Cd, Cr, Cu, Ni, Pb and Zn) and for three metals (MEQ/3=Cu, Pb and Zn) to determine whether the extra number of elements effected enrichment calculations (Table 5). A close correlation between the two data sets (r=0.953, $p<0.05$) supports similar results, which show metals are invariably closely correlated with each other, e. g. the three metals (Cu, Pb, and Zn) were closely correlated with a suite of six metals for Sydney estuary (r = 0.959, $p<0.05$), Hawkesbury River (r=0.932, $p<0.05$), New York Harbour (r=0.843, $p<0.05$) and for Tampa Bay (r=0.825, $p<0.05$) (Birch et al., 2008) and in many other locations (Zhang et al.,2009).

Enrichment has been calculated in the present work based on a novel elemental normalisation procedure employing variable concentrations of Al to accommodate for regional changes in local clay mineral chemical assemblages. This approach has been investigated recently in great detail (Birch, 2020) and is discussed here only in its application to the WHP. The concentration of the Al normaliser varied across the 10 WHP datasets from 20K Al (Rio de Janeiro) to 70 K Al (Darwin) and was most commonly between 32K and 35K Al. The normaliser value used was estimated from the relationship between sediment size and total Al concentration, which was available for six (Darwin, Derwent, Hong Kong, Rio de Janeiro, Ria de Vigo and Sydney) of the 10 harbours. For harbours without sediment size information, normaliser values were estimated from total Al alone, which introduced speculation and no normalisation could be undertaken for harbours without sediment size, Al, or Fe data (Auckland and Canale Candiano in Ravenna).

An opportunity to test the validity of normalisation and enrichment determined by elemental normalisation (Al and Fe) was afforded by the availability of size-fractionated metals data from Sydney estuary. Enrichment based on size-normalised data and 35K Al normalisation (employing SOPAR (2008) background values for both data sets) was closely related. i. e. 9.1 and 9.8, respectively for Cu, 11 and 13, respectively for Pb and 6.5 and 7.6, respectively for Zn (Table 5). Moreover, enrichment determined by sediment size- and Al normalisation was also closely correlated. i. e. r=0.921 (, $p<0.05$) for Cu and r=0.854 ($p<0.05$) for Zn and less so for Pb (r=0.516, $p<0.05$), which showed moderate scatter due to analytical difficulties. These results gender confidence in the approach being used in the current work based on variable Al elemental normalisation.

The availability of PEN data for Darwin Harbour allowed a comparison between another size-nornalisation process and elemental normalisation. Normalisation of Darwin Harbour data to 70k Al produced similar results to PEN normalisation, i. e. mean concentrations of 15 µg/g, 29 µg/g and 79 µg/g compared to 18 µg/g, 36 µg/g and 87 µg/g for Cu, Pb and Zn, respectively. Normalisation using Fe produced inconsistent results due to anomalously high concentrations of this element for some samples related to the presence of Fe oxyhydroxides (Munksgaard et al., 2013). Mean enrichment, also using 70K Al as a normaliser, was closely correlated, i. e. 0.9, 1.4 and 1.0 for Cu, Pb and Zn, respectively compared to 0.7, 1.0 and 0.9, respectively for PEN data (Table 5). Enrichment using PEN and 70K Al data was moderately correlated (r=0.641, $p<0.05$), however PEN data were less consistent than using 70K Al possibly due to variable carbonate content.

Although Li is the normaliser of choice for Ria de Vigo sediments, these data afforded the opportunity to test the appropriateness of Al- and Fe-normalisation on the same data set. Normalised concentrations produced by 90K Al and 35K Fe were remarkedly similar, i. e. 98 µg/g and 97 µg/g, respectively for Cu, 131 µg/g and 125 µg/g, respectively for Pb, and 244 and 235, respectively for Zn. Similarities in enrichment determined by these two techniques were also close, i. e. 4.9 and 4.9 for Cu; 5.2 and 5.0 for Pb and 2.9 and 2.7 for Zn. MEQ for the two approaches were both 4.1 and correlation between the two techniques for Cu was r=0.964 (p<0.05). These results indicated both Al and Fe may be used as elemental normalisers in the absence of diagenetic modification.

Determining the most appropriate pre-anthropogenic metal concentrations was the second difficulty in assessing enrichment in the WHP. The lack of these data for individual harbours reduced the ability to determine the magnitude of anthropogenic change. In the absence of data derived from sedimentary cores, or from local pristine environments, OSPAR (2008) background metal values were adopted in the present WHP study. Various Al concentrations were used in the normalisation process to accommodate for changes in local clay mineral characteristics however, a single suite of background metal concentrations was applied to all WHP data. Background values will be different for each of the world harbours and should be estimated from local fine-grained down-hole core data, or pristine fine sediment. The absence of size-normalised sediment metal concentrations and valid local background data will introduce errors in enrichment determinations for the WHP.

4.3 Use of concentration, contamination and enrichment factors in assessment of anthropogenic change

Derwent River and Sydney estuary registered high values for all 10 enrichment indices used in the current investigation (Table 6), while Auckland and Darwin resulted in low assessments for most of these tools. Other harbours had mixed values across the spectrum of indices with Ria de Vigo, Rio de Janeiro and Santander having slightly elevated outcomes. An attempt has been made to combine the outcomes of assessment factors calculated in the current work to give an overall quantification for the 10 estuaries in the WHP (Table 6). The classification schemes for the EF (Rubio et al., 2000), mDC (Abrahim and Parker, 2008), mPI (Brady et al., 2015) and MEQ (Birch and Olmos 2008) techniques are substantially similar providing a unique opportunity to produce an overall classification scheme for these enrichment factors. Enrichment factors of EF <1.5; 1.5-3; 3 to 5; 5–10; 10 –25; > 25 were classified as not enriched; slightly enriched; moderately enriched; highly enriched; extremely enriched; and severely enriched, respectively. Based on this approach, the overall score for the Derwent River was 20, for Sydney estuary 14, for Santander 12, for Ria de Vigo and Dublin 11, for Rio de Janeiro 9, for Hong Kong 5 and for Darwen 4. Insufficient normalised data were available to rank Canale Candiano of Ravenna and Auckland, however these harbours probably have scores of <4 considering the low total metal concentrations.

A generalised observation of the 10 metrics used in the current study (Table 6) showed that the Nemerow Pollution Index (*PI*) and the Metal Pollution Index (*MPI*) values were high, while the Geo-accumulation index (*Igeo*) for both total sediment and for Al-normalised data were low with respect to results from other indices. PI values were higher than reported in the literature (Brady et al., 2015) possibly due to unusually elevated metal concentration in some of the WHP estuaries, whereas *Igeo* figures are commonly cited low, or negative (Abrahim and Parker, 2008). The Surface Enrichment Factor (*SEF*), Enrichment Factor (*EF*), the Modified Degree of Contamination (*mDC*) and the Mean Enrichment Quotient (*MEQ*) results are similar. An outcome of these assessments was that, although the factors are based on different attributes, the ranking produced was similar for all assessment tools. A further outcome was that the Concentration Factor (*CF*) (un-normalised data), *mDC*, *EF*, *mPI* and the *MEQ* are closely correlated (r values between 0.942 and 0.959, $p<0.05$), while the *Igeo* and the *PI* are poorly correlated with the previous group of factors, probably due to the different basis on which these indicators are calculated.

TABLE 6

Estimation of metal background concentrations has a substantial influence in the determination of anthropogenic change established by contamination and enrichment factors. Four types of background value were used in the study of Ria de Vigo (Northwest Spain) (Rubio et al., 2000). One background value was derived from local geology, a second from global shale and two further background values were based on regional studies. An assessment of contamination varied substantially when each of these background concentrations were used to assess contamination. Abrahim and Parker (2008) found that using continental shale Fe values as a normalising element resulted in a significant increase in *EF* compared to using Fe concentrations from the base of local cores and warned that using global material as background to calculate enrichment should be undertaken with caution. Background metal concentrations used in calculating the Degree of Contamination (DC) were derived from pristine sediments by Hakanson (1980) based on sediment from 50 lakes in Europe and North America already influenced to varying degrees by anthropogenic activity and also possibly by variable grain sizes. Background values were determined by adding one standard deviation to the mean, which resulted in doubling of the final background concentrations due to considerable variation in the data. Resulting background concentrations are high relative to other reported pre-anthropogenic values, nevertheless this technique remains in use globally and is frequently cited in the literature.

The original Geo-accumulation Index (*Igeo*) (Müller 1969, 1979; 1986) was based on fine sediment samples and background metal concentrations, however recently different backgrounds have been used (global shale) (Ghani et al., 2013) and various sediment sizes (total sediment) have been included in the computation (Buruaem et al., 2012; Pang et al., 2015). resulting in confusion and incompatible outcomes. More recently confounding due to variable size when using total sediment has been taken into account by normalising to Al and adjusting the data to 100 % mud (Kim et al., 2018; 2019). Geo-accumulation index values were low and often negative in the current work, similar to other studies where results for most elements were also negative, e. g. Cevik et al. (2009); Kaushik et al. (2009); Thuong et al. (2013), Abrahim and Parker, (2008) and Kim et al. (2018).

The original Degree of Contamination (DC) included seven specific metals (As, Cd, Cu, Cr, Hg, Pb, and Zn) and an organic pollutant (PCB) and required a minimum of five samples. The numeric sum of the eight specific contamination factors expressed overall degree of contamination and all eight contaminants had to be included in the calculation. The limited and specific number of pollutants led Abrahim and Parker (2008) to modify the factor to include any number of metallic contaminants and the analysis of at least three samples of impacted sediments. Background values were determined from the lower sections of cores and the six-division classification scheme was modified accordingly. Abrahim and Parker (2008) restricted examination to fine-grained samples for both contemporary and background materials.

Single-element pollution indicators present a number of limitations and do not take into account the complex interaction of metal contamination in mixed urban and industrial environments. These limitations have led to the development of multi-element indices, e. g. *mPI*, *DC* and *mDC*, which include a suite of metals to make a more integrated assessment of contamination.

The skewed nature of some contaminant data has also led to modification of the *PI* index. In the case where one metal is highly enriched and the calculation is averaged over a suite of metals, the impact of the enriched element is subdued. This problem has been addressed by including the maximum concentration of the elevated element as a separate factor in the weighted-average value. The *mPI* also uses enrichment factors, which accounts for the non-conservative nature of contaminated sediments. However, no guidance is provided of how to identify an 'enriched' element, or how to conduct the calculation if there is not one. In the WHP datasets, Zn was always the highest concentration, however it not clear whether this element should be considered 'anomalously' elevated and included as a separate factor, or not in the computation. Inclusion of Zn as a separate factor in the current study resulted in an over estimation of *mPI* values, e. g. in the Derwent River and Sydney estuary, and production of values that are far in excess of other assessment types in the current study and of *mPI* results in others work (Brady et al., 2015).

4.4 Ecological risk posed by sedimentary metals

Only sediment from Derwent River was rated high risk (MERMQ>1.5), followed by Sydney and Santander estuaries at moderate risk (MERMQ>0.50). Auckland and Darwin sediments exhibited minimal risk and sediment in the remaining harbours (Dublin, Hong Kong, Ravenna, Ria de Vigo and Rio de Janeiro) was assessed at slight risk to benthic communities (Table 7). The statistic that separates Derwent River from other harbours is the number of samples with at least one element with concentrations >3 times ERM values (51 samples, 45%) and >5 times ERM levels (40 samples, 36%) (Table 8). Ecological risk for sediments of the Derwent River are driven by high Cd, Pb and Zn concentrations, Sydney by high Pb and Zn concentrations and Santander by Ni and Zn concentrations (Table 8).

TABLE 7

A more detailed examination of harbours exposed to slight and minimal risk shows Auckland and Darwin with only a few samples >ERL for any one metal (Table 8). Harbours mantled with sediment assessed at slight risk of adverse effects (Dublin, Hong Kong, Ravenna, Ria de Vigo and Rio de Janeiro) have a high proportion (54 % - 88%) of samples with at least one metal >ERL values, suggesting possible risk.

TABLE 8

The second popular effects-based sediment quality guideline for single contaminants, i. e. the Probable Effects Level (PEL) (MacDonald et al., 2000) and for chemical mixtures, i. e. the mean PEL quotient (MPELQ) provide the highest values the Derwent River (1.34), followed by Sydney 0.97) and Santander (0.77), similar to results produced by the MERMQ. The MERMQ for three metals (Cu, Pb and Zn) and for six metals are consistent, except for Sydney where the MERMQ for six metals has been reduced by low Cr and Ni values.

A more extensive evaluation of the highly impacted harbours was made by assessing areas and proportions of harbours adversely affected by sedimentary metals. Greater than 80% of the Derwent River and Sydney estuary are mantled in sediment enriched >5 times over pre-anthropogenic times, while Rio de Janeiro sediments exhibit a large range of enrichments. Sediments in Hong Kong and Ria de Vigo Harbours are mainly enriched between 1.5 and 5 times. Sediments in more than 25% of Derwent River are at high ecological risk (MERMQ>1.5). while only 2% of Sydney estuary was at this risk level. Over 90% of the area of the remaining harbours (Hong Kong, Ria de Vigo and Rio de Janeiro) had a slight to moderate ecological risk (MERMQ = 0.1 - 0,5)

4.5 Overall magnitude of anthropogenic change and ecological risk

An overall assessment of anthropogenic change and ecological risk has been undertaken by ranking enrichment (Table 5), environmental indices (Table 6) and MERMQ (Table 7) for eight harbours (enrichment data were not available for Auckland and Canale Candiano of Ravenna) (Table 9). Ranking was remarkably consistent across the three schemes, i. e. the Derwent River, Sydney and Santander estuaries were placed first, second and third most impacted environments, respectively for all assessments, while Darwin Harbour was the least influenced by human activities. The remaining harbours changed only one or two places between schemes.

TABLE 9

A new categorisation scheme (Birch, 2018) has been applied to results of enrichment and ecological risk obtained in the current study to assess overall anthropogenic change and ecological risk (Table 10). Derwent River, Sydney and Santander estuaries are highly enriched, while Rio de Janeiro is moderately enriched. Dublin, Hong Kong and Ria de Vigo are slightly enriched, whereas Darwin is not enriched. Only the Derwent River is at high ecological risk, while Sydney and Santander estuaries are at moderate risk. Auckland and Darwin are at minimal risk and Dublin, Hong Kong, Ravenna Ria de Vigo and Rio de Janeiro are at slight ecological risk.

TABLE 10

5 Conclusions

Sediments of Derwent River are distinctive with very high total mean concentrations of Cd, Pb and Zn. Sydney estuary sediments contain the highest mean Cu concentrations and Santander Harbour sediments are characterized by the highest mean concentrations of Cr and Ni of the 10 WHP ports.

An innovative technique for Al and Fe normalisation was applied and tested against accepted size-normalisation and post-extraction (PEN) methods, which satisfactorily allowed measurement of anthropogenic change. Metals enrichment followed total metal concentration and the mean enrichment for multiple sedimentary metals (MEQ) was high for Derwent River, Santander Harbour and Sydney estuary (>5.0), moderate for Rio de Janeiro and Dublin Port (3.0-5.0), slight for Hong Kong (1.5-3.0) and minimal for Darwin (<0.15) (no sediment size. Al, or Fe data were available for Canale Candiano of Ravenna and Auckland.

Only sediment from Derwent River was rated at high ecological risk (MERMQ>1.5), followed by Sydney and Santander estuaries with moderate risk (MERMQ>0.50). Dublin, Hong Kong, Ravenna, Ria de Vigo and Rio de Janeiro were assessed at slight risk to benthic communities and Auckland and Darwin sediments exhibited minimal ecological risk.

All 10 enrichment indices used in the current investigation showed elevated values for Derwent River and Sydney estuary, while Auckland and Darwin registered low values for most of these tools. Other harbours had mixed values across the spectrum of indices. A unique, multi-index classification scheme provided an overall score of 20, 14, 12, 11, 9, 5 and 4 for the Derwent River, Sydney estuary, Santander, Ria de Vigo and Dublin, Rio de Janeiro, Hong Kong and Darwen, respectively. Insufficient data were available to rank Canale Candiano of Ravenna and Auckland, however these harbours are considered to score <4 considering total metal concentrations.

A new categorisation scheme applied to results of the current study assessed overall anthropogenic change and ecological risk. Derwent River, Sydney and Santander estuaries were rated highly enriched, while Rio de Janeiro was moderately enriched. Dublin, Hong Kong and Ria de Vigo were slightly enriched, whereas Darwin was not enriched. Only the Derwent River was at high ecological risk, while Sydney and Santander estuaries were at moderate risk. Dublin, Hong Kong, Ravenna Ria de Vigo and Rio de Janeiro were at slight ecological risk and Auckland and Darwin were at minimal risk. The similarity in the ranking of the harbours in assessment of enrichment and ecological risk is reassuring and the minor difference for Rio de Janeiro is due to the different criteria used in the two assessment techniques.

The wide range in environments and a large variety in types of data provided by partner organisations resulted in a useful critique and development of methodologies used in assessment of sediment quality in maritime regions. It is important to restate that these assessments are the result of a screening procedure to identify and prioritise contaminants and region of concern and that further evaluation of other risk factors, e. g. bioaccumulation, bioavailability and toxicity, are required to determine potential impact.

Recommendations

Sample coverage was inconsistent amongst WHP partners and tended to be focused on perceived point sources and nearshore environments, often leaving large central areas un-surveyed, which prevented a full spatial assessment for 40% of the harbours. Sufficient sample density for regional coverage was estimated at ~0.5-1.0 samples/km^2, while for areas of concern, or high variability, a density of 5-10 samples/km^2 is recommended.

The suite of analytes also varied within the WHP and no consistent combination of chemicals other than metals (and even these were not consistent) were available for assessment. Ideally, a full set of metallic and organic contaminants would be required to conduct a satisfactory environmental assessment, however evidence is available to show that metals are strongly correlated to other organic pollutants.

Most analyses were undertaken using weak (HCl) to moderately strong acid (aqua regia) mixtures, which are suitable for assessing the adsorbed phases required to assess the magnitude of anthropogenic change and to establish ecological risk. The use of stronger acids, e. g. HNO_3/$HCLO_4$ (nitric plus perchloric acid) would extract inert mineral forms and may make assessment of ecological risk problematic.

A global inadequacy exists in the availability of suitable data for setting pre-anthropogenic sedimentary metal concentrations. Background values should be estimated from local, fine-grained down-hole, core data and will be different for each of the WHP locations. Cores used for background estimation should be recovered from undisturbed areas of deposition and subsurface bioturbation and post-depositional physical and chemical remobilisation should be avoided. Instead, a single suite of background metal concentrations had to be applied to all WHP data, introducing possible error in enrichment assessments of the 10 harbour estuaries.

Some form of normalisation is essential for enrichment assessment to moderate confounding by varying grain size. WHP data frequently lacked data necessary for assessing metal enrichment, i.

e. sediment size, Al and Fe. Size-fractionated metal data are the preferred data for enrichment estimation, however tests conducted in the current work confirm the use of both Al and Fe as normalisation elements and the use of PEN data for determining human-induced change in the absence of elevated carbonate content.

The individual schemes comprising the plethora of indices now available for estimating metals enrichment have not yet been thoroughly tested for validity and some are based on uncertain assumptions. Indices supporting multiple elements, include a classification scheme and based on normalised data and background information are recommended and results from these schemes are closely correlated (r>0.95), i. e. Enrichment Factor (EF), modified Degree on Contamination (*mDC*) and the Mean Enrichment Quotient (MEQ). The original Geo-accumulation Index (*Igeo*) and the modified version (*mIgeo*) exhibits reduced sensitivity and the Nemerow Pollution Index (*PI*) and the modified version (*mPI*) over emphasises elevated metals resulting in loss of discretionary power. Despite the different formulations on which the 10 indices are based, ranking of index results was similar for all assessment tools and as many as possible indices should be tested in assessing anthropogenic change.

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Table(s)

Table 1. Data availability, sampling device used and analytical method

Location	Years available	Years used	Sampling device	Analytical method	Extraction technique	Acid	RM	Available data			Comments
								Al	Fe	Size	
Auckland	2010,11,12,13	2008	na	ICP-MS	HNO_3/HCl	M	?Y	N	N	N	
Darwin	2012	2012	corer	ICP-MS	HNO_3/$HClO_4$	S	Y	Y	Y	Y	PEN data
Derwent	1998,99,2001,06,09,10,11,12,13	2000	corer	ICP-OES	na	?	Y	N	Y	Y	SN
Dublin	1991,95,96,97,2003,08,13,14	2006	corer	ICP-OES	HNO_3	M	?	Y	Y	N	
Hong Kong	1987-2015; 2003-2015	2015/16	v v grab	ICP-MS	HNO_3	M	?	Y	Y	Y	
Ravenna	1994,2004,09,18	2004	na	GF-AAS	HNO_3/HCl	M	Y	N	N	N	
Ria de Vigo	2011	2011	na	SP	HNO_3	M	Y	Y	Y	Y	
Rio de Janeiro	2005,06[1]	2005/06	v v grab	ICP-OES	6M HCl	W	N	Y	Y	Y	
Santander	2005,6,7,8,9,10,11,12,13,14,15	2015	v v grab	ICP-MS	HNO_3/HCl	M	Y	Y	Y	N	
Sydney	2010-14	2010-14	Box corer	ICP-OES	Aqua regia	W	Y	Y	Y	Y	SN

Notes: PEN=Post Extraction Normalised; SN=size normalised; S=strong; W=weak; M=Moderate; v v=Van Veen; RM=reference material used

ICP=Inductivity coupled plasma; MS=mass spectrometry; OES=optical emission spectrometry;

SP=spectrophotometer; GF-AAS=graphic furness atomic adsorption spectroscopy; na=not available

HNO_3= nitric acid; HCl=hydrochloric acid; $HClO_4$=perchloric acid; aqua regia=HCl/HNO_3

[1] mean of four surveys

Table 2. Data availability and reliability

Location	Number of samples	Harbour area (km^2)	Sample density sample/km^2	Map type	Distribution	Reliability L M H
Auckland	121	800	0.15	P	Sites mainly in bays & tributaries with central area unsampled	M
Darwin	298	1220	0.24	P	Sites restricted to intertidal flats with tidal channels unsampled	H
Derwent	123	200	0.62	FC	Excellent distribution, all locations and environments covered	H
Dublin	42	3.267	12.9	P	Moderate number of sites mainly in shipping basins	M
Hong Kong Harbour	9	63.0	0.14	FC	Excellent coastal dataset but only harbour sites used	L
Ravenna	52	3.62	14.4	P	High density sampling in shipping channels	H
Ria de Vigo	39	156	0.25	FC	Good systematic grid covering all locations & environments	H
Rio de Janeiro	28	449 [1]	0.06	FC	All areas covered but low sample density	M
Santander	10	22.5	4.58	P	Few sites located mainly in marginal areas	L
Sydney	1175	50	23.5	FC	Good distribution, high sample density covers all areas	H

H= high; M=moderate; L=low; FC=filled contour maps; P=point maps

[1] Guanabara Bay area

Table 3. Attributes of concentration and enrichment Factors/Indices used globally

No.	Factor/Index Name	Symbol	Author(s)	Background		Normalis-ation	Multi-element	Classificat-ion Scheme	Score
				Global	Local				
Concentration Factors (no background, or normalisation)									
1	Metal Pollution Index	PI	Usero et al.,1996	N	N	N	Y	N	1
Contamination Factors (background values, but no normalisation)									
2	Contamination Factor	CF	Brady et al., 2015	Y	N	N	N	N	1
3	Nemerow Pollution Index	PI	Nemerow, 1991	N	N	N	Y	N	1
4	Surface Enrichment Factor	SEF	Riba, 2002a	Y	Y	N	N	N	2
Enrichment Factors (apply both background and normalisation procedures)									
5	Enrichment Factor	SEF	Kemp et al., 1976; Rubio et al., 2000	Y	Y	Y	N [1]	N	3
6	Geo-accumation Index (fine sediment)	*Igeo* (fine)	Muller, 1980	Y	Y	Y	N	Y	4
7	Geo-accumation Index (total sediment)	*Igeo* (total)	Xu et al., 2014	Y	Y	Y	N	Y	4
8	Geo accumation Index (total sediment)	*Igeo* (mud %)	Kim et al., 2018	Y	Y	Y	N	Y	4
9	Degree of Contamination	DC	Hakanson, 1980	Y	N	Y	Y	Y	4
10	Modified Nemerow Pollution Index	mPI	Brady et al., 2015	Y	Y	Y	Y	Y	4
11	Mean Enrichment Quotient	MEQ	Birch & Olmos, 2008; Birch et al., 2013	Y	Y	Y	Y	Y	5
12	Modified Degree of Contamination [2]	MDC	Abrahim & Parker, 2008	Y	Y	Y	Y	Y	5

[1] combined elements as overlays on maps; [2] use 'fine-grained' sediments

Table 4. Mean, minimum and maximum concentrations (µg/g, dry weight) for total sediment

Harbour	Cd (1.2; 9.6)			Cr (81; 370)			Cu (34; 270)			Ni (20.9; 51.6)			Pb (46.7; 218)			Zn (150; 410)		
	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max
Auckland	0.1	0.0	0.1	15	3.1	23	13	3.1	36	na	na	na	22	5.4	44	90	16	210
Darwin	0.1	0.01	0.5	18	6.6	95	5.4	0.7	23	8.8	1.5	27	10	1.8	50	25	4.6	190
Darwin [1]	0.1	bd	0.9	45	44	230	15	1.0	147	22	3.5	113	29	6	459	79	6.8	1730
Derwent	14	1.0	128	36	2.0	71	112	1.0	591	17	1.0	31	450	6.0	1880	2130	22	14600
Dublin 2013	3.6	0.1	20	136	25	316	60	3.3	155	90	58	164	138	10	1130	660	22	5240
Dublin 2008	0.7	0.1	2.3	24	3.7	47	27	1.3	69	19	1	39	44	1.9	192	152	9.2	470
Dublin 2006	1.1	0.4	2.1	35	9.3	66	49	8.5	111	29	12	55	81	11	243	217	60	420
Hong Kong [2]	0.2	0.1	0.7	31	17	67	31	7.0	160	18	10	29	41	19	100	121	51	330
Hong Kong [3]	0.3	0.1	1.7	37	22	55	67	23	135	18	14	24	45	29	74	148	72	275
Ravenna	1.6	1.0	2.4	74	46	124	30	8.6	72	na	na	na	49	11	126	106	67	180
Ria de Vigo	0.3	bd	1.3	70	4.2	198	82	4.2	479	29	6.1	43	111	5.0	450	199	13	1490
Rio de Janeiro	0.8	bd	2.4	72	1.4	205	62	0.3	224	21	0.2	113	66	2.7	200	318	4.2	2040
Santander	1.3	0.1	2.6	77	7.5	214	33	2.5	67	46	4.2	126	83	12	145	463	52	1050
Sydney	1.0	bd	52	77	bd	298	133	bd	1060	15	bd	118	210	bd	1930	518	bd	11300
Mean	1.8	0.3	17	54	15	144	51	5.0	237	28	11	74	98	8.7	502	371	32	2960
Maximum	14.0	1.0	128	136	46	316	133	23	1060	90	58	164	450	29	1930	2130	72	14600

[1] for <62.5 µm fraction; [2] coastal region; [3] for Harbour area only; bd=below detection

ERL= Effects Range Low; ERM=Effects Range bd=Below detection; Median; Figures in brackets are ERL; ERM values

Table 5. Mean and maximum enrichment based on various normalising techniques

Location	Cd (0.2 µg/g)		Cr (60 µg/g)		Cu (20 µg/g)		Ni (30 µg/g)		Pb (25 µg/g)		Zn (90 µg/g)		MEQ		Normalisor & concentration
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max	n=6	n=3	
Auckland	na	na	na	na	na	na	na	na	na	na	na	na	na	na	No Al or Fe
Darwin	0.7	11	0.7	3.8	0.7	3.9	0.7	3.8	1.0	7.5	0.9	19.0	0.8	0.9	PEN
Darwin	1.6	11	1.2	4.5	0.9	4.1	1.0	2.1	1.4	5.6	1.0	5.6	1.2	1.1	70K Al
Derwent	77	430	0.8	2.7	5.6	22	0.7	2.1	19	57	23	129	21	16	32K Fe
Dublin 2006	10	45	1	1.6	4.1	7.7	1.8	5.3	5.4	12	4.2	8	4.5	4.6	25K Al
Hong Kong [1]	1.9	24	1.0	1.1	5.1	8.8	1.0	1.3	2.9	5.1	2.6	3.8	2.4	3.5	35K Al
Hong Kong [2]	1.2	6.4	0.8	1.6	2.5	11	1.4	2.6	2.5	6.5	2.1	7.8	1.7	2.2	35K Al
Ravenna	na	na	na	na	na	na	na	na	na	na	na	na	na	na	No size, Al, Fe
Ria de Vigo	1.9	7.3	1.4	3.2	4.9	19	1.2	3.9	5.2	19	2.7	10	2.9	4.1	90K Al
Ria de Vigo	1.8	5.8	1.3	3.1	4.9	4.0	1.2	2.7	5.0	17	2.6	16	2.8	4.1	35K Fe
Rio de Janeiro	5.4	16.7	1.5	4.0	4.0	13	0.9	4.4	3.1	9.3	4.6	26	3.2	3.5	20K Al
Santander	9.9	21	3.5	13	2.5	3.3	4.0	16	5.2	7.3	9.5	18	5.8	5.8	27K Al
Sydney	9.5	69	2.4	7.5	9.8	35	0.8	5.3	13	53	7.6	30	4.5	9.6	35K Al
Sydney	5.1	25	2.0	5.8	9.1	36	0.7	2.1	11	52	6.5	21	5.7	8.6	SN
Mean	11	56	1.5	4.3	4.5	14	1.3	4.3	6.2	21	5.6	25	4.7	5.3	
Maximum	77	430	3.5	13	9.8	36	4.0	16	19	57	23	129	21	16	

Figures in brackets are background values; MEQ=Mean Enrichment Quotient; na= not available
MEQ n=6 is for Cd, Cr, Cu, Ni. Pb and Zn; MEQ n=3 is for Cu, Pb and Zn; PEN=post-extraction normalisation; SN=size normalised; K=1000 µg/g

[1] coastal region; [2] for Harbour area only

Table 6. Results of enrichment computations using multiple indices

	Concentration Factor	Contamination Factors (background, no normalisation)				Enrichment Factors (background and normalisation applied)						
	MPI	CF	PI	SEF	Igeo (total)	EF	Igeo (Al)	mPI	mDC	MEQ	WoE	Rank
Harbour	Metal pollution index	Contamination Factor	Nemerow pollution index	Surface enrichment factor	Geo-accumulation index total sediment	Enrichment factor	Igeo Al normalised	Modified Nemerow pollution index	Modified degree of contamination	Mean enrichment quotient	Total score	
Auckland	7.5	0.6	49	-0.4	-5.6	na	na	na	0.6	na	na	na
Darwin	5.0	0.3	46	-0.5	-2.0	1.0	-0.8	0.2	0.3	1.1	4	8
Derwent	99	20	2070	23	1.3	25.0	2.2	5.3	20	16.0	20	1
Dublin	31	2.5	117	1.8	0.4	5.0	0.5	0.6	2.5	5.8	11	6
Hong Kong	16	1.1	86	0.1	0.5	1.8	0.5	1.5	1.1	2.2	5	7
Ravenna	26	1.8	81	1.2	0.1	na	na	na	2.2	na	na	na
Ria de Vigo	12	2.4	320	1.7	0.4	6.1	0.9	1.1	2.4	4.1	9	5
Rio de Janeiro	34	2.5	335	1.7	1.9	2.8	0.9	2.5	2.5	2.5	11	4
Santander	40	3.0	208	2.4	0.5	5.0	1.8	1.2	3.0	5.8	12	3
Sydney	50	4.5	1740	4.2	0.8	8.7	1.7	5.6	4.5	8.6	14	2

na=not available; WoE=Weight of evidence based on classification schemes for EF, mDC, mPI and MEQ techniques, see text (Section 4.3); Rank Least influenced 1 to most impacted 8

Table 7. Mean Effects Range Median (MERM) for individual metals and for metal mixtures (Mean Effects Range Median Quotients, MERMQ)

Harbour	MERM (Cd, Cr, Cu, Ni, Pb, Zn)						MERMQ
	Cd	Cr	Cu	Ni	Pb	Zn	
Auckland	0.01	0.02	0.05	na	0.11	0.24	0.09
Darwin	0.01	0.05	0.02	0.17	0.05	0.06	0.06
Derwent	1.42	0.10	0.41	0.32	2.04	5.20	1.58
Dublin 2006	0.1	0.1	0.18	0.56	0.37	0.53	0.31
Hong Kong [1]	0.02	0.09	0.12	0.35	0.19	0.30	0.17
Hong Kong [2]	0.03	0.02	0.25	0.35	0.21	0.36	0.20
Ravenna [3]	0.16	na	na	na	0.18	0.43	0.26
Ria de Vigo	0.04	0.15	0.44	0.48	0.6	0.59	0.38
Rio de Janeiro	0.09	0.20	0.23	0.41	0.28	0.78	0.33
Santander	0.13	0.21	0.12	0.87	0.37	1.25	0.51
Sydney	0.09	0.22	0.43	0.27	0.8	0.95	0.53

[1] coastal region; [2] for Harbour area only; [3] for Cd, Pb and Zn only; na= not available

Table 8. Effects range low (ERL) and effects range median (ERM) quotients and numbers and percentages of samples >ERL and >ERM

Harbour	Sample	ERLQ (Cd, Cr, Cu, Ni, Pb, Zn)			ERMQ (Cd, Cr, Cu, Ni, Pb, Zn)						MERLQ	MERMQ
	No.s	Mean	Samples >ERL [1]		Mean	Samples >ERM [1]		No. samples exceeding ERM			Cu, Pb, Zn	Cu, Pb, Zn
			No.	%	ERMQ	No.	%	1-3	3.1-5	5.1-6		
Auckland	121	0.48	0	0	0.08	0	0	0	0	0	0.48	0.12
Darwin	298	0.21	2	<1	0.06	0	0	3	0	0	0.18	0.04
Derwent	123	6.50	102	83	1.60	111	90	51	20	40	8.70	2.56
Dublin 2006	42	1.23	36	88	0.34	2	5	2	0	0	1.43	0.45
Hong Kong	9	0.67	9	100	0.23	0	0	0	0	0	0.87	0.27
Ravenna [3]	52	0.89	26	54	0.20	0	0	0	0	0	0.88	0.20
ria de Vigo	39	1.46	34	87	0.35	6	15	5	1	0	2.04	0.43
Rio de Janeiro	28	1.31	17	60	0.33	4	15	4	1	0	0.78	0.40
Santander	10	1.57	9	90	0.51	8	80	8	0	0	2.07	0.92
Sydney	207	2.00	195	94	0.53	109	53	107	2	0	2.75	0.51

[1] samples with any one metal >ERL or > ERM; [2] for mean Cd, Cr, Cu. Ni. Pb and Zn; [3] for mean Cr, Cu, Pb and Zn only

ERL= Effects Range Low; ERM=Effects Rage Median; PEL= Probable Effects Level; Q=Quotient

Table 9. Habour ranking for Mean Enrichment Quotient (MEQ), ten environmental indices and Mean Effects Median Quotient (MERMQ)

Harbour	MEQ	Environmental Indices	MERMQ	Rank [1] Total	Rank [1] Place
Auckland	na	na	9	na	na
Darwin	8	8	10	26	1
Derwent	1	1	1	3	8
Dublin 2006	4	6	6	16	4
Hong Kong	7	7	8	24	2
Ravenna	na	na	7	na	na
Ria de Vigo	5	5	4	14	5
Rio de Janeiro	6	4	5	15	3
Santander	3	3	3	9	6
Sydney	2	2	2	6	7

[1] Least influenced 1 to most impacted 8; na= not available

Table 10. Magnitude of anthropogenic change (MAC) and Ecological risk posed by sedimentary contaminants (ERA)

Harbour	Magnitude of anthropogenic change (MAC) [1]		Ecological risk posed by sedimentary metals (ERA) [2]	
	MEQ	Enrichment/Modification	MERMQ	Ecological Risk
Auckland	na	na	0.09	Minimal risk
Darwin	1.2	Not enriched	0.06	Minimal risk
Derwent	21	Highly enriched	1.58	High risk
Dublin	5.7	Slightly enriched	0.31	Slight risk
Hong Kong Harbour	1.7	Slightly enriched	0.20	Slight risk
Ravenna	na	na	0.26	Slight risk
Ria de Vigo	2.8	Slightly enriched	0.38	Slight risk
Rio de Janeiro	3.2	Moderately enriched	0.33	Slight risk
Santander	5.8	Highly enriched	0.51	Moderate risk
Sydney	5.7	Highly enriched	0.53	Moderate risk

MEQ= Mean enrichment quotient; MERMQ= Mean effects median quotient; na=not available

[1] MEQ <1.5 - not enriched; 1.5-3.0 - slightly enriched; 3.0-5.0 - moderately enriched; >5.0 - highly enriched

[2] MERMQ <0.1 - minimal risk; 0.1 - 0.5 - slight risk; 0.5 - 1.5 - moderate risk; >1.5 high risk

Figure Captions

Figure 1. The ten world harbour estuaries assessed in the current WHP

Figure 2. Sample sites in six of the WHP locations

Figure 3. Distribution of fine (<62.5 µm) sediment in six of the WHP locations

Figure 4. Distribution of Zn in total sediment for six of the WHP locations

Figure 5. Distribution of Zn enrichment for six of the WHP locations

Figure 6. Distribution of Mean Enrichment Quotient (MEQ) (Cu, Pb and Zn) for six of the WHP locations

Figure 7. Distribution of Ecological Risk Assessment (ERA) for six of the WHP locations. ERL=Effects Range Low; ERM=Effects Range Median

Figure 8. Distribution of Mean Effects Range Median Quotient (MERMQ) for six of the WHP locations

Figure 9. Ecological Risk for world harbour estuaries assessed in the current WHP expressed as Effects Range Median (ERM) with Mean Effects Range Median Quotient (MERMQ for six metals) (a) including the Derwent River and (b) excluding the Derwent River to emphasise remaining locations


Dublin
Santander
Vigo
Ravenna
Hong Kong
Darwin
Rio de Janeiro
Auckland
Sydney
Derwent

Figure 1.

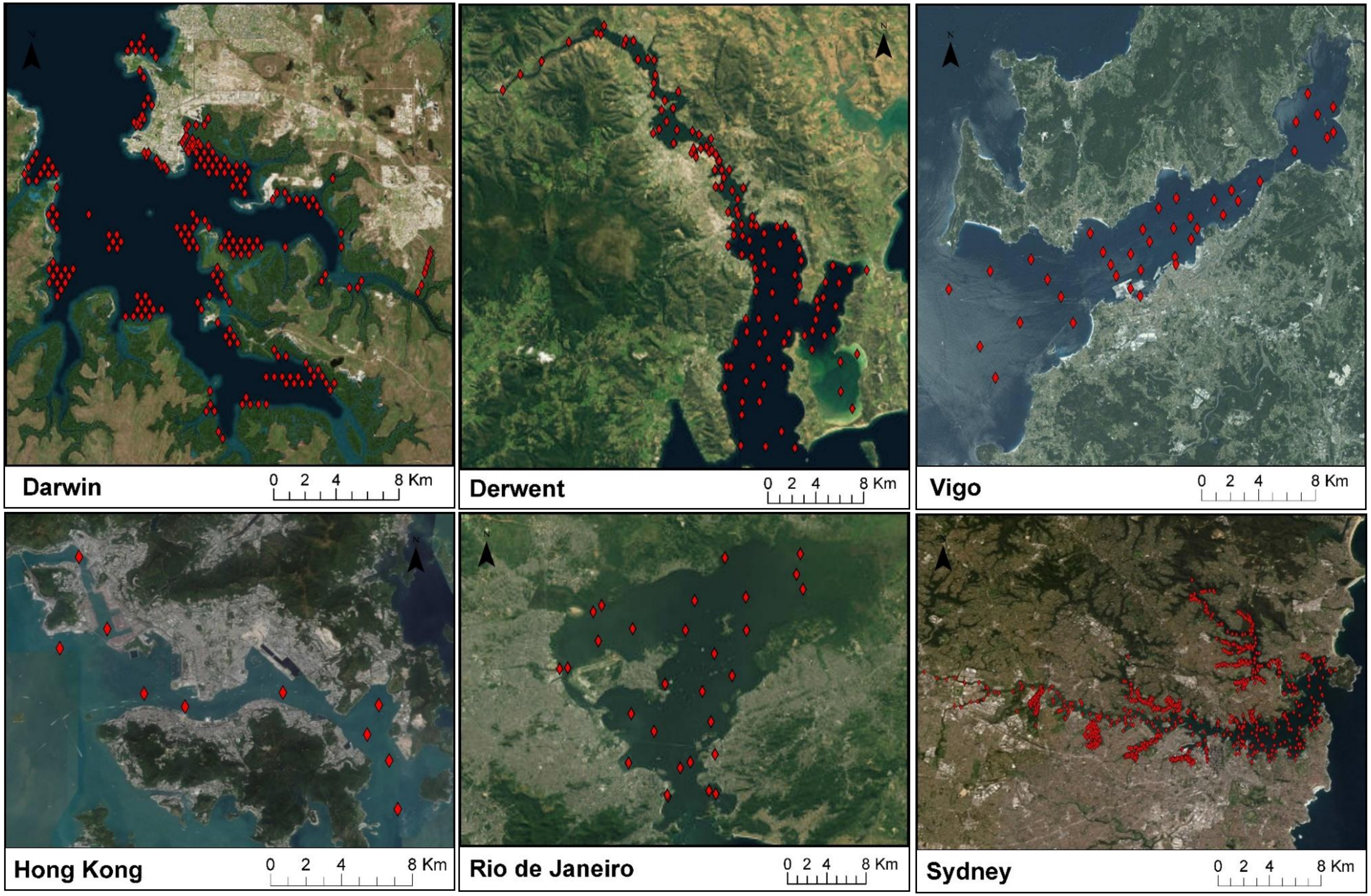

Darwin
0 2 4 8 Km
Derwent
0 2 4 8 Km
Vigo
0 2 4 8 Km
Hong Kong
0 2 4 8 Km
Rio de Janeiro
0 2 4 8 Km
Sydney
0 2 4 8 Km

Figure 2.

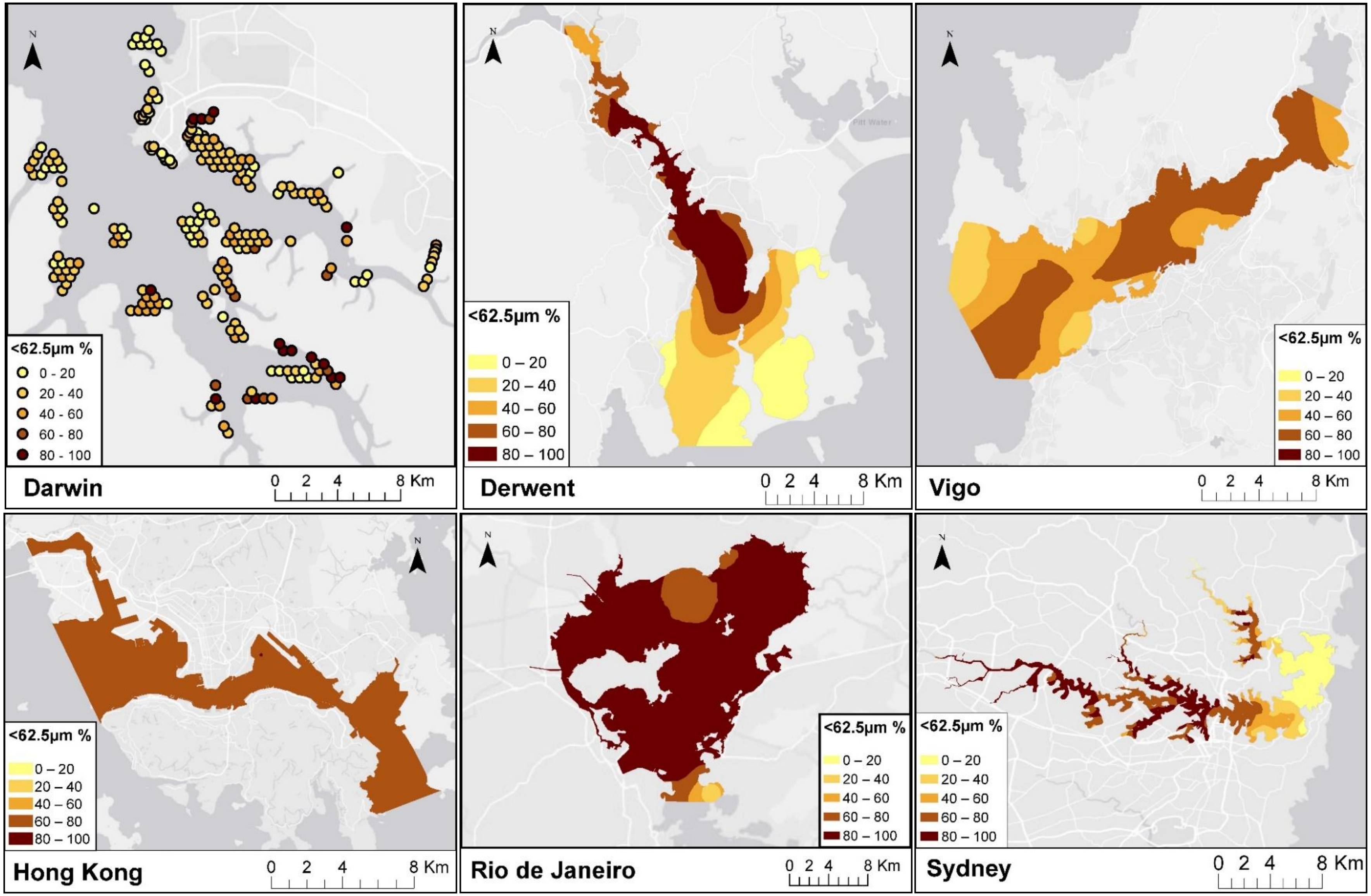
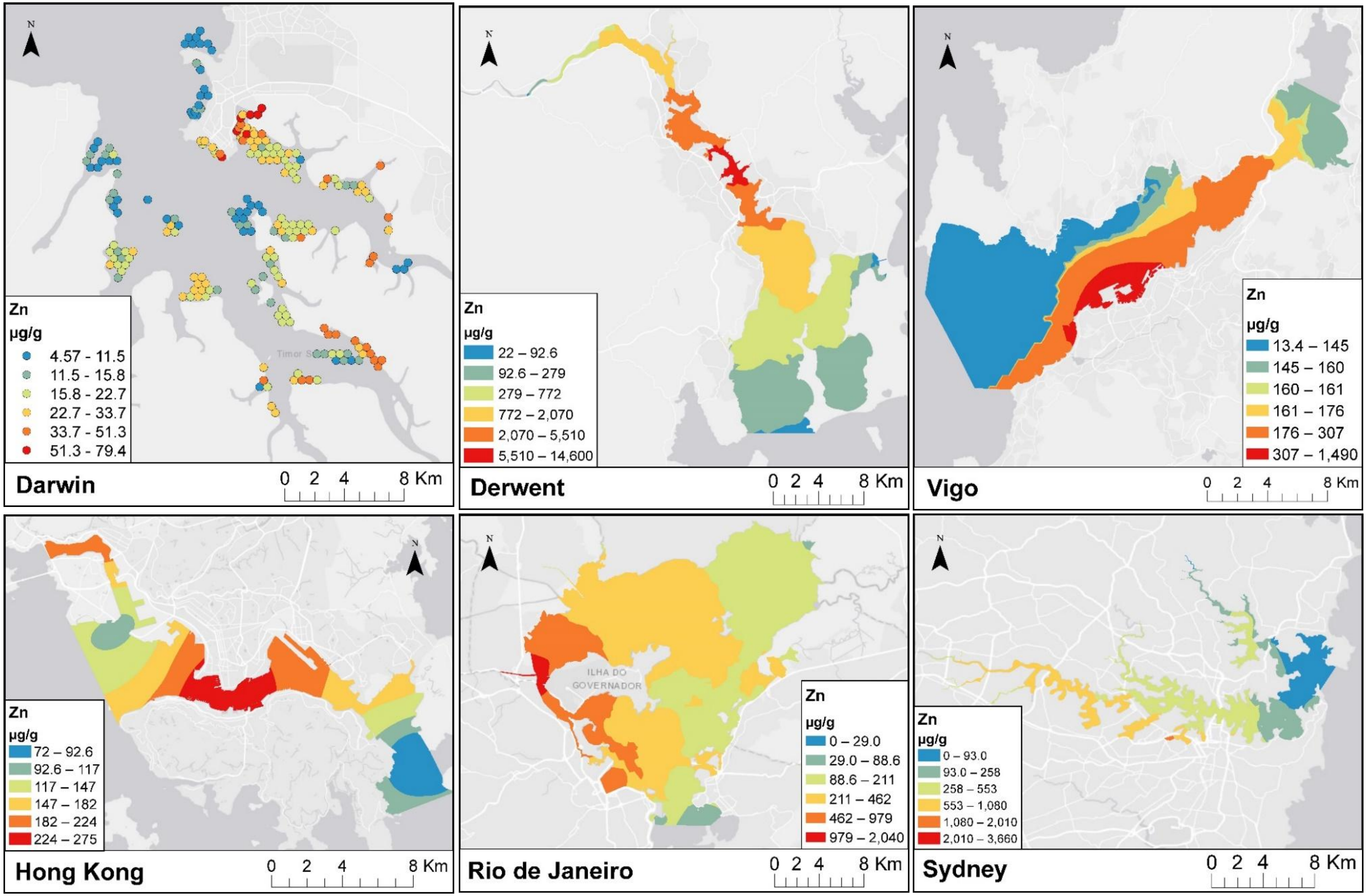

Darwin
Derwent
Vigo
Hong Kong
Rio de Janeiro
Sydney
<62.5µm %
0 - 20
20 - 40
40 - 60
60 - 80
80 - 100
0 2 4 8 Km

Figure 3.



Zn
µg/g
4.57 - 11.5
11.5 - 15.8
15.8 - 22.7
22.7 - 33.7
33.7 - 51.3
51.3 - 79.4
Darwin
0 2 4 8 Km
Zn
µg/g
22 – 92.6
92.6 – 279
279 – 772
772 – 2,070
2,070 – 5,510
5,510 – 14,600
Derwent
0 2 4 8 Km
Zn
µg/g
13.4 – 145
145 – 160
160 – 161
161 – 176
176 – 307
307 – 1,490
Vigo
0 2 4 8 Km
Zn
µg/g
72 – 92.6
92.6 – 117
117 – 147
147 – 182
182 – 224
224 – 275
Hong Kong
0 2 4 8 Km
ILHA DO
GOVERNADOR
Zn
µg/g
0 – 29.0
29.0 – 88.6
88.6 – 211
211 – 462
462 – 979
979 – 2,040
Rio de Janeiro
0 2 4 8 Km
Zn
µg/g
0 – 93.0
93.0 – 258
258 – 553
553 – 1,080
1,080 – 2,010
2,010 – 3,660
Sydney
0 2 4 8 Km

Figure 4.

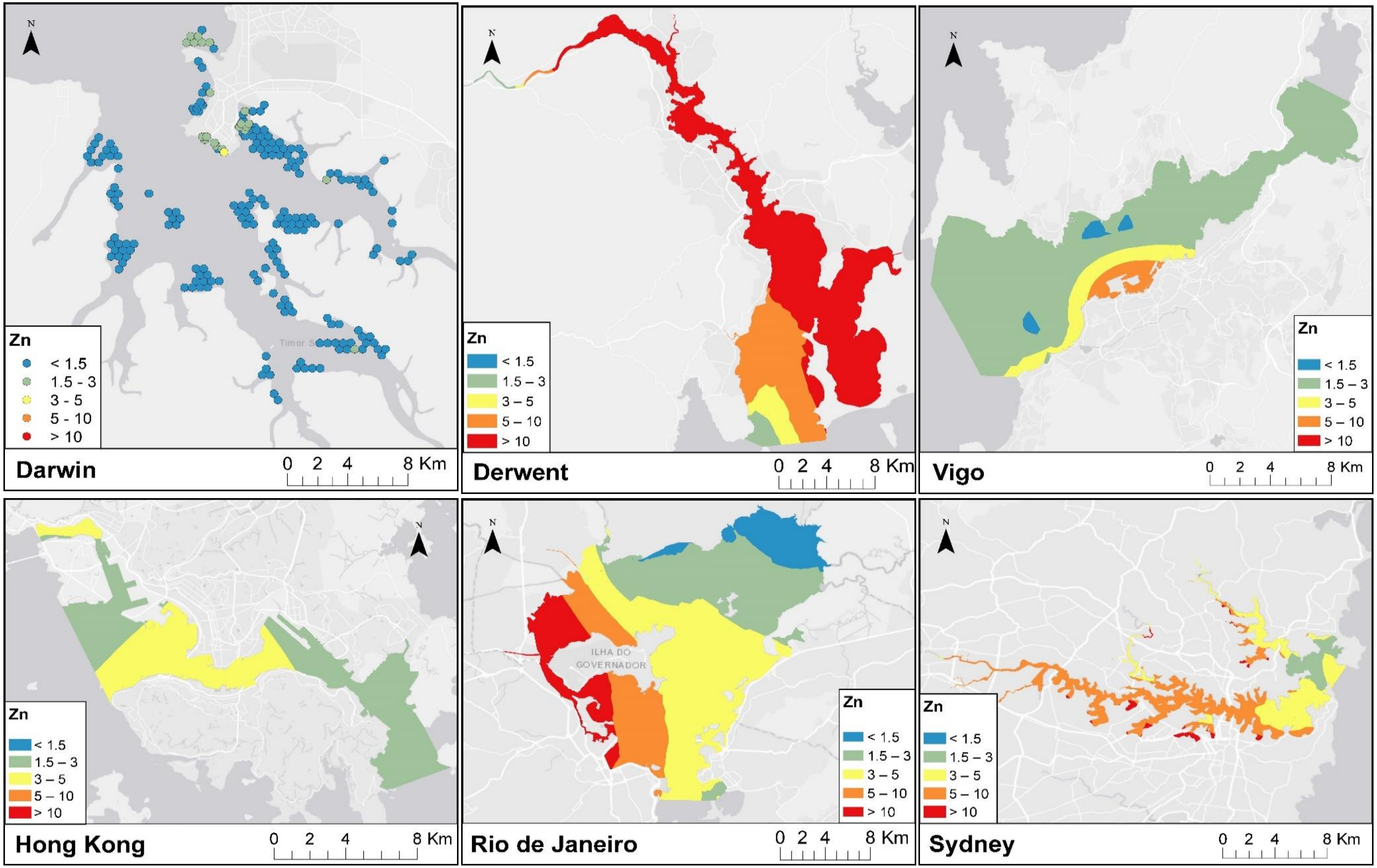

Zn
< 1.5
1.5 - 3
3 - 5
5 - 10
> 10
Darwin
0 2 4 8 Km
Zn
< 1.5
1.5 – 3
3 – 5
5 – 10
> 10
Derwent
0 2 4 8 Km
Zn
< 1.5
1.5 – 3
3 – 5
5 – 10
> 10
Vigo
0 2 4 8 Km
Zn
< 1.5
1.5 – 3
3 – 5
5 – 10
> 10
Hong Kong
0 2 4 8 Km
ILHA DO GOVERNADOR
Zn
< 1.5
1.5 – 3
3 – 5
5 – 10
> 10
Rio de Janeiro
0 2 4 8 Km
Zn
< 1.5
1.5 – 3
3 – 5
5 – 10
> 10
Sydney
0 2 4 8 Km

Figure 5.

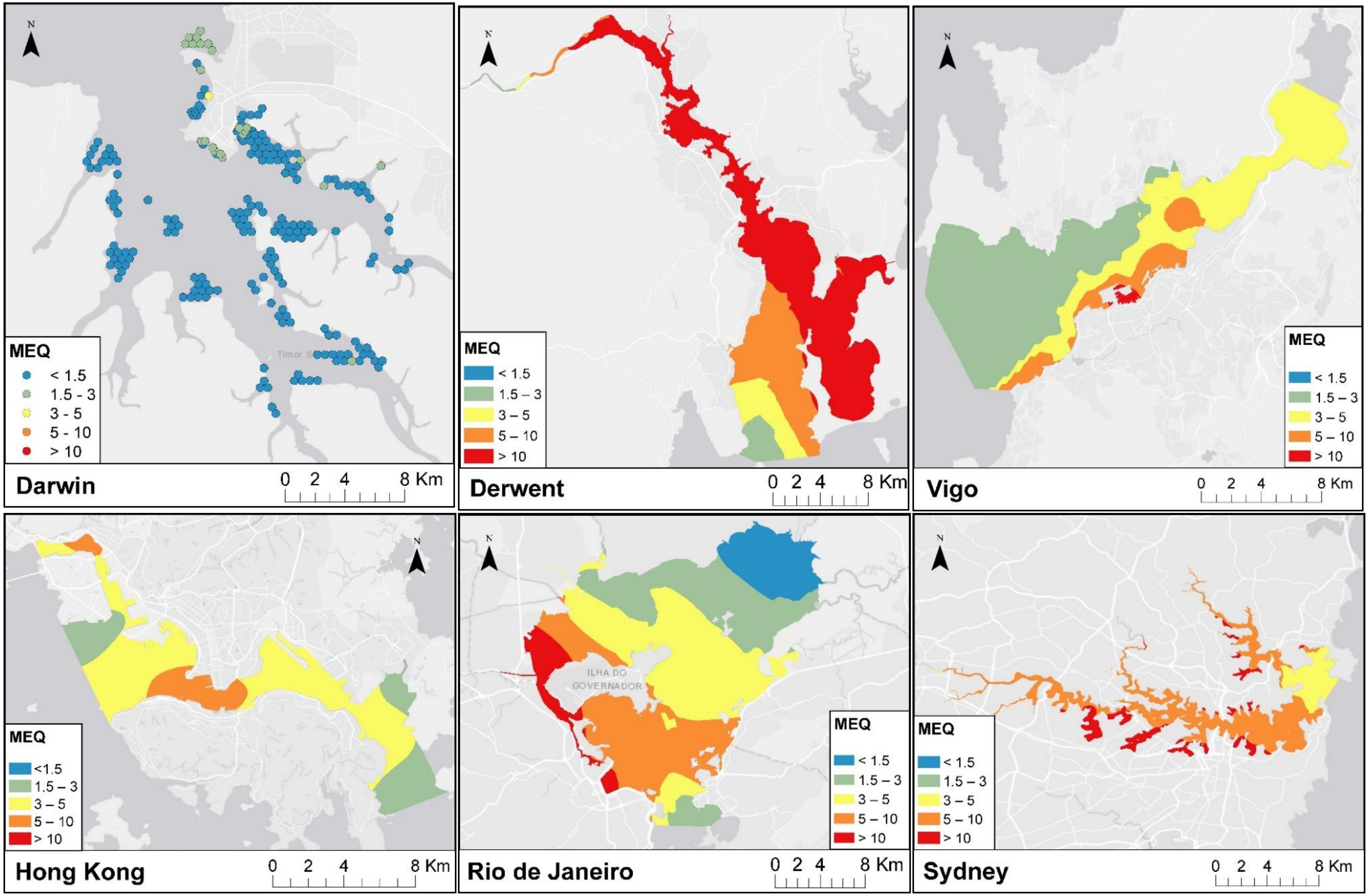
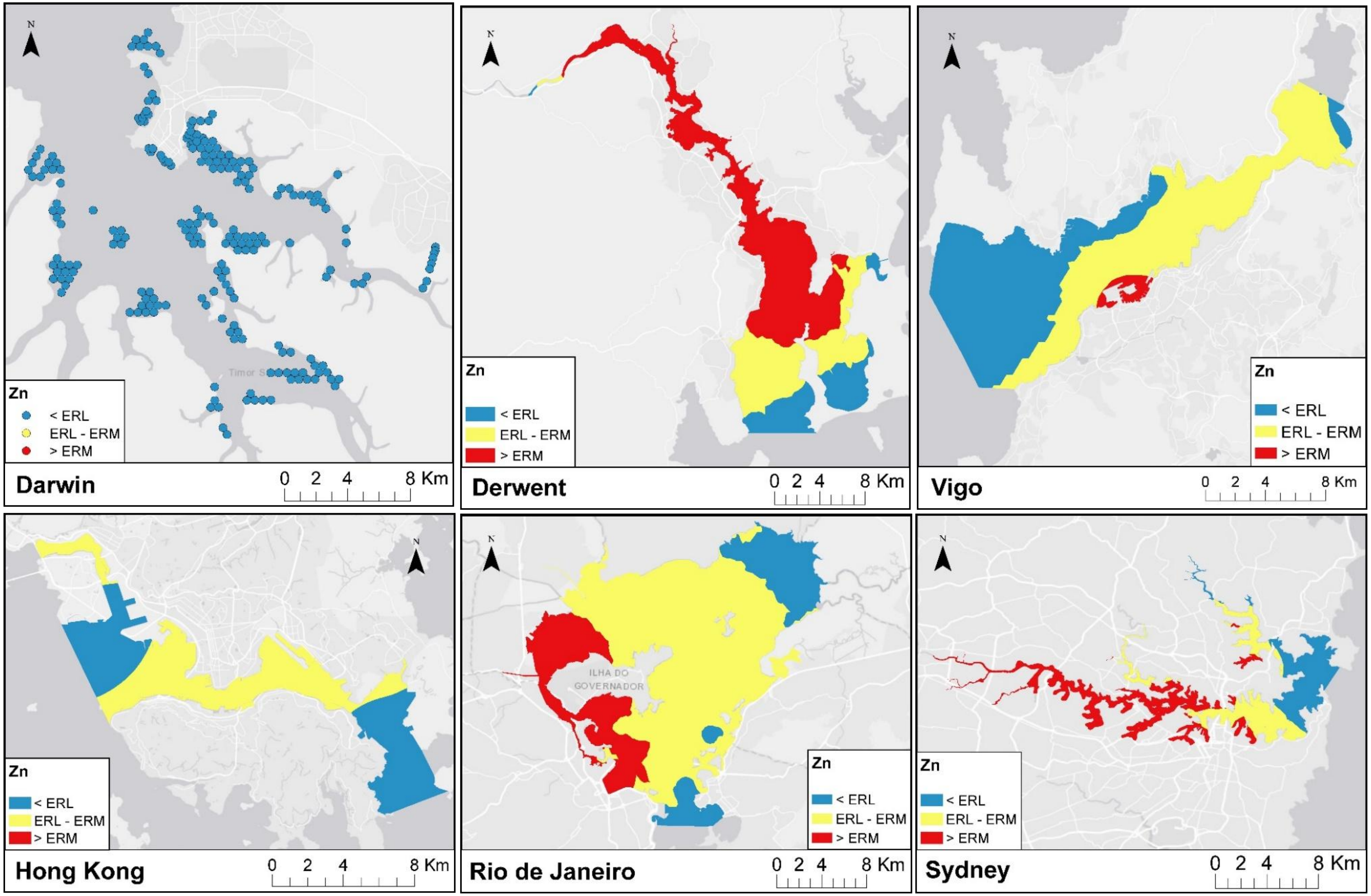
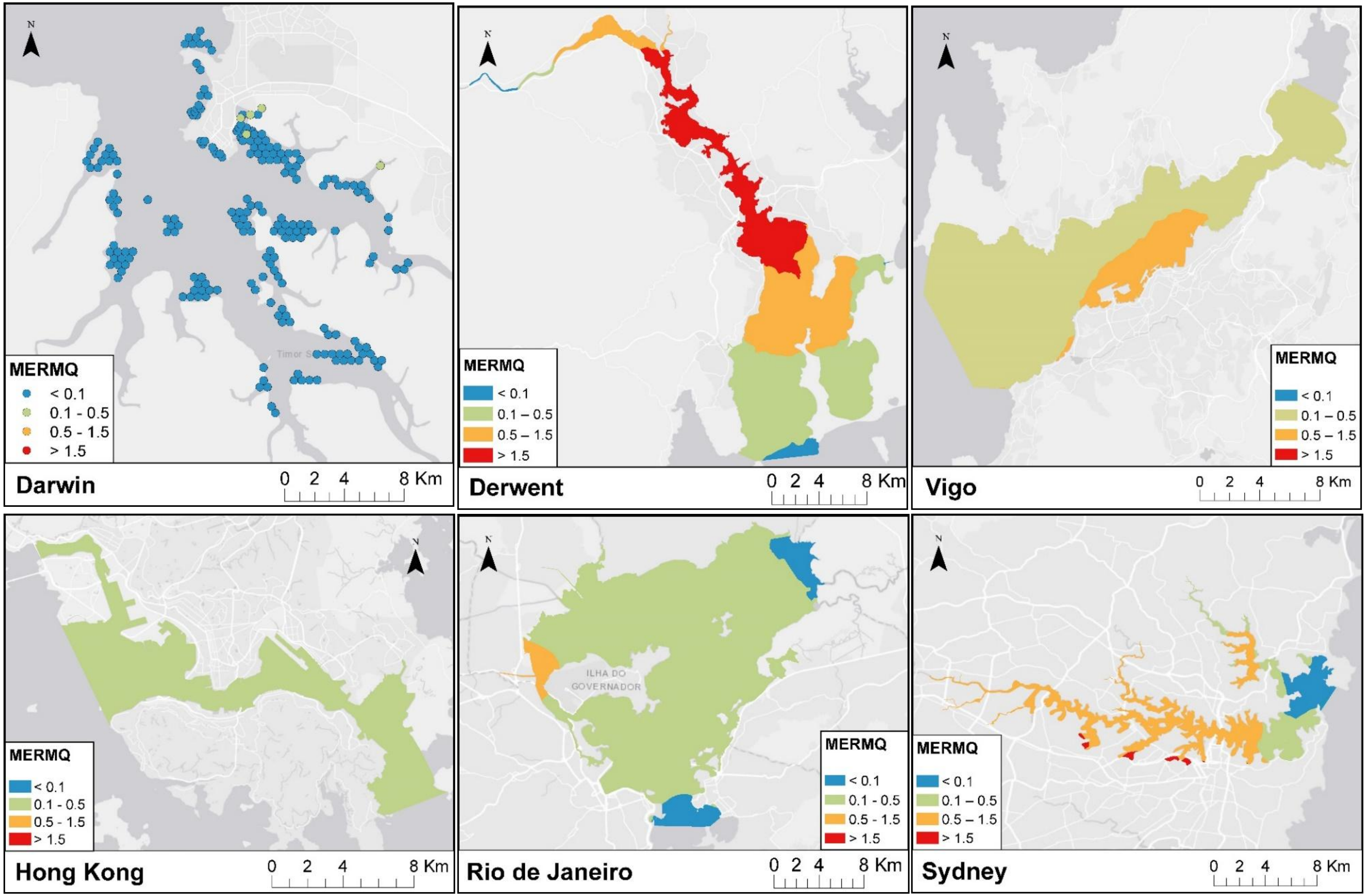

MEQ
< 1.5
1.5 - 3
3 - 5
5 - 10
> 10
Darwin
0 2 4 8 Km
Derwent
Vigo
Hong Kong
Rio de Janeiro
ILHA DO GOVERNADOR
Sydney

Figure 6.



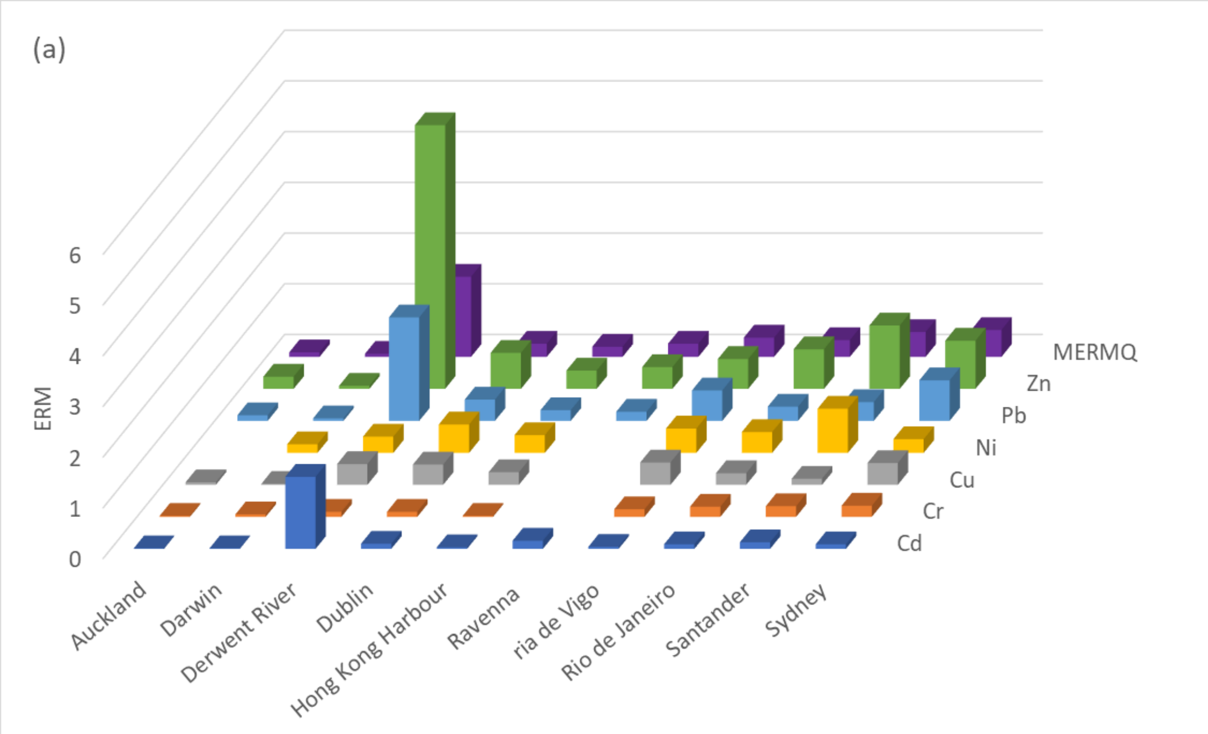
Darwin
Zn
< ERL
ERL - ERM
> ERM
0 2 4 8 Km
Derwent
Zn
< ERL
ERL - ERM
> ERM
0 2 4 8 Km
Vigo
Zn
< ERL
ERL - ERM
> ERM
0 2 4 8 Km
Hong Kong
Zn
< ERL
ERL - ERM
> ERM
0 2 4 8 Km
Rio de Janeiro
ILHA DO GOVERNADOR
Zn
< ERL
ERL - ERM
> ERM
0 2 4 8 Km
Sydney
Zn
< ERL
ERL - ERM
> ERM
0 2 4 8 Km

Figure 7.



MERMQ
< 0.1
0.1 - 0.5
0.5 - 1.5
> 1.5
Darwin
0 2 4 8 Km
MERMQ
< 0.1
0.1 – 0.5
0.5 – 1.5
> 1.5
Derwent
0 2 4 8 Km
MERMQ
< 0.1
0.1 – 0.5
0.5 – 1.5
> 1.5
Vigo
0 2 4 8 Km
MERMQ
< 0.1
0.1 - 0.5
0.5 - 1.5
> 1.5
Hong Kong
0 2 4 8 Km
ILHA DO
GOVERNADOR
MERMQ
< 0.1
0.1 - 0.5
0.5 - 1.5
> 1.5
Rio de Janeiro
0 2 4 8 Km
MERMQ
< 0.1
0.1 – 0.5
0.5 – 1.5
> 1.5
Sydney
0 2 4 8 Km

Figure 8.


(a)
ERM
0
1
2
3
4
5
6
Auckland
Darwin
Derwent River
Dublin
Hong Kong Harbour
Ravenna
ria de Vigo
Rio de Janeiro
Santander
Sydney
MERMQ
Zn
Pb
Ni
Cu
Cr
Cd

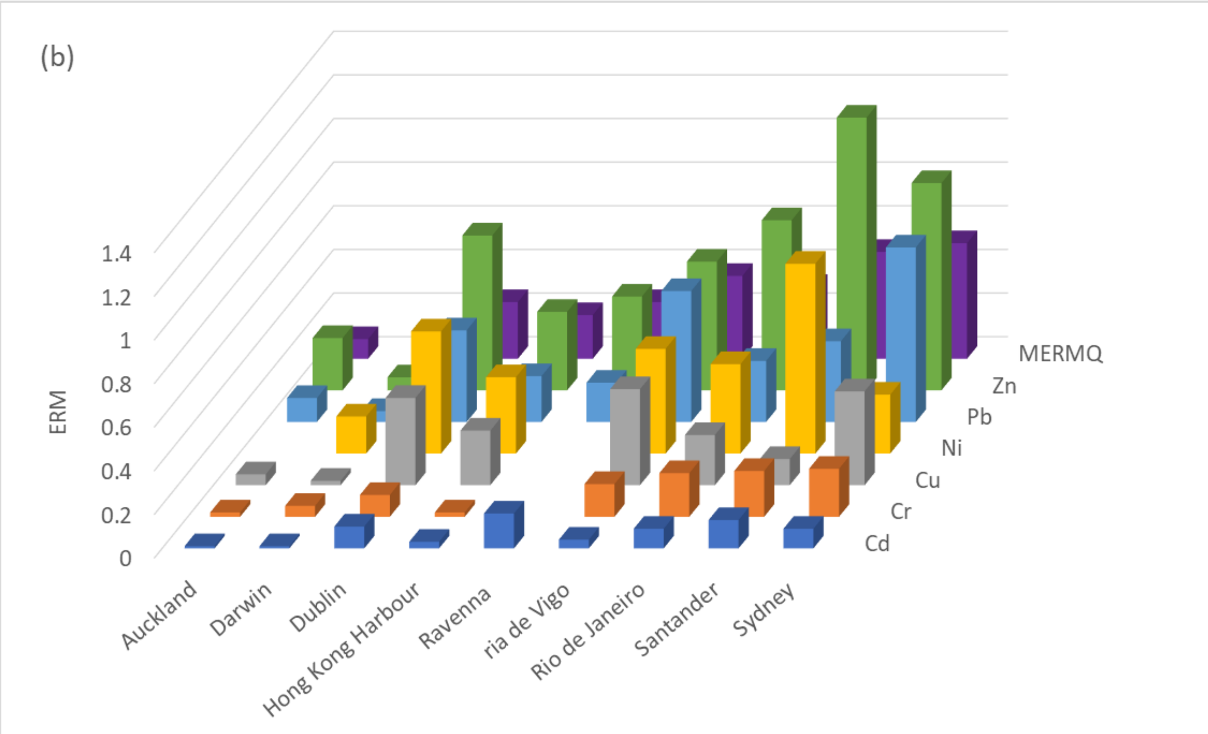

(b)
ERM
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Auckland
Darwin
Dublin
Hong Kong Harbour
Ravenna
ria de Vigo
Rio de Janeiro
Santander
Sydney
MERMQ
Zn
Pb
Ni
Cu
Cr
Cd

Figure 9.

Credit Author Statement

G F Birch wrote most of the paper and undertook most of the computations

J-H Lee drafted the maps and diagrams and undertook some of the computations. He also read many versions of the early drafts

E Tanner managed the project, provided advise on the locations and co-authors and read many drafts of early versions of the paper

The remaining co-authors provided data on the harbours and read drafts of early versions of the paper