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

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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.

1 Sediment metal enrichment and ecological risk assessment of ten ports and estuaries in the
2 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

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74 1. INTRODUCTION

75 Substantial anthropogenic stress on coastal marine environments has reduced sediment and
76 water quality in many global harbours and estuaries resulting in threatened benthic and pelagic
77 populations (Costanza et al., 1997; Chapman and Wang, 2001; Costanza et al., 2014). It is
78 important that the extent of contamination of an estuarine environment is assessed as accurately
79 as possible and that the level of threat to the health of these sensitive environments is determined
80 with care. Choosing an appropriate methodology to assess environmental condition is complex
81 and requires an integrated strategy (Rees et al., 2008). Ecosystem indicators used to assess
82 anthropogenic stress are commonly compromised by natural spatial and temporal variability.
83 This confounding of natural and anthropogenic-induced stress results in inappropriate and often
84 erroneous assessment (Hogg and Norris, 1991). Increasingly, sediments are being used to assess
85 the status of aquatic environments due to the advantage sediments have in faithfully recording
86 and time integrating environmental events, both temporally and spatially (Rodrigues et al., 2006;
87 Birch et al., 2008). Moreover, sediments greatly influence the quality of overlying and interstitial
88 water and are an extensive habitat to a large number of faunal and floral species (Simpson et al.,
89 2015).

90 The condition of estuarine environments may be described using a wide range of approaches, e.
91 g. ecological risk indicators (Singh et al., 2005), concentration factors/indicators (Guo et al.,
92 2010) and enrichment factors/indicators (Caeiro et al., 2005). However, from a management
93 perspective, it is important to know by how much the system has deviated from the pristine
94 condition, i. e. the magnitude of anthropogenic change, and the degree of risk of potential harm
95 posed by sedimentary contaminants to biological communities (Birch, 2016). These two types of
96 information differ fundamentally and are based on different types of data. A full and
97 comprehensive assessment of sediment health is complex and requires a raft of chemical,
98 sedimentological and ecological approaches (Ponti et al., 2009; Birch, 2016; Birch, 2018),
99 however information on the degree of anthropogenic change and level of ecological risk posed
100 by sedimentary chemicals provides a useful initial screening assessment of environmental quality
101 in marine environments.

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

107

108 1.1 The WHP Concept

109 The WHP was initiated by the Sydney Institute of Marine Science (SIMS) and aims to develop
110 resilient urban harbours through a global network of collaborating researchers (Steinberg et al.,

111 2016). The project brings together international research institutions and agencies concerned
112 with the health of these heavily urbanised waterways and the increasing challenges these
113 environments face. Like Sydney, many of the great cities of the world, such as Auckland, Rio
114 de Janeiro and Hong Kong, are located on the coast. These working harbours are part of the
115 fundamental fabric of those communities and the relationship between the residential, industrial
116 and marine environments require ongoing study and management. The WHP tackles issues
117 surrounding the multiple uses of harbours through global collaborative projects and targeted
118 workshops. The Project works to facilitate and link programs across major international
119 harbours, with a proactive focus on investigating and restoring ecosystem functioning and the
120 consequent development of management best-practices that can be applied by all partner cities

121 1.2 Harbours of the WHP

122 The morphodynamic characteristics of estuaries influence benthic contaminant distributions and
123 concentrations through tidal patterns, flushing and structural control (Roy et al., 2001; Birch et
124 al., 2016). Numerous classification schemes have been developed in an attempt to combine
125 diverse physical, biological and ecological characteristics of coastal waterways (Dalrymple et al.,
126 1992; Edgar et al., 2000; Roy et al., 2001). The ten harbour estuaries assessed in the current work
127 (Fig. 1) have been loosely separated into five morphodynamic groups, namely (1) funnel-shaped,
128 wave-dominated, drowned-valley estuaries: Derwent River (Tasmania, Australia), Sydney
129 estuary (New South Wales, Australia), Ría de Vigo (Spain) and Auckland Harbour (Waitemata
130 Bay, New Zealand); (2) tide-dominated, drowned-valley estuaries: Darwin Harbour (Australia)
131 and Santander Harbour (Spain); (3) open ocean embayments: Hong Kong; (4) partially enclosed
132 embayments: Rio de Janeiro, Guanabara Bay, (Brazil); and (5) river mouths/canals: Dublin
133 Harbour (Ireland) and Ravenna Harbour (Italy).

134 Auckland Harbour, Waitemata Bay, New Zealand

135 The Waitemata Harbour (80 km²) is the largest east coast estuary in the Auckland region and is
136 comprised of tidal creeks, embayments and a central basin (Aguirre et al., 2016). Sediment
137 studies have been mainly confined to urban and rural tidal creeks, local harbours and
138 embayments, which receive the major contaminant loads, leaving the central basin largely un-
139 surveyed. These peripheral environments are predominantly muddy and fringed by mangrove
140 mudflats. The catchment (185 km²) comprises mainly urban (21%), rural (25%), forest (21%)
141 and minor industrial landuses. Urbanised catchments have been identified as major sources of
142 fine sediment and metals to the harbour (Aherns, 2008; Mills et al., 2012; Mills and Williamson,
143 2014). Henderson Creek, which drains the largest urban subcatchment, as well as a substantial
144 area of rural land, contributes the largest loads of sediment and metals to Central Waitemata
145 Harbour. Present-day surface sediments show spatially-variable concentrations of metals with
146 maximum concentrations occurring on intertidal flats near tidal creek outlets and stormwater
147 drains in the south western embayment of Central Waitemata Harbour and upper Shoal Bay.
148 Marked increases of metal discharge was initiated around 1950 coinciding with the beginning of

149 rapid urbanisation and reached a maximum more than 20 years ago, while declining slightly to
150 the present time.

Darwin Harbour, Northern Territory, Australia

151 Darwin Harbour (~1220 km²) is approximately 35 km long and 5 km wide at the mouth. The
152 waterway is macro-tidal (range up to 8m) and comprises extensive mudflats (containing
153 substantial calcium carbonate from shell material) fringed by large stands of mangroves
154 separated by deep tidal channels. Parts of the Harbour are relatively poorly flushed, especially in
155 the dry season when the residence time in the upper arms is ~20 days. Most (85%) of the
156 catchment (~2010 km²) is open space, while urban and light industry occupy 7% (no heavy
157 industry), horticulture makes up about 1-2 % of the area and rural/residential comprises 6 %.
158 Although sedimentary metal concentrations are generally low, moderate environmental concern
159 is for elevated metals along the developed eastern side of Darwin Harbour and in the vicinity of
160 the sewage treatment plant outfall north of the city (Munksgaard et al., 2012; 2013; 2015; 2018).
161 Metal loads have declined as a consequence of treatment system improvements, however
162 emerging sources of metals are from removal of marine sediments associated with coastal
163 development and dredging activities.

164 Derwent River, Tasmania, Australia

165 The Derwent River is approximately 45 km long, occupies 200 km² and is relatively deep (av. 25
166 m) (Whitehead et al., 2010), The waterbody is stratified in the narrow upper reaches and well
167 mixed in the lower, broad seaward area. The tidal range is 1 m and average flushing time is 12
168 days. The catchment (8,900 km²) is mainly agriculture and forest (76%) and urban/industry (8%)
169 and supports 40% of the state population. The main environmental issues are metal
170 contamination of water and sediment from a zinc smelter and nutrients from a paper mill and
171 waste water treatment plants. Nutrient loads have declined, but Zn, mainly from groundwater,
172 remains elevated.

173 Dublin Harbour, Ireland

174 Dublin Bay hosts Dublin, the capital city of Ireland (population >1m) (Brooks et al., 2016) and
175 Dublin Port, busiest shipping port in Ireland, which accounts for half of the nation's annual
176 imports and exports (DPC, 2014). Dublin Port (3.267 km²) has developed on both sides of the
177 Liffey channel, but most of the shipping docks are on the northern side, while the southern port
178 encompasses major infrastructure. Technical development and regulation backed by
179 environmental monitoring has considerably reduced most adverse effects of deliberate
180 contamination. Despite such controls, input of contaminants to the port from discharge of sewage
181 and industrial waste, spillage of cargo, or ship lubricants, stormwater runoff and warm water
182 from power stations still occurs. Riverine inputs (mainly from the Liffey River), which drain the
183 highly urbanized and rural areas around Dublin city, are a major source of contaminants into
184 Dublin Bay (EPA, 2006; 2015; Brooks et al., 2016; Murphy et al., 2016; Cunningham, 2018).

185 Resuspension of contaminated sediments may occur due to strong tidal forces, storm surges, or
186 increased water movement from boats (Davoren et al., 2005; Macken et al., 2008; Bedri et al.,
187 2011; Briciu-Burghina et al., 2014).

188 Hong Kong Harbours

189 Hong Kong is situated in the Pearl River Estuary (PRE), and covers about 8000 km² (Chen et al.,
190 2013). The estuary (1649 km²) is up to 30 m deep (av. <15 m) and is microtidal with a <2 m
191 average tidal range (Mao et al., 2004). Bottom sediment is mainly mud with subordinate sand
192 and gravel (Tanner et al., 1993). Sedimentary metals are significantly higher in harbours, e. g.
193 Tolo Harbour and Victoria Harbour, than in offshore areas (Chan et al., 2016; Blackmore, 1998;
194 Zhou et al., 2007a, b; Tang et al., 2008; Chen and Jiao, 2010; Liu et al., 2015; Chen et al., 2013).
195 The territory (1108 km²) supports >7.4 million people and comprises Hong Kong Island, Lantau
196 Island, Kowloon Peninsula, the New Territories and 261 islands with a complex and long
197 coastline (1200 km) (EPD, 2017; SMO, 2018). Hong Kong is a highly urbanized (81 %), coastal
198 city receiving substantial metal loads from industrial and municipal waste waters, especially
199 during the 1950s-1980s (Morton, 1989). Metal contamination of marine sediment is mainly
200 attributed to: (1) historical discharge of untreated industrial wastewater and partially treated
201 sewage (e. g., Victoria Harbour and Tolo Harbor); (2) surface runoff from Pearl River and local
202 rivers (e. g. Deep Bay), and (3) other sources, including infiltration from septic tanks and
203 leachate of antifouling compounds from shipping (Chen and Jiao, 2010; Liu et al., 2015).
204 Improved conditions since the late 1980s are due to industry moving to the New Territories,
205 Southern China and other areas of Asia (Morton, 1996; Blackmore, 1998) and improved
206 treatment of domestic sewage (Lai et al., 2016). However, metal contamination persists due to
207 release from legacy contaminated sediments.

208 Ravenna Harbour, Italy

209 Ravenna is the largest harbour (3.62 km²) in the western Adriatic and is one of the most
210 extensive commercial seaports in Italy. The harbour was established in lagoonal systems
211 surrounding the city and is structured as a major 'canal' port extending for 11 km from the centre
212 of Ravenna to the tourist seacoast. The canal is directly connected to surrounding lagoons
213 (Pialassa Baiona and Pialassa Piomboni), which are included in the southern part of the Po River
214 Delta Park, inscribed in the World Heritage List. Construction of two large converging jetties
215 (2400 m long each) to protect the harbour from siltation has altered sediment transport and has
216 re-shaped nearby tourist beaches. Environmental concerns include degradation of natural
217 habitats, contamination of sediments and management of highly urbanised areas (Airoldi et al.,
218 2016). Ravenna Harbour and coastal lagoons receive civil and industrial wastewater carrying
219 nutrients, pollutants and cooling water from two power stations and industrial plants. Although
220 discharges now comply with current laws, lax legal constraints between 1958 and 1976 resulted
221 in sediment of Pialassa Baiona being heavily impacted by industrial metals, including Hg (Fabbri
222 et al., 1998; 2000; 2001; McRae et al., 2000; Guerra, 2012; Guerra et al., 2014). However,

223 sediment resuspension due to frequent maintenance dredging and to deepen the port have had
224 minimal effects on macrobenthic assemblages inhabiting the lagoons (Guerra et al., 2007; 2009;
225 Ponti et al., 2009; 2011).

226 Ría de Vigo, Spain

227 Ría de Vigo (156 km²) is the most populated (411,363 inhabitants) and developed
228 (approximately 7% industrial, 12% construction) ria in Galicia and is home to Vigo city
229 (population 292,986) (Galician Institute of Statistics, 2017; <http://www.ige.eu>). The ria is
230 approximately 30 km long and 12 km wide at the mouth. The waterway is relatively deep (av. 16
231 m, max. 45 m) and the water column is well mixed with a tidal range of 4 m and an average
232 flushing time of 3-4 days (Barton et al., 2015). Sediments are predominantly organic-rich and
233 fine grained. The catchment (578.2 km²) is heavily urbanised and industrialised (>21%)
234 (Fernández et al., 2016) and activities include shipbuilding, canning, automobile and steel
235 manufacturing. Metal pollution is restricted to the inner estuary as a result of urban and industrial
236 discharges and to intense activity of the Port of Vigo with chronic Pb pollution due to discharge
237 from a ceramic factory located at the head of the estuary (Rubio et al., 2000; Prego and Cobelo-
238 García, 2003; Alvarez Iglesias et al., 2006; 2007; Quelle et al., 2011). Other sources are natural,
239 related to catchment and upwelling processes (Quelle et al., 2011). Mariculture rafts in the
240 northern estuary have influenced the distribution of metals by increasing the carbon content and
241 decreasing grain size producing metal sinks. Tidal currents act to redistribute metals from
242 accumulation zones.

243 Rio de Janeiro, Guanabara Bay, Brazil

244 Guanabara Bay (449 km²) is located in the southeastern Brazil Marine Ecoregion in the most
245 economically developed region of the country. The bay comprises a large, shallow (av. 5.1 m)
246 inner semi-circular water body with a maximum length of 48.2 km and a narrow inlet with a
247 main central channel depth of 58 m. Mean spring tidal range is 1.05 m. The catchment is the
248 largest of this ecoregion (~3700 km²) (Kjerfve et al., 1997; Kjerfve et al., 2001) and supports
249 Rio de Janeiro, the second largest Brazilian city (6.5 million people). The drainage basin of the
250 Guanabara Bay (4180 km²) is drained by approximately 45 rivers (JICA, 1994) and the main
251 rivers are the Macacu, Iguaçu, Estrela and Sarapuí. The Guanabara Bay catchment includes,
252 partially or totally, 12 municipalities with a population of almost 10 million inhabitants,
253 equivalent to 80% of the population of the State of Rio de Janeiro. As a consequence of urban,
254 agricultural, and industrial development, the bay is one of the most altered and polluted in the
255 country (Carreira et al., 2002; Xavier de Brito et al., 2002; Silva et al., 2013; Camargo et al.,
256 2017, Cordeiro et al., 2015; Baptista Neto et al., 2017). Anthropogenic metal sources to the bay
257 include direct discharges of untreated and treated industrial waste, domestic sewage, inputs from
258 rivers, atmospheric fallout, dockyards and agricultural activities, landfill and road runoff
259 (Rebello et al., 1986; Abuchacra et al., 2015; Aguiar et al., 2018). Metal loads to the bay have
260 increased substantially over the last 70 years caused by population growth in the metropolitan
261 region (from ~2.5 to 12 million) accompanied by extensive urbanization, deforestation and

262 industrial and agricultural growth (Moraes, 2012; Covelli et al., 2012; Figueiredo Jr. et al.,
263 2014). Higher concentrations of metals located in the inner bay from river discharge and in
264 sediments adjacent to harbours (Baptista Neto et al., 2006; Cordeiro et al., 2015; Aguiar et al.,
265 2018) exhibit significant ecotoxicological effects on aquatic organisms (Moraes et al., 2000;
266 Maranhão et al., 2009; 2010; Campos et al., 2019).

267 Santander Bay, Spain

268 Santander Bay (22.5 km²) is one of the most important and largest estuaries in northern Spain
269 (Biscay Gulf) and includes a Special Protection Area (SPA) (Gómez et al., 2014). The bay is a
270 natural harbour and hosts a major commercial port. The bay is characterized by a semidiurnal
271 tidal regime with a medium tidal range of 2.9 m and interacts with freshwater discharges from
272 the Cubas River (Puente et al., 2002). The estuary is dominated by extensive, shallow water
273 (max. depths 10–12 m) intertidal areas (67%), which have been greatly modified by urban
274 development and port activity (Ondiviela et al., 2013). Anthropogenic activities began in Roman
275 times (Vigurí et al., 2007) reaching a maximum impact during the 1970s (Vigurí et al., 2007).
276 Since marsh reclamation in 1903, the inner bay has undergone intensive industrial expansion of
277 mainly metallurgical and chemical industries. During the last 150 years between 37% and 50%
278 of the original intertidal zone has been reclaimed (Vigurí et al., 2007; Remoundou et al., 2015;
279 Calleja et al., 2017) and used as grasslands, to expand the Port, and to create new industrial and
280 residential areas, including the city of Santander. Continuous, untreated industrial discharges
281 ceased in 2001 when a new sewer system came into operation (López et al., 2013; Echávarri et
282 al., 2007) and all direct discharges to the bay were eliminated in 2010 when a new wastewater
283 treatment plant was commissioned. Industrial contaminant sources are mainly located in the
284 inner bay and on the western shore, where the port is located. Maximum metal concentrations
285 occur in the subtidal and inner estuary related to industrial sources and are minimal in the
286 intertidal flats (Puente et al., 2002).

287 Sydney estuary, New South Wales (NSW), Australia

288 Sydney estuary is approximately 30 km long and up to 3 km wide with an area of 50 km², while
289 the catchment (500 km²) is highly industrialized and urbanized (76%) (Birch et al., 2015; 2016;
290 Birch, 2016) and supports the City of Sydney (population 5.5m). Estuarine water is generally
291 well-mixed marine, but becomes stratified after prolonged heavy rain (Lee et al., 2011; Birch and
292 McCready, 2009). Typical flushing times are 5 to 10 days, however in the upper reaches of the
293 waterway it may be up to 130 days. Sediments in the estuary are mainly muddy in the upper
294 reaches and sandy in the mid- and lower estuary. Sediments are significantly contaminated by
295 metals and organic compounds (Birch et al., 2000a; 2008; 2013; McCready et al., 2004; 2006;
296 Birch, 2017) and the waterway is classified as “severely modified” (NLWRA, 2002; Birch and
297 Taylor, 2000a). Until recently, the harbour was a busy commercial and naval port and the
298 shoreline was lined by factories, however, industries have moved away from Sydney and the area
299 has converted into a mainly tourist and recreational hub (Birch and Taylor, 2000b, c).

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2. METHODS AND MATERIALS

2.1 Analytical Methods

Auckland Harbour

Total recoverable metals were determined on the <500 µm fraction by hot acid digestion (HNO₃/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 HNO₃/HClO₄ (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°C, crushed and sieved at 2mm. Samples were digested in HNO₃ 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 (HNO₃) (ISO, 1995) and analysed by ICP-MS (USEPA, 1994).

Ravenna Harbour

Samples were digested in closed Teflon vessels by a mixture of HNO₃ + 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).

332 TABLE 1

333

334 Ría de Vigo

335 Total sediment was digested with a strong acid mix of HNO₃/HCl/HF in Teflon digestion bombs
336 using a microwave oven and analysed by spectrophotometer. Quality assurance systems using
337 Certified Reference Materials (BCSS-1 and BEST-1, National Research Council of Canada).

338 Rio de Janeiro

339 Sediments were digested using a microwave-assisted procedure with concentrated HNO₃
340 solution (USEPA, 2007a) and analysed by ICP-OES. Analytical quality control was assessed by
341 analysing a certified reference material (NIST 2782 Industrial Mud).

342 Santander Harbour

343 Sediment samples were collected with a Van Veen grab and grain size was determined by dry
344 sieving. Metals analysis was for the <63 µm fraction and followed the U.S. Standard method
345 (US EPA 6020, 2007b) using a HNO₃/HCl/HF mix and analysed by ICP-MS and a Certified
346 Reference Material (Loamy Clay, CRM 052, Resource Technology Corporation, US).

347

348 Sydney estuary

349 The fine (<63 µm) fraction and total sediment were analysed by aqua regia digestion
350 (HCl/HNO₃) (modified US EPA 200.8 Rev 4.4 method) (US EPA 1994) and analysed by ICP-
351 OES using a reference material (AGAL-10), procedural blanks and blind replicates (Siaka et al.,
352 1998; Birch and Taylor, 2000b).

353

354 2.2 Data availability and sample distribution

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

363

364 TABLE 2

365

366 Duplicate samples from 45 sites for the years 1995 to 2015 (n=2676) were available for the Hong
367 Kong coastal region, however only the most recent vintage (2015/16) of samples (n=9) confined
368 to the harbour areas (63.0 km²) were used for mapping in the present assessment. Several of the
369 canals of Ravenna Harbour have been sampled, but lacked Al, Fe, or size data and only
370 sediments (n=52) of Canale Candiano (3.52 km²) have been assessed. The 39 samples taken in
371 2011 in Ria de Vigo estuary were well distributed and provided a good spatial spread of data
372 throughout the embayment. Although sampling was undertaken for multiple years between 2005
373 and 2015 in Santander Harbour, sites were sparsely distributed and the data for 2015 (n=10)
374 mapped in the present study were located close to the shoreline with an absence of samples in the
375 central harbour (22.5 km²). Approximately decadal sampling has been undertaken in Sydney
376 Harbour between the years 1975 to 2015. The 2000-2015 dataset (n=1175) used in the current
377 assessment was well distributed throughout the estuary and provided an excellent spatial
378 platform for mapping and assessing contaminants.

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

386

387 2.3 Differentiation between ‘anthropogenic enrichment’ and ‘sediment quality’

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

403

404 2.4 Techniques to measure anthropogenic change (enrichment) in the WHP

405 Two complications with the WHP dataset, i. e. that background concentrations for metals were not
406 available for all locations and that size-normalised data were accessible for only three locations
407 (Derwent River, Ria de Vigo and Sydney) and Post-Extraction Normalisation (PEN) was
408 undertaken for Sydney and Darwin. In the PEN technique, the $>63 \mu\text{m}$ fraction is removed by
409 sieving after digestion thereby capturing metals associated with the total sediment, providing an
410 advantage over the usual size-normalisation procedure, which only measures contaminants in the
411 $<63 \mu\text{m}$ fraction (Birch and Taylor, 2000; Birch, 2003). The lack of these data restricted the
412 ability to determine the magnitude of anthropogenic change, i. e. sedimentary metals enrichment.

413 Early researchers used global average upper crust and marine shale metal concentrations as
414 ‘standard reference materials’ (SRMs), (Taylor, 1964; Bowen, 1979; Turekian and Wedepohl
415 1961; Wedepohl, 1995). SRM values are not site, or material, specific and the preferred methods
416 of determining background are identification of a nearby ‘pristine environment’, or the use of
417 sedimentary cores to obtain sediment from below the level of anthropogenic influence.
418 Nevertheless, SRMs are still being used extensively and are entrenched in the literature (Pekey,
419 2006; Karbassi et al., 2008; Kabir et al., 2011).

420 The European Union has been concerned with the problem of establishing background metal
421 values for their community for some time and the OSPAR Coordinated Environmental Monitoring
422 Programme (CEMP) working group on monitoring (MON) have declared that core data will form
423 the basis by which background is determined for the OSPAR region using only fine-grained
424 and/or sieved samples (size normalised) to reduce the confounding of variable grain size and, if
425 possible, samples should be taken from sediment older than 1850 AD (OSPAR, 2008). Using data
426 from multiple studies, OSPAR (2005; 2008) established a single background metals dataset for the
427 entire northeast Atlantic region. An investigation of background metal concentrations for 52
428 harbours and estuaries globally showed a remarkably narrow range of concentrations (Birch,
429 2016) with means of $27 \mu\text{g/g}$, $33 \mu\text{g/g}$ and $97 \mu\text{g/g}$ for Cu, Pb and Zn, respectively. A similar
430 study conducted as part of the current work, but exclusively for $<63 \mu\text{m}$ data, gave values of 17
431 $\mu\text{g/g}$, $26 \mu\text{g/g}$ and $79 \mu\text{g/g}$, respectively, which compared closely with the OSPAR concentrations
432 of $20 \mu\text{g/g}$, $25 \mu\text{g/g}$ and $90 \mu\text{g/g}$, respectively for fine sediment. Background metal concentrations
433 are strongly influenced by geology, climate and soil processes (Birch, 2018) and will be different
434 for each of the WHP harbours. However, in the absence of local information on background
435 concentrations, the OSPAR pre-anthropogenic values have been adopted in the present study in
436 order that results be consistent between the 10 harbours being assessed and that WHP outcomes
437 can be related to other global studies.

438 The second difficulty in assessing the magnitude of human-induced change in ports of the WHP,
439 i. e. the absence of normalised metals data, was addressed using a unique elemental-
440 normalisation procedure. Aluminium has been used as a normalising element (denominator) for
441 some time (Rubia et al., 2000; Caeiro et al., 2005; Brady et al., 2015), however an increasing
442 number of studies are using an assumption that sediment containing 100% clay mineral material
443 has an Al concentration of $50,000 \mu\text{g/g}$ Al and that total metal concentrations can be normalised
444 to this concentration of Al (OSPAR, 2005; 2008; Munksgaard et al., 2012; 2013; 2015; 2018).
445 Further assumptions are that all metals are associated with the clay mineral phase and that the Al
446 concentration used for normalisation ($50,000 \mu\text{g/g}$ Al) was the same for all locations. These

447 assumptions were tested by comparing normalisation and enrichment determined by size-
448 normalised core data with that determined using 50 000 µg/g Al for the Sydney estuary dataset.
449 Pearson (product moment) correlation was used to determine the linear association between size-
450 fractionated metals and metals normalized to various concentrations of Al. The relationship
451 between Al and sediment size for the Sydney estuary dataset showed that a considerably lower
452 concentration of Al corresponded to the composition of 100% clay mineral phase, i. e. 35,000
453 µg/g Al (and 35,000 µg/g for Fe, another normalising element). A unique opportunity to
454 comprehensively study the relationship between Al (and Fe) and sediment size was made
455 available by a large body of data obtained from 41 central NSW estuaries, which included
456 sediment size, total sediment and size-normalised metals (Birch et al., 2016). Results from this
457 study showed that the relationship between Al (and Fe) concentrations in total sediment and the
458 fine fraction content was unique for each estuary. The procedure of choosing the appropriate Al
459 concentration for normalisation is described in detail in Birch (2020). This understanding has led
460 to a break-through in an ability to normalise metals data using unique Al normalising
461 concentrations for each individual WHP harbour (the Canale Candiano of Ravenna and
462 Auckland had neither Al and/or Fe) The use of Al and Fe in normalisation procedures should be
463 used cautiously as Al enrichment in glacial sediments (Loring, 1991) and elevation of Fe by
464 diagenetic processes, is well documented (Grant and Middleton, 1990; Whalley et al.,1999).

465

466 2.5 Indicators used to estimate the magnitude of anthropogenic change (MAC) (sedimentary metal
467 enrichment)

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

479 TABLE 3

480

481 2.6 Ecological Risk Assessment (*ERA*) Risk of adverse effects to benthic populations posed by
482 anthropogenic sedimentary chemicals

483

484 Chemical concentrations *per se* do not provide an effective means for determining potential
485 adverse effects on benthic resources. To assess the ecological significance of contaminants bound

486 to sediments information on toxicity, bioaccumulation and effect on the structure of biological
487 communities are needed. These measurements require a high degree of expertise, are time
488 consuming and expensive and, as in the case of the WHP, are frequently not available. Instead,
489 sediment quality guidelines (SQG) are commonly used to make preliminary assessments of
490 sediment toxicity when direct biological effects information is unavailable. Empirical methods,
491 employing matching sediment chemistry and biological effects data, have been used in
492 development of SQGs for determining adverse outcomes of contaminants on ecological
493 populations using total sediment chemistry. Numerical-effects based SQGs are now in common
494 use globally as a screening management tool to identify and prioritise contaminants and regions of
495 concern.

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

509 Contaminants do not occur as single chemicals within marine sediments and a number of schemes
510 have been developed to assess the effects of chemical mixtures for aquatic sediments. The mean
511 ERM quotient (MERMQ) scheme has been used to estimate adverse ecological effects of chemical
512 mixtures in this WHP (Long and MacDonald, 1998). The MERMQ method requires normalising
513 the concentration of each chemical with respect to its ERM value, summing the quotients for each
514 substance and dividing by the number of chemicals for which guidelines are being used. MERMQ
515 ranges of >1.5; 1.5-0.5; 0.5-0.1 and <0.1 have been related to the probability of toxicity (76%,
516 49%, 21% and 9%, respectively) in amphipod assemblages. The number of ERL and ERM
517 exceedances has also been related to toxicity through whole sediment bioassays. However, these
518 toxicity relationships should be used with caution due to area-specific nature of benthic
519 populations and sedimentary chemicals and instead the MERMQ is considered in the current
520 assessment as a level of risk of adverse effects to sediment-dwelling animals, rather than as a
521 probability of toxicity.

522

523 3. RESULTS

524 For harbours with adequate sample density (Darwin, Derwent, Hong Kong, Ria de Vigo, Rio de
525 Janeiro and Sydney) figures are presented as filled contour maps (Figs. 2-8) and for the
526 remaining locations (Auckland, Dublin, Ravenna and Santander) distributions are given as points

527 in Supplementary Material (Figs. S1-S7). Because distributions of most elements being considered
528 in this work co-occur, only Zn is depicted in figures to limit the number of diagrams. Total metal
529 concentrations (Table 4, Fig. S8), enrichment (Table 5, Fig. S9), contamination and enrichment
530 indices/factors (Table 6) and ecological risk (Tables 7 and 8, Fig. 9) are described for each of the
531 WHP locations below.

532

533 Auckland Harbour

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

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

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

542

543 TABLE 4

544

545

546 Darwin Harbour

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

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

555 Concentration and contamination factors were low, suggesting no to slight contamination.
556 Enrichment values indicated sediments were generally uncontaminated with mean values of 0.9,
557 1.4 and 1.0 for Cu, Pb and Zn, respectively, except for the tidal flat sediment near Darwin City
558 and port where enrichment was generally >2.5.

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

563

564 TABLE 5

565

566 Derwent River

567 Mean and maximum total sediment Cd (14 µg/g and 128 µg/g, respectively), Pb (450 µg/g and
568 1880 µg/g, respectively) and Zn (2130 µg/g and 14600 µg/g, respectively) concentrations were
569 extremely high and the maximum concentration for Zn is possibly the highest recorded. Total
570 sediment, mean and maximum Cu concentrations were moderately high and Cr and Ni
571 concentrations were slightly elevated. A very strong down-stream gradient was apparent for Cd,
572 Cu, Pb and Zn with maximum concentrations centered on the Glenorchy area.

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

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

585

586 Dublin Port

587 The total sediment metal concentrations reported for three vintages (2006, 2008 and 2013) of
588 data for Dublin Port varied greatly. Vintages 2006 and 2008 had similar spatial distributions
589 covering most of the harbour area, while 2013 data were mainly confined to the Alexandra Basin
590 loading dock. Metal total sediment concentrations in 2006 (Cu, Pb and Zn concentrations were
591 49 µg/g, 81 µg/g and 217 µg/g, respectively) were substantially higher than in 2008 (mean 27
592 µg/g, 44 µg/g and 152 µg/g, respectively), but lower than in Alexandra dock in 2013 (mean 60
593 µg/g, 138 µg/g and 663 µg/g, respectively). In particular, the 2006 vintage data were normalised
594 using 25K Al (mean Al 15,900) resulting in increased enrichment and a MEQ of 4.6. However,
595 for the 2008 survey which covered the majority of the harbour, sediment metal concentrations
596 exceeded ERL values only in a minor part of the inner harbour, while one site exceeded ERM
597 values for Pb and Zn. As a result, the overall risk for this vintage was low and the MERMQ was
598 0.31. Concentrations of Cu, Pb and Zn displayed similar distribution patterns, i. e. increasing
599 towards the inner harbour with a moderate elevation in a dock in the central harbour area (based
600 on 2008 data).

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

614

615 Hong Kong Harbour

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

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

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

630 Ravenna

631 Sediments in the Canale Candiano were moderately rich in total mean Cd and Pb concentrations
632 ($1.6 \mu\text{g/g}$ and $49 \mu\text{g/g}$, respectively) and metal concentrations increased towards the city of
633 Ravenna. Concentration and contamination indicators were slightly elevated, however no
634 enrichment factors could be determined due to an absence of sediment size data and normalising
635 elements for the Canale Candiano. Ecological risk was low ($MERMQ=0.26$) with Zn posing the
636 highest concern ($MERM=0.43$).

637 Rio de Janeiro

638 Rio de Janeiro Bay was almost entirely mantled in muddy sediments ($>80\%$) and total sediment
639 metals were moderately high for Cu and Pb (means $62 \mu\text{g/g}$ and $66 \mu\text{g/g}$, respectively) and high

640 for Zn (mean 318 µg/g). All metals increased towards the SW and were greatest adjacent to Rio
641 de Janeiro city and the Rio Pauvna and lowest in the sandy sediment off San Francisco Beach in
642 the SE. Maximum concentration for Zn was third highest (2039 µg/g) for the 10 harbours
643 studied.

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

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

654

655 Ria de Vigo estuary

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

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

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

674

675 Santander Harbour

676 Sediments in Santander Harbour contained the second highest total Cr (83 µg/g) and Ni (48
677 µg/g) concentrations in the WHP. Lead and Zn sediment metal concentrations were high in the

678 dockland area west of the harbour and Pb and Cu concentrations were also elevated in the
679 embayment to the south. An apparent decreasing metals gradient from the upper embayment in
680 the south towards the harbor mouth in the northeast requires verification with additional
681 sampling.

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

687 Mean total Cr, Ni and Pb concentrations exceeded ERL values and mean Zn concentrations were
688 $>ERM$. With a spatially limited dataset it was difficult to determine accurately the areas exposed
689 to ecological risk by sediments, however it appeared that large parts of the port may be at risk for
690 Cu, Pb and Zn. Overall ecological risk was moderate ($MERMQ=0.51$). Additional sampling and
691 mapping is required to verify the risk distribution.

692

693 Sydney estuary

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

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

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

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

721

722 4. Discussion

723

724 4.1 Sampling and Analytical methods

725 Sediment samples used by WHP institutions were recovered by grab (van Veen), corer or box
726 corer. When using these different sampling devices, it is important to remove only the uppermost
727 sediment layer so as to sample only the most recently deposited material and not to mix this
728 surficial material with underlying, pre-anthropogenic substrate. Sampling design, density and
729 distribution needs to be consistent. However, sampling was frequently focused on perceived
730 source locations and points of interest with low density cover over the remaining (sometimes
731 majority) waterway preventing a full spatial assessment. Sample density should be relative to
732 small-scale spatial variance and proximity to discharge locations to provide optimal coverage for
733 source identification and dispersion tracking. Sample density, which provided satisfactory
734 regional coverage for reasonably consistent abundances was approximately 0.5-1.0 samples/km²,
735 but increased to 5-10 samples/km² in areas of interest, or in places of high variability based on
736 data provided in the current study.

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

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

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

780

781 4.2 Magnitude of anthropogenic change

782

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

791 Enrichment (MEQ) was calculated for six metals (MEQ/6=Cd, Cr, Cu, Ni, Pb and Zn) and for
792 three metals (MEQ/3=Cu, Pb and Zn) to determine whether the extra number of elements
793 effected enrichment calculations (Table 5). A close correlation between the two data sets
794 ($r=0.953$, $p<0.05$) supports similar results, which show metals are invariably closely correlated

795 with each other, e. g. the three metals (Cu, Pb, and Zn) were closely correlated with a suite of
796 six metals for Sydney estuary ($r = 0.959$, $p < 0.05$), Hawkesbury River ($r = 0.932$, $p < 0.05$), New
797 York Harbour ($r = 0.843$, $p < 0.05$) and for Tampa Bay ($r = 0.825$, $p < 0.05$) (Birch et al., 2008) and in
798 many other locations (Zhang et al., 2009).

799 Enrichment has been calculated in the present work based on a novel elemental normalisation
800 procedure employing variable concentrations of Al to accommodate for regional changes in local
801 clay mineral chemical assemblages. This approach has been investigated recently in great detail
802 (Birch, 2020) and is discussed here only in its application to the WHP. The concentration of the
803 Al normaliser varied across the 10 WHP datasets from 20K Al (Rio de Janeiro) to 70 K Al
804 (Darwin) and was most commonly between 32K and 35K Al. The normaliser value used was
805 estimated from the relationship between sediment size and total Al concentration, which was
806 available for six (Darwin, Derwent, Hong Kong, Rio de Janeiro, Ria de Vigo and Sydney) of the
807 10 harbours. For harbours without sediment size information, normaliser values were estimated
808 from total Al alone, which introduced speculation and no normalisation could be undertaken for
809 harbours without sediment size, Al, or Fe data (Auckland and Canale Candiano in Ravenna).

810 An opportunity to test the validity of normalisation and enrichment determined by elemental
811 normalisation (Al and Fe) was afforded by the availability of size-fractionated metals data from
812 Sydney estuary. Enrichment based on size-normalised data and 35K Al normalisation (employing
813 SOPAR (2008) background values for both data sets) was closely related. i. e. 9.1 and 9.8,
814 respectively for Cu, 11 and 13, respectively for Pb and 6.5 and 7.6, respectively for Zn (Table 5).
815 Moreover, enrichment determined by sediment size- and Al normalisation was also closely
816 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 ($r = 0.516$,
817 $p < 0.05$), which showed moderate scatter due to analytical difficulties. These results gender
818 confidence in the approach being used in the current work based on variable Al elemental
819 normalisation.

820 The availability of PEN data for Darwin Harbour allowed a comparison between another size-
821 normalisation process and elemental normalisation. Normalisation of Darwin Harbour data to 70k
822 Al produced similar results to PEN normalisation, i. e. mean concentrations of 15 $\mu\text{g/g}$, 29 $\mu\text{g/g}$
823 and 79 $\mu\text{g/g}$ compared to 18 $\mu\text{g/g}$, 36 $\mu\text{g/g}$ and 87 $\mu\text{g/g}$ for Cu, Pb and Zn, respectively.
824 Normalisation using Fe produced inconsistent results due to anomalously high concentrations of
825 this element for some samples related to the presence of Fe oxyhydroxides (Munksgaard et al.,
826 2013). Mean enrichment, also using 70K Al as a normaliser, was closely correlated, i. e. 0.9, 1.4
827 and 1.0 for Cu, Pb and Zn, respectively compared to 0.7, 1.0 and 0.9, respectively for PEN data
828 (Table 5). Enrichment using PEN and 70K Al data was moderately correlated ($r = 0.641$, $p < 0.05$),
829 however PEN data were less consistent than using 70K Al possibly due to variable carbonate
830 content.

831 Although Li is the normaliser of choice for Ria de Vigo sediments, these data afforded the
832 opportunity to test the appropriateness of Al- and Fe-normalisation on the same data set.
833 Normalised concentrations produced by 90K Al and 35K Fe were remarkably similar, i. e. 98
834 $\mu\text{g/g}$ and 97 $\mu\text{g/g}$, respectively for Cu, 131 $\mu\text{g/g}$ and 125 $\mu\text{g/g}$, respectively for Pb, and 244 and
835 235, respectively for Zn. Similarities in enrichment determined by these two techniques were

836 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
837 approaches were both 4.1 and correlation between the two techniques for Cu was $r=0.964$
838 ($p<0.05$). These results indicated both Al and Fe may be used as elemental normalisers in the
839 absence of diagenetic modification.

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

851

852 4.3 Use of concentration, contamination and enrichment factors in assessment of
853 anthropogenic change

854

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

871 A generalised observation of the 10 metrics used in the current study (Table 6) showed that the
872 Nemerow Pollution Index (*PI*) and the Metal Pollution Index (*MPI*) values were high, while the
873 Geo-accumulation index (*I_{geo}*) for both total sediment and for Al-normalised data were low with
874 respect to results from other indices. PI values were higher than reported in the literature (Brady
875 et al., 2015) possibly due to unusually elevated metal concentration in some of the WHP

876 estuaries, whereas *Igeo* figures are commonly cited low, or negative (Abraham and Parker,
877 2008). The Surface Enrichment Factor (*SEF*), Enrichment Factor (*EF*), the Modified Degree of
878 Contamination (*mDC*) and the Mean Enrichment Quotient (*MEQ*) results are similar. An
879 outcome of these assessments was that, although the factors are based on different attributes, the
880 ranking produced was similar for all assessment tools. A further outcome was that the
881 Concentration Factor (*CF*) (un-normalised data), *mDC*, *EF*, *mPI* and the *MEQ* are closely
882 correlated (r values between 0.942 and 0.959, $p < 0.05$), while the *Igeo* and the *PI* are poorly
883 correlated with the previous group of factors, probably due to the different basis on which these
884 indicators are calculated.

885

886 TABLE 6

887

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

906 The original Geo-accumulation Index (*Igeo*) (Müller 1969, 1979; 1986) was based on fine
907 sediment samples and background metal concentrations, however recently different backgrounds
908 have been used (global shale) (Ghani et al., 2013) and various sediment sizes (total sediment)
909 have been included in the computation (Buruaem et al., 2012; Pang et al., 2015). resulting in
910 confusion and incompatible outcomes. More recently confounding due to variable size when
911 using total sediment has been taken into account by normalising to Al and adjusting the data to
912 100 % mud (Kim et al., 2018; 2019). Geo-accumulation index values were low and often
913 negative in the current work, similar to other studies where results for most elements were also
914 negative, e. g. Cevik et al. (2009); Kaushik et al. (2009); Thuong et al. (2013), Abraham and
915 Parker, (2008) and Kim et al. (2018).

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

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

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

941

942 4.4 Ecological risk posed by sedimentary metals

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

952

953 TABLE 7

954

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

960

961 TABLE 8

962

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

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

978

979

980 4.5 Overall magnitude of anthropogenic change and ecological risk

981

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

989

990 TABLE 9

991

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

1000

1001 TABLE 10

1002

1003

1004 5 Conclusions

1005 Sediments of Derwent River are distinctive with very high total mean concentrations of Cd, Pb
1006 and Zn. Sydney estuary sediments contain the highest mean Cu concentrations and Santander
1007 Harbour sediments are characterized by the highest mean concentrations of Cr and Ni of the 10
1008 WHP ports.

1009 An innovative technique for Al and Fe normalisation was applied and tested against accepted
1010 size-normalisation and post-extraction (PEN) methods, which satisfactorily allowed
1011 measurement of anthropogenic change. Metals enrichment followed total metal concentration
1012 and the mean enrichment for multiple sedimentary metals (MEQ) was high for Derwent River,
1013 Santander Harbour and Sydney estuary (>5.0), moderate for Rio de Janeiro and Dublin Port (3.0-
1014 5.0), slight for Hong Kong (1.5-3.0) and minimal for Darwin (<0.15) (no sediment size. Al, or Fe
1015 data were available for Canale Candiano of Ravenna and Auckland.

1016 Only sediment from Derwent River was rated at high ecological risk (MERMQ>1.5), followed
1017 by Sydney and Santander estuaries with moderate risk (MERMQ>0.50). Dublin, Hong Kong,
1018 Ravenna, Ria de Vigo and Rio de Janeiro were assessed at slight risk to benthic communities and
1019 Auckland and Darwin sediments exhibited minimal ecological risk.

1020 All 10 enrichment indices used in the current investigation showed elevated values for Derwent
1021 River and Sydney estuary, while Auckland and Darwin registered low values for most of these
1022 tools. Other harbours had mixed values across the spectrum of indices. A unique, multi-index
1023 classification scheme provided an overall score of 20, 14, 12, 11, 9, 5 and 4 for the Derwent
1024 River, Sydney estuary, Santander, Ria de Vigo and Dublin, Rio de Janeiro, Hong Kong and
1025 Darwin, respectively. Insufficient data were available to rank Canale Candiano of Ravenna and
1026 Auckland, however these harbours are considered to score <4 considering total metal
1027 concentrations.

1028 A new categorisation scheme applied to results of the current study assessed overall
1029 anthropogenic change and ecological risk. Derwent River, Sydney and Santander estuaries were
1030 rated highly enriched, while Rio de Janeiro was moderately enriched. Dublin, Hong Kong and
1031 Ria de Vigo were slightly enriched, whereas Darwin was not enriched. Only the Derwent River
1032 was at high ecological risk, while Sydney and Santander estuaries were at moderate risk. Dublin,
1033 Hong Kong, Ravenna Ria de Vigo and Rio de Janeiro were at slight ecological risk and
1034 Auckland and Darwin were at minimal risk. The similarity in the ranking of the harbours in
1035 assessment of enrichment and ecological risk is reassuring and the minor difference for Rio de Janeiro is
1036 due to the different criteria used in the two assessment techniques.

1037 The wide range in environments and a large variety in types of data provided by partner
1038 organisations resulted in a useful critique and development of methodologies used in assessment
1039 of sediment quality in maritime regions. It is important to restate that these assessments are the result
1040 of a screening procedure to identify and prioritise contaminants and region of concern and that further
1041 evaluation of other risk factors, e. g. bioaccumulation, bioavailability and toxicity, are required to
1042 determine potential impact.

1043 Recommendations

1044 Sample coverage was inconsistent amongst WHP partners and tended to be focused on perceived
1045 point sources and nearshore environments, often leaving large central areas un-surveyed, which
1046 prevented a full spatial assessment for 40% of the harbours. Sufficient sample density for
1047 regional coverage was estimated at ~0.5-1.0 samples/km², while for areas of concern, or high
1048 variability, a density of 5-10 samples/km² is recommended.

1049 The suite of analytes also varied within the WHP and no consistent combination of chemicals
1050 other than metals (and even these were not consistent) were available for assessment. Ideally, a
1051 full set of metallic and organic contaminants would be required to conduct a satisfactory
1052 environmental assessment, however evidence is available to show that metals are strongly
1053 correlated to other organic pollutants.

1054 Most analyses were undertaken using weak (HCl) to moderately strong acid (aqua regia)
1055 mixtures, which are suitable for assessing the adsorbed phases required to assess the magnitude
1056 of anthropogenic change and to establish ecological risk. The use of stronger acids, e. g.
1057 HNO₃/HClO₄ (nitric plus perchloric acid) would extract inert mineral forms and may make
1058 assessment of ecological risk problematic.

1059 A global inadequacy exists in the availability of suitable data for setting pre-anthropogenic
1060 sedimentary metal concentrations. Background values should be estimated from local, fine-
1061 grained down-hole, core data and will be different for each of the WHP locations. Cores used for
1062 background estimation should be recovered from undisturbed areas of deposition and subsurface
1063 bioturbation and post-depositional physical and chemical remobilisation should be avoided.
1064 Instead, a single suite of background metal concentrations had to be applied to all WHP data,
1065 introducing possible error in enrichment assessments of the 10 harbour estuaries.

1066 Some form of normalisation is essential for enrichment assessment to moderate confounding by
1067 varying grain size. WHP data frequently lacked data necessary for assessing metal enrichment, i.

1068 e. sediment size, Al and Fe. Size-fractionated metal data are the preferred data for enrichment
1069 estimation, however tests conducted in the current work confirm the use of both Al and Fe as
1070 normalisation elements and the use of PEN data for determining human-induced change in the
1071 absence of elevated carbonate content.

1072 The individual schemes comprising the plethora of indices now available for estimating metals
1073 enrichment have not yet been thoroughly tested for validity and some are based on uncertain
1074 assumptions. Indices supporting multiple elements, include a classification scheme and based on
1075 normalised data and background information are recommended and results from these schemes
1076 are closely correlated ($r > 0.95$), i. e. Enrichment Factor (EF), modified Degree on Contamination
1077 (*mDC*) and the Mean Enrichment Quotient (MEQ). The original Geo-accumulation Index (*Igeo*)
1078 and the modified version (*mIgeo*) exhibits reduced sensitivity and the Nemerow Pollution Index
1079 (*PI*) and the modified version (*mPI*) over emphasises elevated metals resulting in loss of
1080 discretionary power. Despite the different formulations on which the 10 indices are based,
1081 ranking of index results was similar for all assessment tools and as many as possible indices
1082 should be tested in assessing anthropogenic change.

1083

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1087

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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 furnace atomic adsorption spectroscopy; na=not available

HNO₃= nitric acid; HCl=hydrochloric acid; HClO₄=perchloric acid; aqua regia=HCl/HNO₃

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-accumulation Index (fine sediment) | <i>I_{geo}</i> (fine) | Muller, 1980 | Y | Y | Y | N | Y | 4 |
| 7 | Geo-accumulation Index (total sediment) | <i>I_{geo}</i> (total) | Xu et al., 2014 | Y | Y | Y | N | Y | 4 |
| 8 | Geo accumulation Index (total sediment) | <i>I_{geo}</i> (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 | Abraham & 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 ($\mu\text{g/g}$, 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 | 1 | 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 | 0 | 2130 | 22 | 0 |
| Dublin 2013 | 3.6 | 0.1 | 20 | 136 | 25 | 316 | 60 | 3.3 | 155 | 90 | 58 | 164 | 138 | 10 | 0 | 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 | 0 | 518 | bd | 0 |
| 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 | 0 | 2130 | 72 | 0 |

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

| Harbour | Concentration Factor | Contamination Factors (background, no normalisation) | | | | Enrichment Factors (background and normalisation applied) | | | | | WoE | Rank |
|----------------|-----------------------|--|-------------------------|---------------------------|---------------------------------------|---|--------------------|----------------------------------|----------------------------------|--------------------------|-------------|------|
| | MPI | CF | PI | SEF | Igeo (total) | EF | Igeo (AI) | mPI | mDC | MEQ | | |
| | Metal pollution index | Contamination Factor | Nemerow pollution index | Surface enrichment factor | Geo-accumulation index total sediment | Enrichment factor | Igeo AI 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 No.s | ERLQ (Cd, Cr, Cu, Ni, Pb, Zn) | | | ERMQ (Cd, Cr, Cu, Ni, Pb, Zn) | | | | | | MERLQ Cu, Pb, Zn | MERMQ Cu, Pb, Zn |
|----------------------|----------------|-------------------------------|---------------------------|-----|-------------------------------|------------------------------|----|------------------------------|-------|-------|---------------------|---------------------|
| | | Mean | Samples >ERL ¹ | | Mean ERMQ | Samples >ERM ¹ | | No. samples exceeding ERM | | | | |
| | | | No. | % | | 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 Range Median; PEL= Probable Effects Level; Q=Quotient

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

| Harbour | MEQ | Environmental Indices | MERMQ | Rank ¹ | |
|----------------|-----|-----------------------|-------|-------------------|-------|
| | | | | Total | 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



Figure 1.

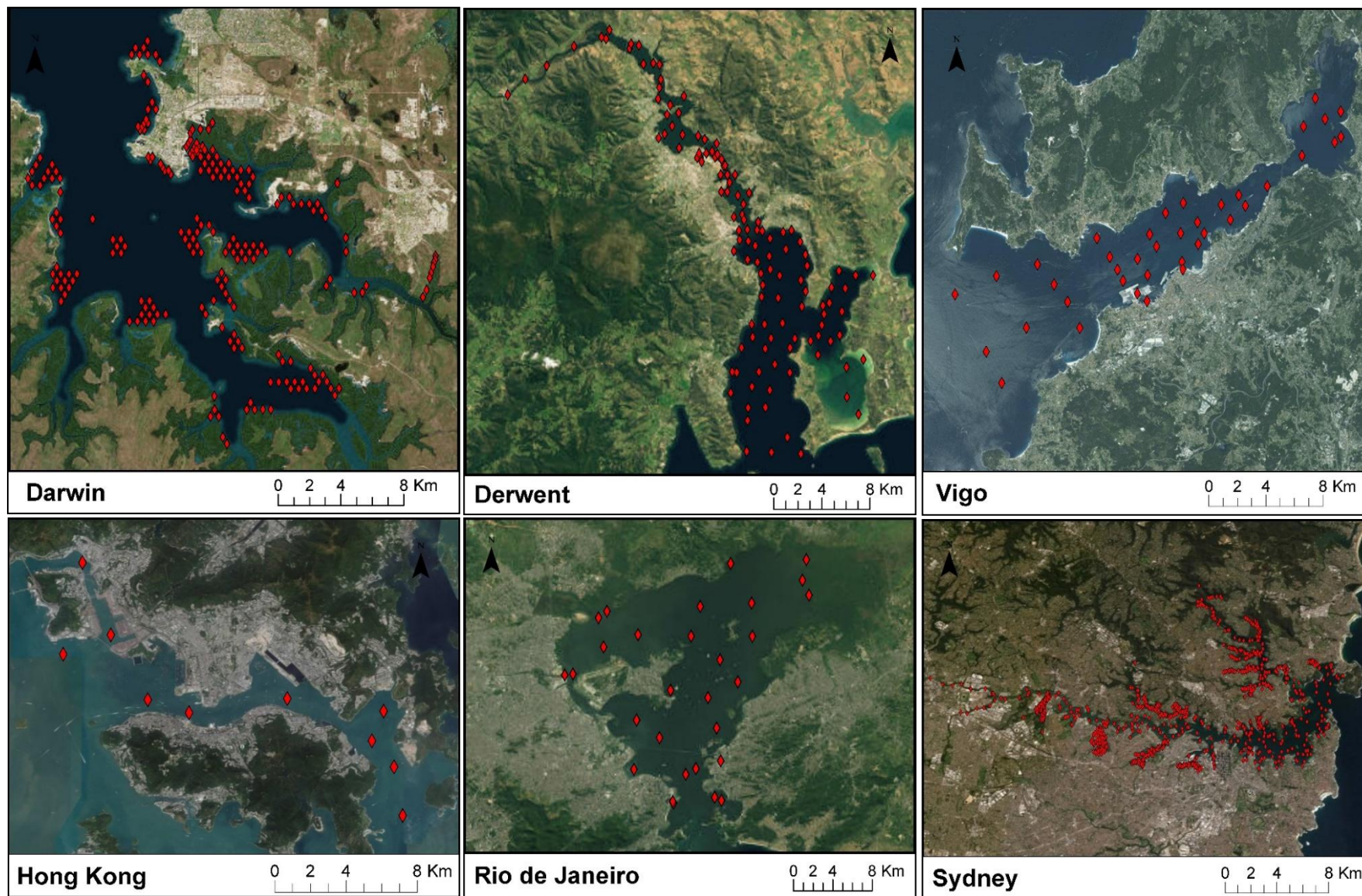


Figure 2.

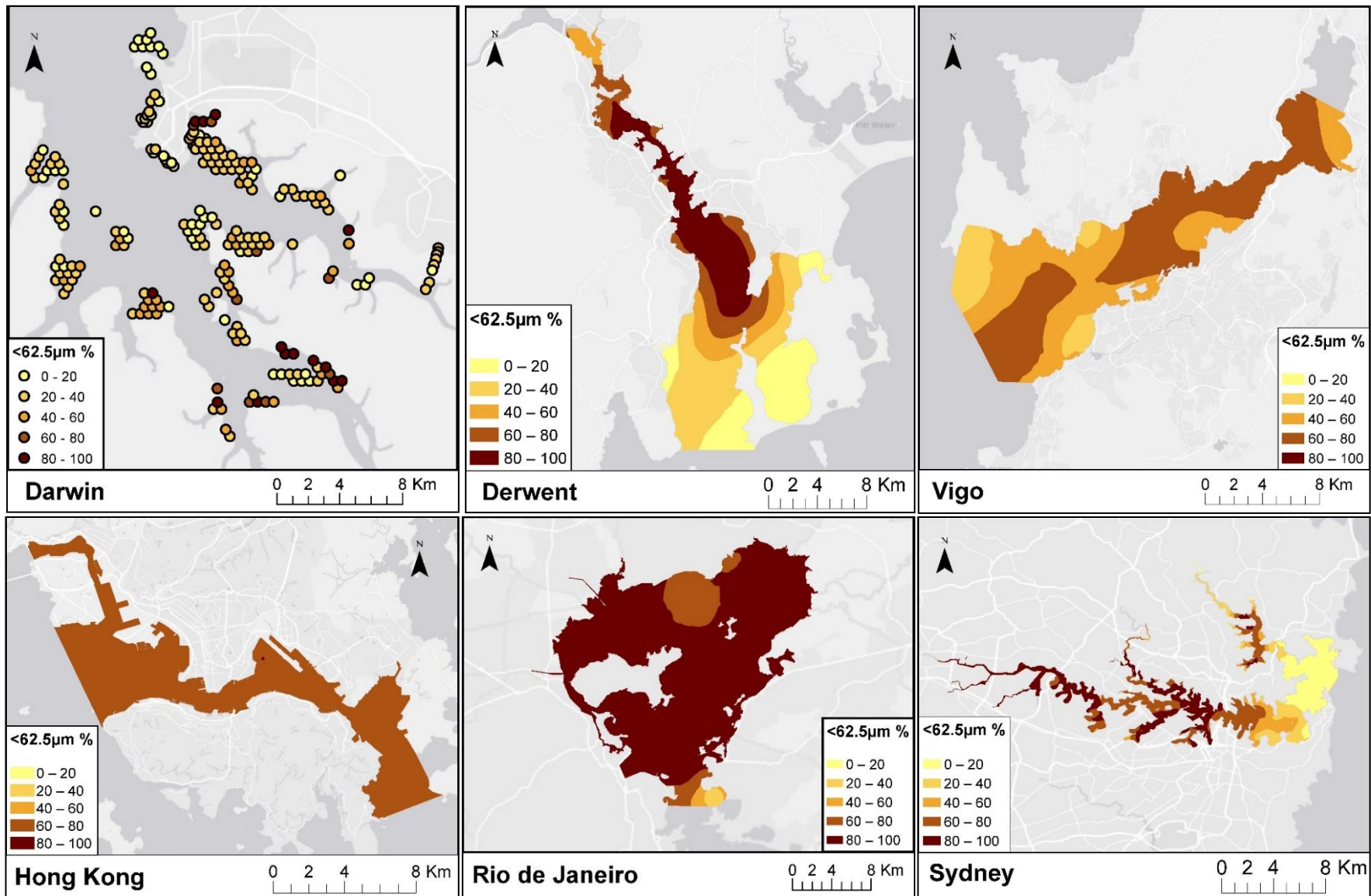


Figure 3.

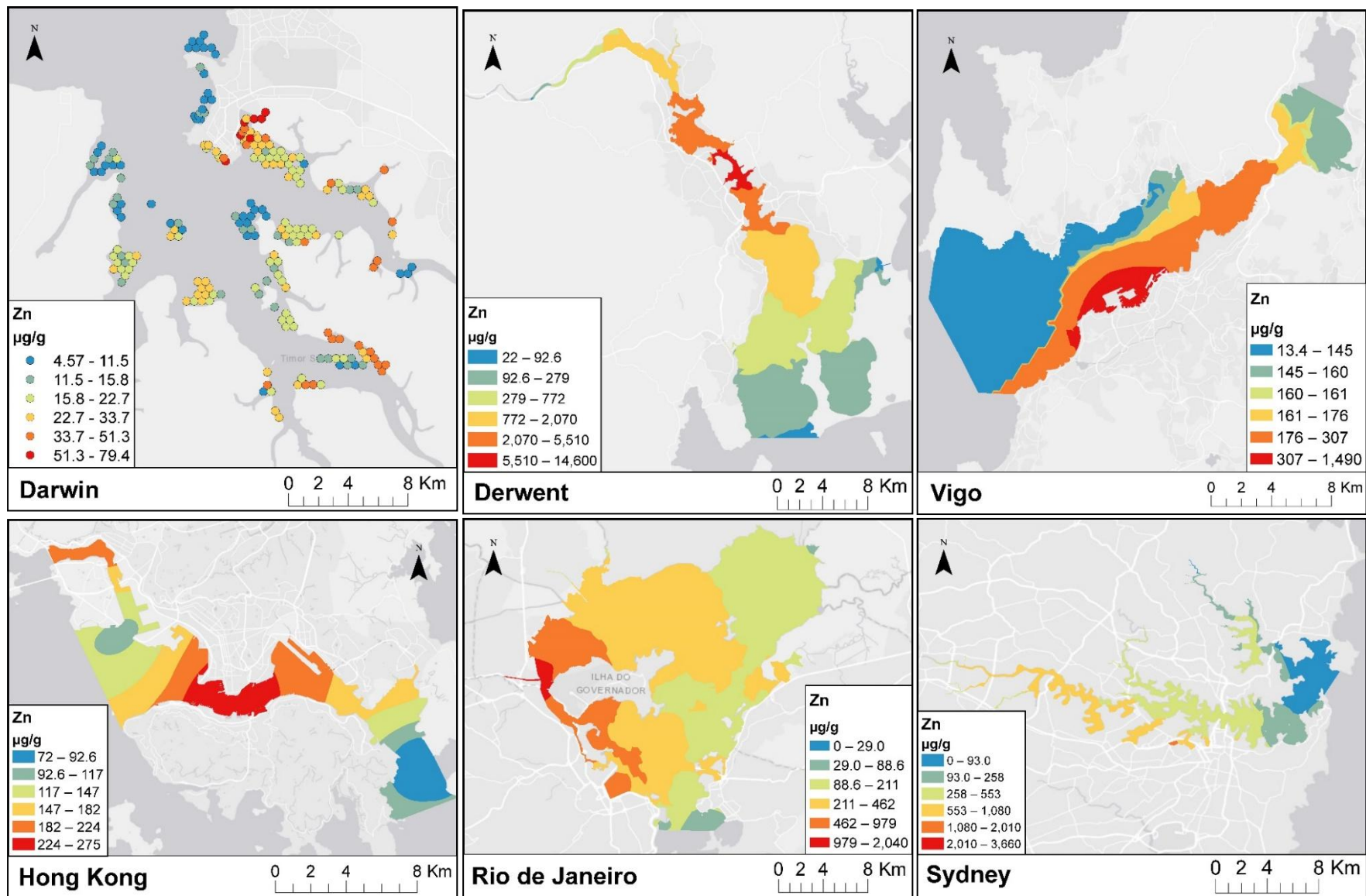


Figure 4.

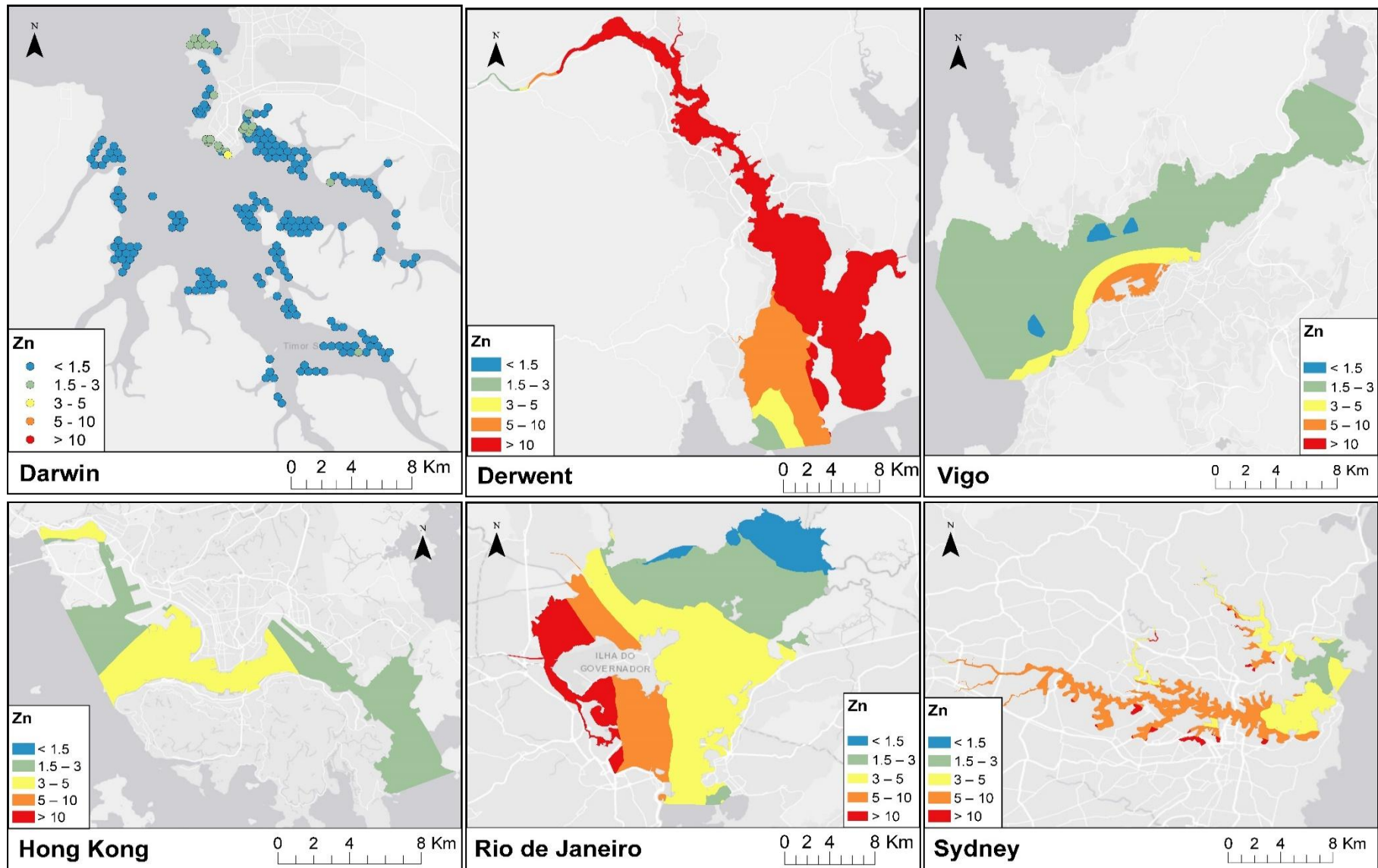


Figure 5.

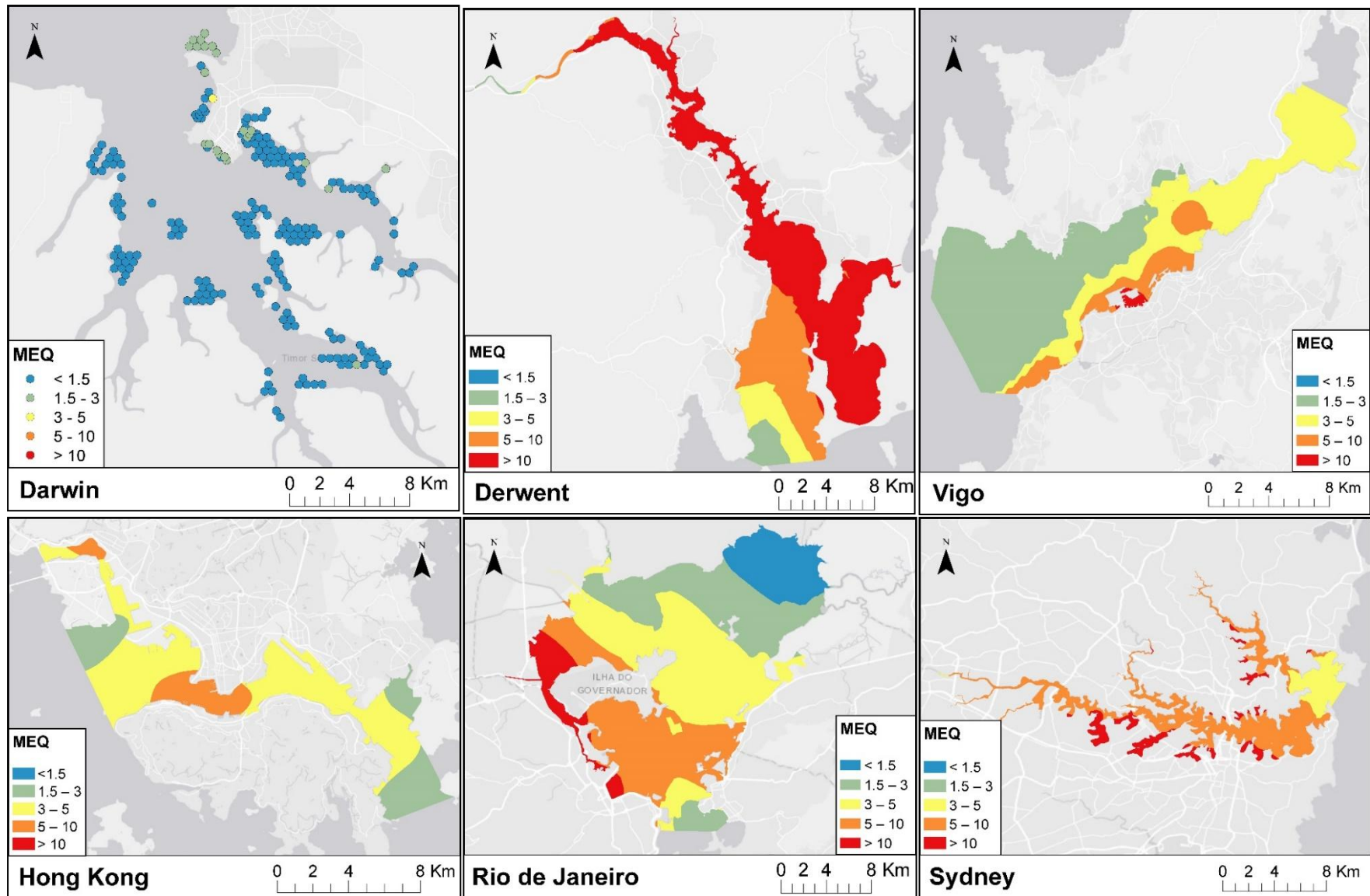


Figure 6.

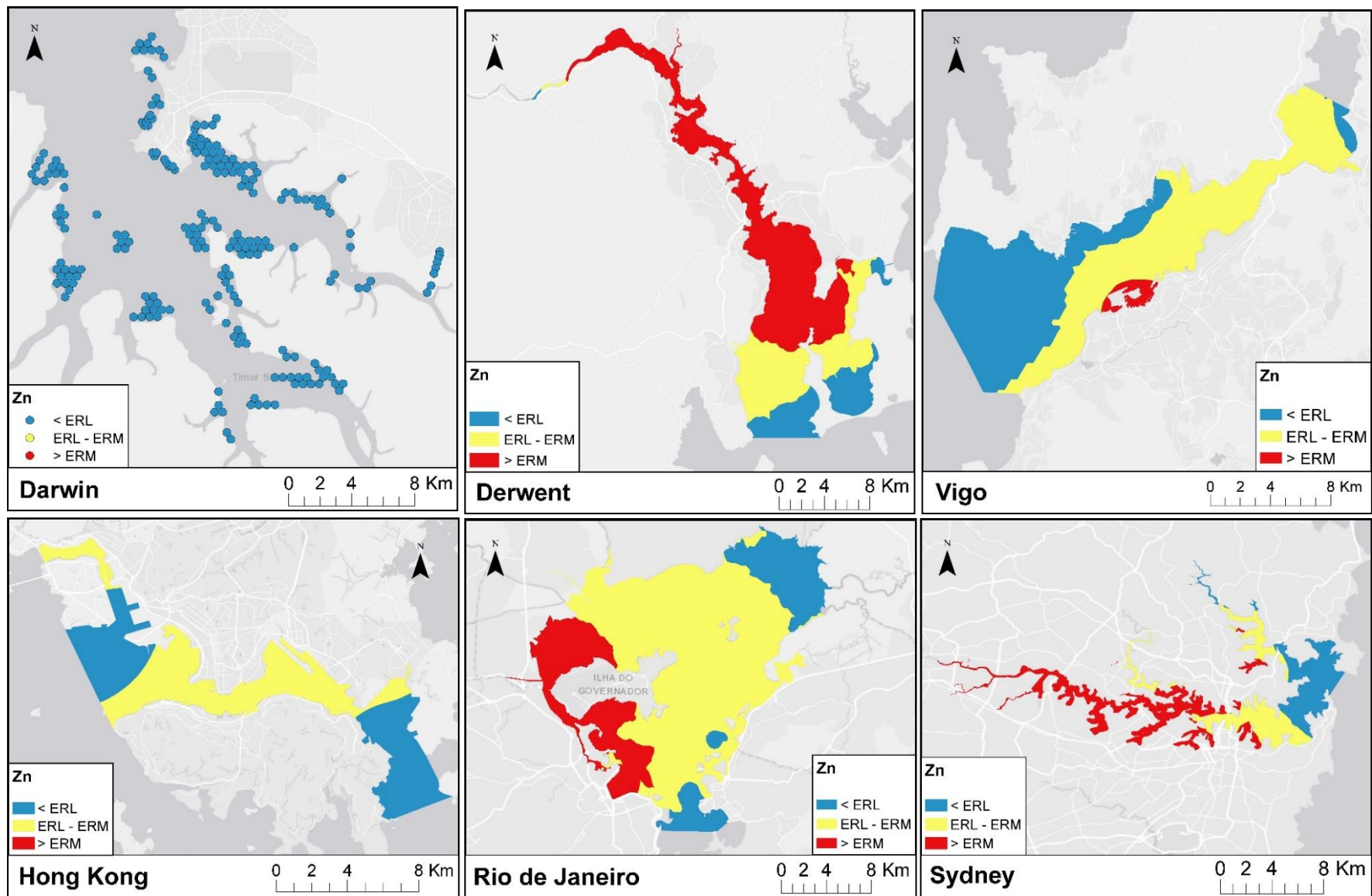


Figure 7.

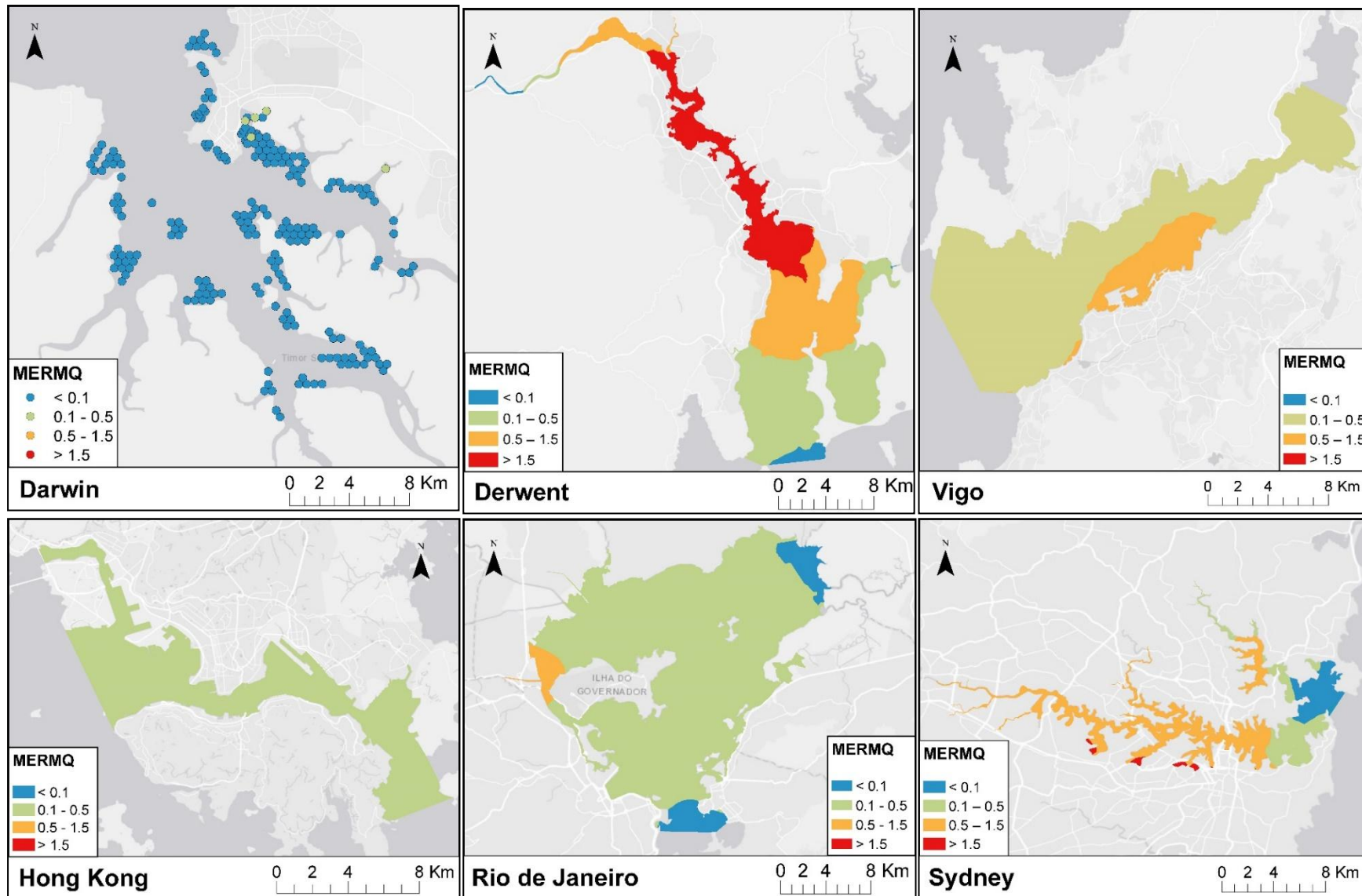


Figure 8.

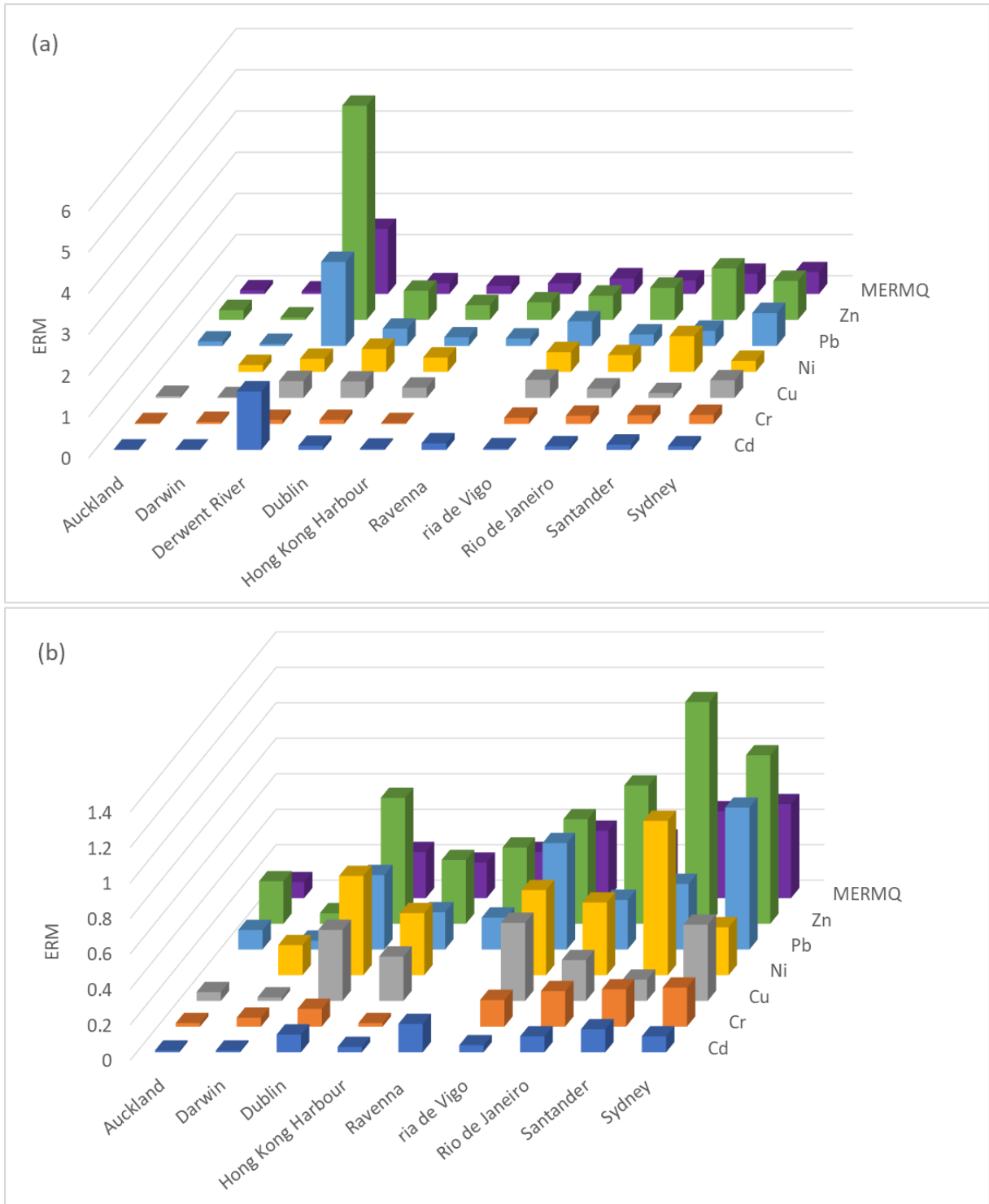


Figure 9.

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