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Assessment of human-induced change and biological risk posed by contaminants in estuarine/harbour sediments: Sydney Harbour/estuary (Australia)

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ABSTRACT

A rapid, simple yet scientifically sound scheme providing two important types of information used in assessment of estuarine sediments is presented. The mean enrichment quotient (MEQ) (fine contemporary sediment metal concentration/fine fraction background metal concentration) for Cu, Pb and Zn provides the magnitude of human-induced change, (deviation from the pristine condition), while sediment quality guidelines (SQGs) assess the risk posed by sedimentary contaminants to the benthic community.

Maximum metal enrichment for sediment in Sydney estuary (Australia) is >100 times for Cu, Pb and Zn and the MEQ is >10 times for most of the estuary. Adverse effect on benthic populations due to Cu, Pb and Zn are expected in 2%, 50% and 36% of the waterway, respectively. SQGs for contaminant mixtures predict ~2% of the estuary has the highest risk of adverse effects, while 25% has intermediate risk. The scheme is well suited to initial assessments of estuarine sediments worldwide.

1. Introduction

Estuaries are diverse and biologically productive ecosystems with high conservation and ecological value (Costanza et al., 1997, 2014; Boyes and Elliott, 2006). More than half the world population live within 100 km of a shoreline (Niemi et al., 2004) and estuaries are commonly the foci of industrial, commercial and recreational activities (Birch et al., 2015a, 2015b). Substantial anthropogenic stress has resulted in reduction in sediment and water quality, which threatens benthic and pelagic populations (Chapman and Wang, 2001). It is therefore important that the extent of contamination of estuarine environments is assessed accurately and that the level of threat to the health to these sensitive environments be determined comprehensively.

1.1. Environmental indicators

Choosing an appropriate ecosystem indicator to assess environmental condition is complex and requires an integrated strategy to quantify the effects of human activities on the marine environment (Magni, 2003; Magni et al., 2004). Ecosystem condition indicators need to be easily and inexpensively employed to accurately and appropriately measure numerous biological, chemical and physical processes. A weight-of-evidence approach is considered most effective for assessment of multiple indicators within a decision framework in assessing ecosystem health (Simpson et al., 2005).

Ecosystem indicators used to assess anthropogenic stress are commonly compromised by significant natural spatial and temporal variability. This confounding results in inappropriate and erroneous ecosystem assessment rendering it difficult to discriminate between natural- and human-induced stress under complex conditions (Hogg and Norris, 1991; Olmos and Birch, 2010). The original (pristine) condition of an estuary is rarely known and to determine whether present distributions of flora and fauna indicate good or poor condition is difficult to establish (McLoughlin, 1985). To determine the magnitude of human-induced change and adverse biological effects requires historic baseline information (control sites), which is commonly not available, especially on high-population seaboards.

1.2. Sediments as ecosystem indicators

The use of sedimentary indicators in assessment of environmental condition has been poorly understood and greatly undervalued and underutilised. The preferred media for assessment of estuarine health has traditionally been the water column and biological indicators (Rainbow, 1995, 2006). However, water is dynamic and highly variable in the short- and long-term requiring large numbers of samples to spatially and temporally characterise this medium with confidence (Birch and Olmos, 2008). Water chemical concentrations are low and analyses are difficult and expensive, which compromises data quality and interpretation (Bubb et al., 1990; Siaka et al., 1998; Birch and Taylor, 2000b). Analysis of floral and faunal distributions is often difficult due to significant natural temporal and spatial variance and the chemistry of tissue is variable between individuals, species, genders, organs and age.

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Increasingly, sediment is being used preferentially to assess the status of aquatic environments rather than other traditional media. However, these materials should be used in combination with other screening tools for a comprehensive assessment of aquatic systems (Belin et al., 2014). The great advantage sediments have over other indicators of environmental condition is that they faithfully record and time integrate environmental events within the aquatic system, commonly referred to as 'the memory of sediments'. The integration of environmental events over time provides useful spatial and temporal information (Birch, 2007; Birch et al., 2013) and allows prediction of future environmental change and status (Birch et al., 2010, 2012, 2013). Sediments greatly affect the quality of overlying and interstitial water through physical (re-suspension, Peterson et al., 1997; Simpson et al., 2000), biological (bioturbation, Reible et al., 1996) and chemical (desorption and benthic diffusion, Rivera-Duarte and Flegal, 1994.) processes. Sediments are an extensive habitat and a large storage for contaminants and therefore have an extensive influence on the biological health in the marine environment. The majority of toxicants adsorb to fine-grained particles and therefore sediments are important in the transport of contaminants in the water column. Contaminants also have an affinity for finely-disseminated organic matter and therefore sediments influence the feeding habitats of benthic and pelagic animals, as well as being involved in the uptake processes. Sediment quality thus influences, to a large degree, the biodiversity and ecological health of marine systems. Although sediments are appropriate indicators of environmental status, these materials should be used in combination with other media for a comprehensive of aquatic systems. However, as yet no approach has been undertaken to develop indicators to assess potential interactions between the wide range of metallic and non-metallic contaminants, which may be contained within marine sediments. The vast number of combinations of these chemicals may result in synergistic, additive or antagonistic functional effects on benthic and pelagic communities, which remains to be addressed (Part, 2006).

Although sediments are appropriate indicators of environmental status in aquatic systems, their use has sometimes been problematic due to the lack of uniformity in analysis and difficulties in interpretation of sedimentary data. These issues have been largely overcome and interpretation has become clearer with establishment of accepted analytical protocols (Simpson et al., 2005, 2016) and a more advanced understanding of speciation and particularly partitioning in sedimentary systems. The difficulty in interpreting sediment-derived contaminant data due to the confounding effects of variable grain size is not always fully appreciated. Grain size is the dominant parameter controlling contaminant concentrations in sediments, including proximity to source. A procedure for reducing the confounding caused by variable grain size is essential for interpretation of sediment contaminant data and should be an integral part of the protocol for environmental assessment. Variability in grain size imposes considerable spatial and temporal variance on sediment-derived chemical data and determination of source, dispersion, the pristine condition, magnitude of anthropogenic change (as addressed in the current work), temporal change and comparability of contaminated systems cannot be made without some form of 'normalisation' of the data (see Section 2.1.3) (Forstner, 1982; Loring, 1991; Birch, 2003).

1.3. Assessing the status of estuarine condition

The condition of an estuarine environment may be described using a wide range of approaches, however from a management perspective it is important to know (1) by how much the system has deviated from the pristine condition (magnitude of anthropogenic change), and (2) the degree of risk of potential harm posed by sedimentary contaminants to biological communities. These two types of data are very different – one measures the amount of human-induced change and the other determines potential ecological risk posed by sedimentary anthropogenic chemicals. These two aspects are frequently confused and these data types are often integrated (Caeiro et al., 2005; Mil-Homes et al., 2006).

The objectives of the present work are to briefly review methodologies used in the assessment of anthropogenic change and risk posed by sedimentary contaminants in marine/estuarine environments and then to apply the least complex and most effective approach to sediments of Sydney harbour/estuary, Australia.

2. Methods to assess the magnitude of anthropogenic change

2.1. Pre-anthropogenic, or background concentrations

To calculate the amount of deviation from the pristine condition in marine environments, it is first necessary to estimate the concentrations of chemicals in sediments deposited prior to human influence (pre-anthropogenic, pre-industrial or background concentrations). For anthropogenic chemicals, e.g. organochlorine compounds (OCs) and polychlorinated biphenyls (PCBs), pre-anthropogenic concentrations are zero. However, for chemicals, which have both anthropogenic and natural components, such as metals and polycyclic aromatic hydrocarbons (PAHs), it is necessary that the human contribution first be determined to establish the magnitude of change. The background concentration of PAH is mainly related to bush fire activity and is low (<50 μg/kg) and frequently regarded as zero. Metals are an intrinsic component of minerals comprising sediments and have a natural background concentration even in pristine environments. Pre-anthropogenic concentrations of metals have been determined by statistical and empirical methodologies (Matschullat et al., 2000).

2.1.1. Statistical methods to estimate background metal concentrations

Statistical methods used to determine anthropogenic change identify pristine from contaminated samples to establish a threshold, which separates natural from man-modified material. Statistical methods to determine anthropogenic contributions have been reviewed by Matschullat et al. (2000), Reimann et al. (2005) and Rodriguez et al. (2006).

Pre-anthropogenic metal concentrations are inferred using linear regression of a normalising element (Al, Fe) against total sediment metal concentration. Outliers are identified as those samples that fall outside the 95% confidence limit and are removed and regression recalculated until normality is achieved. Data falling within the predicted interval belong to a pre-anthropogenic population and samples above this band are enriched in metals due to human activities (Matschullat et al., 2000). Modal analyses, relative cumulative frequency curves, iterative standard deviation identification and outlier testing have been used in many studies to estimate background metal concentrations (Matschullat et al., 2000). More recently empirical cumulative distribution functions (ECDF) have been used to detect and remove outliers in large sedimentary metal data sets (Rodriguez et al., 2006). The mean of discrete uni-modal metal populations and the mean of the lowest sub-group for polymodal distributions were inferred as the pre-anthropogenic metal concentrations (Rodriguez et al., 2006).

Sediment chemistry data, however are commonly not normally or log-normally distributed due to the presence of multiple processes controlling elemental distribution and may comprise numerous subgroups (multimodal) (Reimann and Filzmoser, 2000). Also, all sediment samples in some harbour estuaries are contaminated to some degree and two distinct sub-populations (contaminated and pristine) are not present (Birch and Taylor, 2002a).

2.1.2. Empirical methods to estimate background metal concentrations

Empirical techniques use geochemical data from uncontaminated sediment derived from subsurface sediment below the anthropogenic section by coring (Thevenon et al., 2011), or from pristine surficial sediment in control areas of the same ecosystem. Use of pristine estuarine sediment is often not possible due to the global nature of atmospheric contamination and is commonly difficult for highly-populated, contaminated seaboards. The frequently employed global mean concentrations (crustal or shale) as background concentrations do not relate to local conditions and are increasingly being disregarded (Matschullat et al., 2000; Kaber, 2011). The use of catchment geology, soils and fluvial sediments to estimate background estuarine metal concentrations (Carral et al., 1995; Salminen and Tarvainen, 1997; Prohic and Juracic, 1989; Rubio et al., 2000) are more appropriate as data are derived from local source materials, however the relationship between the chemistry of the catchment and mixed saline estuarine conditions is complex.

2.1.3. Normalisation of background metals data

Background concentrations based on total sediment are compromised by grain-size effects, e.g. the lowest metal concentrations in the pre-anthropogenic section would be for quartzitic and calcareous sands, which would have concentrations close to zero. If total sediment is used for background, material of comparable texture and organic content to the material being investigated would have to be selected for each sample being analysed (Maher et al., 1999). This process is tedious and introduces inaccuracy.

Various forms of normalisation have been used to reduce confounding introduced by variable grain size, or more correctly variable grain surface area. (Loring, 1991; Clark et al., 2000; Birch, 2003; Mudge et al., 2003; Birch et al., 2008b), however the most common methods are size- and elemental normalisation techniques.

Chemicals are partitioned primarily to fine sediment particles (<4 mm), typically clay minerals due to an increased surface charge (cation exchange capacity) and exponential increase of surface area with decreasing particle size (Forstner, 1982; Bubb et al., 1990). Finely-disseminated organic material also absorbs surface contaminants. Size normalisation is usually undertaken by physical fractionation by sieving (usually 62.5 μm) (Birch and Olmos, 2008). Elemental methods involve normalisation of anthropogenic metals to a conservative element, which acts as a proxy for fine-grained material and which is not associated with human activity (Matthai and Birch, 2001, Matthai et al., 2002). The most common normalisation elements are Al (Windom et al., 1989) and Fe (Hornung et al., 1989), however these elements should be used cautiously as Al may be regionally specific (Windom et al., 1989) and Fe is a common diagenetic surface oxide and may be affected by redox potential.

2.2. Techniques used to determine the magnitude of anthropogenic change

Methods employed to determine the magnitude of anthropogenic change may, or may not use background concentrations and may incorporate normalised or un-normalised (total sediment) data. Some of these techniques are reviewed by Caeiro et al. (2005), Brady et al. (2015) and Birch, 2016.

2.2.1. Methods using background concentrations and normalised data

The magnitude of human-induced change is frequently estimated by expressing current sediment metal concentrations as enrichment over pre-anthropogenic concentrations. To be valid this approach requires that both the current data and pre-anthropogenic concentrations to be normalised (size or elemental) to reduce the confounding due to variable grain size (Buat-Menard, 1979).

Enrichment Factors (EF) using size-normalised data (Szefer and Skwarzec, 1988) are simply the current metal concentration in sediment fine fraction (<62.5 μm)/metal concentration in fine background material. Alternatively, Enrichment Factors using total sediment chemistry and a normalizing element (Al) (Buat-Menard, 1979) are expressed as (total current sediment metal concentration / total current Al sediment metal concentration) / (total background sediment metal concentration / total sediment Al background metal concentration).

Another popular indicator of contamination level is the Geo accumulation Index expressed as $Igeo = \log_2(\mathrm{Cn} / 1.5 * \mathrm{Bn})$ (Müller, 1979). Where C is the total sediment concentration of metal, B is the geochemical background concentration of the average continental shale. A factor of 1.5 is included for possible variation due to lithogenic effects and an index of enrichment is provided (Müller, 1981). Other methods using background concentrations include, Degree of Contamination, which employs a reference level and the new Geo accumulation Index, which uses regional background based on a range of sediment sizes (Caeiro et al., 2005).

2.2.2. Methods without background concentrations, or normalized data

These techniques include the Pollution Index (PI) (Johansson and Johansson, 1976), which is the highest metal concentration in a location multiplied by a weight based on the reciprocal of the median observed concentration and the Metal Pollution Index (MPI) (Usero et al., 1996), which is the aggregation of concentrations for each element at a location. The Marine Sediment Pollution Index (Shin and Lam, 2001) is the sediment quality rating of a contaminant multiplied by a weight based on the results of principal component analysis. More complex techniques are sorption hypothesis (Song et al., 2014) and calculating pollutant ‘stocks’ in the upper sediment (Critto et al., 2005).

The performance of these environmental indices based on comparability, representativeness, credibility, simplicity, sensitivity and acceptability found the Marine Pollution Index and the Marine Sediment Pollution Index to rank highest (Caeiro et al., 2005). A recent review of indices (Birch, 2016) found the Mean Enrichment Quotient used in the present work amongst to top performing techniques.

3. Assessment of biological risk posed by sedimentary contaminants

Chemical concentrations *per se* do not provide an effective means for determining potential adverse effects on benthic resources. To assess the biological significance of contaminants bound to sediments information on persistence, toxicity, bioaccumulation and effect on the structure of biological communities are needed. These tests require a high degree of expertise, are time consuming and expensive. Instead, sediment quality guidelines (SQG) are commonly used to make preliminary assessments of sediment toxicity when direct biological effects information is unavailable. Empirical methods, employing matching sediment chemistry and biological effects data, have been used in development of SQGs for determining adverse outcomes of contaminants on biological populations using total sediment chemistry. Numerical-effects based SQGs are now in common use globally as a screening management tool to identify and prioritise contaminants and regions of concern (Hyland et al., 2000; Belin et al., 2014; Simpson et al., 2016).

3.1. Schemes based on sediment quality guidelines

There are a number of sediment quality effects-based guidelines, which have been established. The apparent-effects threshold (AET) scheme identifies sediment concentrations above which a statistically significant biological effect is observed for a given chemical. Screening level concentrations (SLC) provide the highest concentration of a contaminant that can co-occur with approximately 95% of a specific infauna. However, the most commonly used SQG for estuarine and marine environments is the US National Oceanic and Atmospheric Administration (NOAA) scheme (Long and Morgan, 1990; Long et al., 1995a, b and 2000). Concurrent sediment chemical and biological data from the laboratory and field for a variety of techniques and benthic end points were tabulated. Chemical concentrations and observed biological effects were sorted to identify the effects range low (ERL, lower tenth percentile of effects) and the effects range median (ERM, fiftieth percentile of effects) concentrations. The former level identifies the concentration below which adverse biological effects are seldom observed and the latter level distinguishes concentrations above which adverse biological effects occur frequently. Concentrations between the two levels are concentrations exhibiting irregular biological response. This approach is similar to the Threshold (effects/no effects concentration) (TEL) and Probable Effects (PEL) Level scheme developed for Florida (MacDonald et al., 1996), which includes no effects data. A wide range of chemicals, including organic and metallic contaminants, has been incorporated into these SQGs and the approach is now well established in North America and in many countries in Europe, Asia, South America and Africa (Long et al., 2000; Hyland et al., 2000; 2003; Belin et al., 2014; Simpson et al., 2016).

Contaminants do not occur as single chemicals within marine sediments and a number of schemes have been developed to assess the effects of chemical mixtures for aquatic sediments (Long et al., 1998, 2000, 2006; Long et al., 1998; Fairey et al., 2001). The mean ERM quotient (MERMQ) scheme requires normalising the concentration of each chemical with respect to its ERM value, summing the quotients for each substance and dividing by the number of chemicals for which guidelines are being used. MERMQ ranges of >1.5; 1.5–0.5; 0.5–0.1 and <0.1 have been related to the probability of toxicity (76%, 49%, 21% and 9%, respectively) in amphipod assemblages (Long et al., 1998). The number of ERL and ERM exceedances has also been related to toxicity through whole sediment bioassays (Long et al., 1998; Birch and Taylor, 2002a, 2002b, 2002c). However, these relationships should be used with caution due to area-specific nature of benthic populations and sedimentary chemicals and instead the MERMQ is considered in this work and in other studies as a level of risk of adverse effects to sediment-dwelling animals, rather than a probability of toxicity (Birch and Taylor, 2004; Birch et al., 2008a; Birch and Olmos, 2008). Hyland et al. (2000) found sediments to be degraded at considerably lower levels than predicted by MERMQs due to the increased sensitivity of multiple species and to long-term chemical exposure under marine field conditions,

Although PEL/TEL and ERL/ERM SQGs are the most widely used methods of assessing the quality of sediment, a vast array of other methodologies, also based on sediment guidelines, has been employed to estimate benthic effects due to sedimentary contaminants (Caeiro et al., 2005). The Pollutant Load Index (PLI) (Wilson and Jeffery, 1987) includes a minimum threshold associated with degradation, or reduction in estuarine quality; the Equation Sub-index Sediment Quality (Ferreira, 2000) is evaluated by sediment contamination, bioaccumulation and biodiversity; the Logistic Regression Model (Field et al., 2002) evaluates the probability of acute toxicity based on amphipod mortality tests; and the Potential Ecological Risk Index (Riba et al., 2002) compares sediment concentrations to the highest level of metal having no adverse biological effect. The Mean Sediment Quality Guideline Quotient of Ingersoll and MacDonald (1999) and another by Fairey et al. (2001) of the same name (SQGQ1) are similar to the MERMQ developed by Long et al. (2006). When these indices are judged for performance based on comparability, representativeness, credibility, simplicity, sensitivity and level of uncertainty, the NOAA SQGs were found to be superior (Caeiro et al., 2005). A new sediment assessment method, the 'Hazard Index' a complex scheme incorporating 58 physio-chemical parameters and several 'normalisation' procedures, produced the same result as the MERMQ (Mali et al., 2016).

3.2. Schemes not based on sediment quality guidelines

Other approaches, not associated with SQGs, include equilibrium partitioning, assessment of bioavailability, tissue burden, AVS-SEM (acid volatile sulfides-simultaneously extracted metals) and porewater concentrations. These techniques are at another level of complexity and not without challenges. The equilibrium partitioning approach is based on the assumption that the critical factor controlling sediment toxicity is the concentration of contaminant in sediment porewater. Sediment quality is predicted using LC50 values obtained from water only toxic tests. The method is most applicable to hydrophobic organic chemicals based on a partition coefficient (K_D), which is the ratio of contaminant concentrations in sediment and the concentrations in ambient porewater. Equilibrium partitioning applied to metals may be confounded by metal bioavailability in oxic sediments due to dissolved organic and metal binding phases, i.e. hydrous iron and manganese oxide phases. In anoxic sediments, solubility may be regulated by insoluble metal sulfides. The ratio of acid volatile sulfide (AVS) to the concentration of simultaneously extracted metals (SEM) provides a measure of metal toxicity. If the ratio is less than one, sediments may be toxic. However, if the ratio exceeds unity, no toxicity may be exhibited because total metal concentrations are too low. The unstable nature of AVS may also result in oxidation during sampling or handling or in the natural environment by bioturbation reducing the predictability of the SEM-AVS method (Simpson et al., 2005). Analysis of porewater is difficult due to low concentrations and large matrix complications. Porewater guidelines might be inappropriate in cases where contaminants are formed as a result of chemical and microbial processes. Determining tissue burden is fraught with difficulties associated with physiochemical conditions of the ambient environment and tissue concentrations varies for different species, ages, organs and gender, moreover metals are often regulated or excreted by benthic organisms.

Ultimately, the most comprehensive assessment of the status of estuarine sediment is the use of multiple lines of evidence, usually incorporating sediment chemistry, ecotoxicology and benthic community structure. Additional indicators may be included, e. g. bio-availability, bio-accumulation, EVS-SEM and porewater chemistry and assessed within a weight of evidence (WOE) matrix. The most economic and efficient approach to acquire these data are through a decision tree approach whereby the simplest and least expensive analyses are undertaken first and if the results exceed certain thresholds, additional, more complex/expensive analyses are carried out (ANZECC/ARMCANZ, 2000). Such analyses are beyond the ability of many jurisdictions and are not appropriate for a screening assessment, such as being proposed in the current work.

4. Anthropogenic change and biological risk applied to Sydney estuary sediments

Sydney estuary and the distribution of sedimentary contaminants are described briefly before a discussion on the methodology chosen to assess anthropogenic change and biological risk.

4.1. Sydney estuary

Sydney estuary is central to the largest capital city in Australia and through an extensive system of embayments and tributaries, the waterway is accessible to a large proportion of the four and a half million inhabitants (Fig. 1). 'Sydney estuary' is used in the current paper to describe the entire estuarine system, rather than 'Sydney Harbour' or 'Port Jackson', which refers to restricted parts of the waterway (McLoughlin, 1985; Birch and McCready, 2009). Until recently the harbour was a busy commercial and naval port and the shoreline, especially in the upper reaches, was lined by major industries (Birch et al., 2015a). In the last two decades industries have moved away from Sydney estuary, including shipbuilding and repair yards and army and navy facilities have been relocated. Extensive shoreline industrial sites have been demolished and the foreshore is rapidly changing into prestigious, expensive, high-rise housing communities (Birch et al., 2015b).

Sydney estuary catchment (500 km^2) is highly industrialized and urbanized (76%) (Birch et al., 2015a) and the estuary (30 km long, up to 3 km wide and 50 km^2) is a dendritic, drowned river valley (Roy, 1983), while the water is generally well-mixed marine (Lee et al., 2011; Birch and McCready, 2009), Sediments in the estuary are subject to significant contamination by metals, nutrients, polycyclic aromatic hydrocarbons (PAHs) and organochlorine compounds (OCs) (Birch and Davey, 1995; Birch et al., 1999; Birch and Taylor, 2000a; McCready et al., 2000, 2004, 2006a, 2006b, 2006c) and the waterway is classified as "severely modified" by the National Audit of estuaries

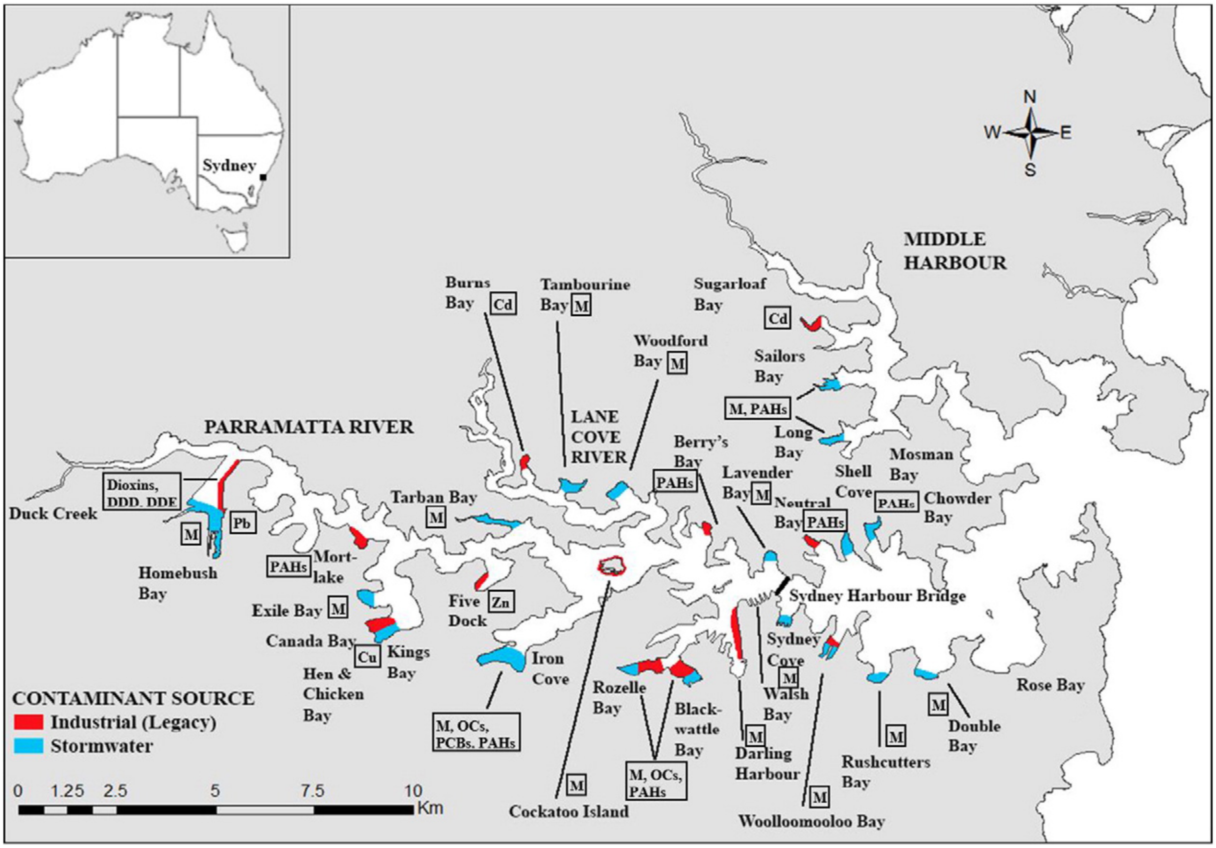

Fig. 1. Sydney estuary with locations mentioned in the text and distribution of stormwater (blue) and industrial (red) sources of contaminant. M = metals; OCs = organochlorine compounds; PAHs = polycyclic aromatic hydrocarbons; PCBs = polychlorinated biphenyls.

(NLWRA) (OzCoast, 2000; NLWRA, 2002). A clear understanding of the severity and distribution of contamination, as well as the risk to benthic populations, are needed before a coherent strategy can be introduced to successfully manage and restore this catchment-estuary system.

4.2. Concentrations of surficial sediment contaminants in a global perspective

Metal concentrations in sediments of Sydney estuary (Tables 1 and 2) are some of the highest reported in New South Wales (Table S1) and Australia (Table 2) (only surpassed by a small number of industrial sites, e. g. Derwent River, Spencer Gulf, Lake Macquarie and Macquarie Harbour) (Birch, 2000) and are more impacted by metals than most global harbours (Birch and Taylor, 1999) for size-normalised (Table 3) and total sediment (Table 2). Maximum metal concentration are generally higher for size-normalised data than for total sediment, however for Cd and Zn this not so, indicating some of these metals are associated with moderately large (>62.5 m), metal-rich particles, possibly marine and fishing debris (Table 1). Minimum metal concentrations for total sediment for a small number of samples are below detection due to these sediments comprising coarse-grained quartzitic or calcareous materials. Minimum fine fraction concentrations approach background values for some elements (Pb) for a restricted area close to the estuary mouth. For other estuaries and harbours, less modified than Sydney, many samples may have normalized metal concentrations approaching local background values.

Surficial sediment OC concentrations are the highest of any Australian estuary and are some of the highest reported for harbours worldwide (Table 4). However, Victoria Harbour, China (total chlordane), Cochin estuary India (hexachlorobenzene, HCB) and Sarasola Bay, USA (H-epoxide) report higher concentrations of some OC compounds. Mean PAH values in Sydney estuary are only surpassed by sediment concentrations in Yangpu Bay, China for naphthalene (Table 5), although Townsville Harbour and Greenwick Bay (Australia) have high levels of several PAH compounds. Sydney estuary sediments contain higher concentrations of Total PAHs, Total polychlorinated biphenyls (PCBs), Total DDTs (dichlorodiphenyltrichloroethane) and fluoranthene compared to studies of single chemicals (Table S2), however Total PAHs, Total PCBs and fluoranthene are high in sediments of South Carolina (USA), Venice (Italy) and Lorain (USA), respectively. Although several harbours have higher OC and PAH concentrations, sediments of Sydney estuary appear to contain anomalously high metal levels compared to global ports.

4.3. Distribution of surficial sediment contaminants in Sydney estuary

Spatial distributions for samples (Fig. 2) and contaminants (Figs. 3 and 4) were determined by kriging interpretation using the Geostatistical Analyst tool in ArcGIS. The distribution and numbers of surficial (<2 cm depth) sediment samples analysed for contaminants are provided in Fig. 2A–C and Table 1, respectively. The field and laboratory methodologies are described in detail in Birch et al. (2013) and were consistent over the last decade that the samples were collected.

Sedimentary metal concentrations decline markedly from the upper reaches of the estuary towards the mouth and with distance from the headwaters of offchannel embayments and tributaries in the central estuary due to stormwater discharge. Sediments of the four south, central embayments of Blackwattle/Rozelle Bay, Iron Cove, Hen and Chicken

Table 1
Contaminant concentrations in fine fraction (<62.5 μm) and total sediment in Sydney estuary.

	No. samples	Minimum	Maximum	Mean	ERL	ERM	ISQG-L	ISQG-H	LOR
Total sediment metals (μg/g)									
Cd	728	Bd	52	1.0	1.2	9.6	1.5	10	0.1
Co	948	Bd	29	5.3	na	na	na	na	na
Cr	836	Bd	298	77	81	370	80	370	0.1
Cu	1168	Bd	1060	133	34	270	65	270	1.0
Ni	1075	Bd	118	15	21	52	21	52	1.0
Pb	1173	Bd	1932	210	47	218	50	220	1.0
Zn	1178	Bd	11,300	486	150	410	200	410	1.0
Fine (<62.5 μm) sediment metals (μg/g)									
Cd	802	Bd	24	1.1	na	na	na	na	na
Co	1082	2.8	33	8.5	na	na	na	na	na
Cr	738	37	346	108	na	na	na	na	na
Cu	1137	9.2	1225	214	na	na	na	na	na
Ni	1088	9.8	118	22	na	na	na	na	na
Pb	1138	38	3841	355	na	na	na	na	na
Zn	1136	71	8411	745	na	na	na	na	na
Total sediment organochlorine compounds (μg/kg)									
Lindane	159	Bd	120	1.5	na	na	0.32	1.0	0.5
Chlordane	158	Bd	416	63	na	na	0.5	6.0	0.5
Diedrin	180	Bd	162	11	na	na	0.02	8.0	0.5
Endrin[a]	12	4.1	24	10	na	na	0.02	8.0	0.5
Total DDT	173	Bd	5384	43	1.6	46	1.6	46	0.5
Hexachlorobenzene	190	Bd	1620	26	na	na	na	na	na
Polychlorinated biphenyls (PCBs) (μg/kg)									
Total PCBs	286	Bd	2601	109	23	180	23	na	5
Total sediment polycyclic aromatic hydrocarbons (PAHs) (μg/kg)									
Naphthalene	213	1.2	13,187	289	160	2100	160	2100	10
2-Menaphthalene	205	Bd	10,056	190	70	670	na	na	10
Acenapthylene	215	0.6	13,072	509	44	640	44	640	10
Acenaphthene	209	Bd	1300	79	16	500	16	500	10
Fluorene	212	Bd	2356	138	19	540	19	540	10
Phenanthrene	223	1.9	26,263	1311	240	1500	240	1500	10
Anthracene	215	0.6	5810	487	85	1100	85	1100	10
fluoranthene	231	3.3	60,361	3034	600	5100	600	5100	10
Pyrene	233	3.9	64,682	3520	665	2600	665	2600	10
Benz(a)anthracene	224	6.7	29,201	1607	261	1600	261	1600	10
Chrysene	224	3.1	26,128	1615	384	2800	384	2800	10
Benzo(a)pyrene	226	3.2	45,323	2292	430	1600	430	1600	10
Dibenz(ah)anthracene	213	Bd	4216	290	63	260	63	260	10
Total PAHs	238	Bd	460,336	21,782	23	180	23	na	20

Bd = below detection; na = not available. ERL = effects range low; ERM = effects range median; ISQG-L and -High = interim sediment quality guidelines-low and -high; LOR = level of reporting.

[a] Not included in Fig. 4D.

Bay and Homebush Bay consistently contain the most widespread distribution and highest concentrations of metals (and most other contaminants) (Fig. 3 for Pb). Moderate metal concentrations are confined to the western embayments of Middle Harbour, especially Long and Sugarloaf Bays. Sediment metal concentrations are generally lower in the upper parts of Lane Cove, Middle Harbour and Parramatta River and are lowest at the estuary mouth.

Individual embayments have distinctive metal distributions in Sydney estuary. Sediments in Homebush Bay generally have only moderate concentrations of all metals, except for high Pb levels in the south east related to paint manufacturing (Fig. 1). Surficial sediments in Hen and Chicken Bay have high Cu concentrations originating from bronze processing, whereas sediments of Iron Cove are elevated in Pb and Cd due to historical industrial discharge. Backwattle/Rozelle Bay is highly enriched in Cu, Pb and Zn from shoreline heavy industry, whereas Cr is anomalously high in sediments of Sugarloaf Bay in northwest Middle Harbour and in Burns Bay in Lane Cove derived from tanning industries.

High concentrations of many OC compounds occur in sediments in restricted parts of the upper reaches of embayments and tributaries throughout the estuary. Chlordane is the most widespread OC and is present in sediments of the four south, central embayments, as well as in southern bays in the lower estuary, whereas DDT and analogues DDD and DDE are in high concentrations mainly as legacy contaminants in Homebush Bay and is associated with stormwater discharge in Iron Cove and southern embayments of the upper estuary. Other cyclodiene compounds (aldrin, dieldrin, heptachlor and heptachlor-epoxide) are present in sediments at lower concentrations, mainly in Iron Cove and small embayments in the upper estuary. PCBs and HCBs are contained in sediments mantling Homebush Bay and the upper reaches of small embayments on the southern shores of central estuary. Total PAHs are elevated in sediments of upper Iron Cove and in the upper reaches of many embayments of the lower estuary. Sediment at Mortlake and Neutral Bay contain extremely high point sources of PAHs (240,000 μg/kg and 380,000 μg/kg, respectively). The PAHs are predominately high-molecular weight compounds, characteristic of high-temperature combustion, suggesting that fuel consumption by internal combustion engine and coal-fired power stations are likely sources of these chemicals (McCready et al., 2000). Sediments in Duck River contain PAHs with a high abundance of low-molecular weight compounds, indicating a source of un-burnt fuel.

High concentrations of organic anthropogenic chemicals are mainly as legacy contaminants in Homebush Bay, Blackwattle/Rozelle Bay and

Table 2
Sydney estuary and global metal concentrations in total surficial sediment (μg/g).

Estuary	Reference	Cd	Cr	Cu	Ni	Pb	Zn
Australian harbour estuaries							
Sydney estuary, Australia	1	1.1	108	214	22	355	745
Corio Bay	2	0.6–15	2–6	6–10	4–9	44–80	45–94
Port Phillip Bay	2	Bd-6	8–115	1–62	2–66	2–197	13–830
Port Adelaide	2	Bd-3.4		11–293		10–329	30–403
Darwin Harbour	2	0.8–3		4–32		22–91	16–270
Brisbane River	2	Bd-2	13–54	3–30		20–82	41–144
Port Hunter	2	Bd-8	21–167	19–283	44–156	25–843	32–5161
Macquarie Harbour	3			666		41	150
				8–1395		6–118	9–380
Lake Macquarie	4	11	20	39	8	134	377
		Bd-168	2–106	2–106	Bd-13	9–836	17–2215
Lake Macquarie	5	23		32		309	525
		2–660		5–420		5–7050	6–6250
Derwent River	3	50–10,400	0.5–258	5–10,100	1–4.2	5–42,000	1–1400
Spencer Gulf	3	Bd-267		3–122	12–19	3–5270	11–16,667
Port Pirie	3	Bd-150	Bd-40	Bd-170		Bd-5000	Bd-6000
International harbour estuaries							
Bristol Channel, UK	6	1.1		54	33	88	255
	6	Bd-24	37–346	9.2–1225	9.8–118	38–3841	71–8411
Fraser River, Canada	6	Bd-0.4	Bd-61		Bd-55	Bd-24	Bd-220
Macao, China	6	0.3–8	4–39			19–67	
Tokyo Bay, Japan	6	0.5–1.4	29–126	16–80	16–44	25–58	106–405
Clyde estuary, UK	6	0.4–9		3–172		12–215	34–590
Ten Greek Gulfs, Greece	6			5–188	40–400	10–500	30–1500
Six South African Harbours	6	Bd-0.6	2–114	3–102	4–28	2–88	17–287
Haifa Bay, Israel	6	Bd-1		1–41		4–30	4–109
Cork Harbour, Ireland	6			Bd-0.2	12–16	18–44	65–124
Forty USA bays/harbours	6	Bd-5.9	23–2296	1–218		2–186	144,820
Venice, Italy	6	Bd-2	41–106	11,902	14–20	17–306	77–306
Hebe Harbour, China	6	Bd-0.9	28–87	21–87	7–13	27–42	87–106
Thames estuary, UK	6	Bd-3	24–123	24–123	21–55	63–465	115–401
Hudson Raritan estuary, USA	7	1.8	154	173	41	182	314
		Bd-6	33–420	3–520	5–130	14–520	30–1400
San Diego, USA	7	Bd	84	84	9	25	154
		Bd-3.1	Bd-340	Bd-660	Bd-69	Bd-250	Bd-1600
Tampa Bay	7	1.0	54	44		56	135
		Bd-76	2–167	0.7–348		1.3–346	2.1–1260

Bd = below detection. Single figures are mean concentrations.
References: 1 This work; 2 Birch and Taylor, 2004; 3 Birch, 2000; 4 Olmos and Birch, 2010; 5 Roy and Crawford, 1984; 6 Birch and Taylor, 1999; 7 in house data.

Table 3
Sydney estuary and global normalised (<62.5 μm) metal concentrations in surficial sediment (μg/g).

Estuary	Reference	Cd	Co	Cr	Cu	Ni	Pb	Zn
Sydney estuary, Australia	1	1.1	8.5	108	214	22	355	745
		Bd-24	2.8–33	37–346	9.2–1225	9.8–118	38–3841	71–8411
Hong Kong, China	2	0.33		49	119	25	54	148
China		0.1–5.3		5–560	1–4000	5–220	9–260	17–790
Quanzhou Bay	3	0.59		82	71	33	68	180
Quanzhou, China		0.3–0.9		51–122	25–120	16–46	34–101	106–242
Tamaki Estuary	4	0.28			35		73	207
Auckland, New Zealand		0.1–1.0			21–47		51–122	138–272
Qua Iboe Estuary	5			0.014	44	21	45	102
Niger Delta, Nigeria				0.01–0.02	43–45	21–21	43–46	102–104
Lima Estuary	6			57	45	14	37	111
Viana do Castelo, Portugal				24–84	16–406	46,447	19–64	59–398
Port of Barcelona	7	1.22		68	183	25	189	391
Barcelona, Spain		0.4–2.8		39–110	71–531	18–34	86–589	183–1133
Gulf of Gemlik			19	117	41	110	29	128
Sea of Marmara, Turkey	8		13–24	71–181	23–58	35–165	0.1–67	88–185
San Pablo Bay		0.21		21	39	37	22	65
San Francisco, USA	9	0.1–0.4		15–39	25–49	27–45	15–27	48–79
Montevideo Harbour	10			161	89	30	85	312
Montevideo, Uruguay				79–253	59–135	26–34	44–128	174–491
Gulf of Paria	11			29	14	18	13	89
Venezuela/Trinidad				10–40	5–22	5–24	1–37	48–158

Bd = Below detection. Single values are mean concentrations.
References: 1 This work; 2 Zhou et al., 2007; 3 Yu et al., 2008; 4 Abrahim and Parker, 2008; 5 Udofia et al., 2009; 6 Cardosa et al., 2008; 7 Guevara-Riba et al., 2004; 8 Ünlü et al., 2008; 9 Lu et al., 2005; 10 Muniz et al., 2004; 11 Rojas de Astudillo et al., 2005.

Table 4
Organochlorine pesticides and PCB concentrations in sediments from Sydney estuary and other Australian and global harbour estuaries (μg/kg).

	Reference	Total chlordane	HCB	Lindane	Dieldrin	Aldin	Heptachlor	H - epoxide	Endrin	Total PCBs	Total DDT
Australian harbour estuaries											
Sydney estuary	1	63	26	1.5	11.1	8.0	3.4	1.2		183	43
		Bd-416	Bd-1620	Bd-120	Bd-162	Bd-391	Bd-70	BD-15		Bd-2601	Bd-5384
Hawkesbury River	1	7.4	0.6	0.5	3.5	12	0.2	0.2			
		Bd-52	Bd-4.1	Bd-13	Bd-38	Bd-391	Bd-7.1	Bd-6.3			
NSW Continental shelf	1	Bd-15	Bd-70	Bd-7.9	Bd-8.0	Bd-5.9	Bd-6.6	Bd-1.3		Bd-3077	
Perth	1									<10	
Derwent River	1									7–47	
Port Philip, offshore	1									<10–59	
Port Philip, inshore	1									18–390	
Corio Bay offshore	1									<10–86	
Corio Bay inshore	1									14–810	
Port River, Adelaide	1	Bd-0.2		Bd	Bd	Bd	Bd	Bd		Bd	
Queensland ports	1									6–550	
International harbour estuaries											
Victoria Harbour, China	1	1.3–2233									1.4–97
San Francisco, USA	1	Bd-2									Bd-9
Sarasota Bay, USA	1	Bd-27			Bd-17	Bd-22	Bd	Bd-43			
Kingston Habour, Jamaica	1			0.5–0.8	Bd-17	9.2–37					
Manukau Harbour, NZ	1	0.2–1.3		Bd-1.4	0.3–0.5		Bd-1.6	Bd-0.3		0.5–14	
Firth of Forth, UK	1			Bd-0.64						Bd-27	Bd-2.5
Cochin estuary, India	2				142				59		163
Port of Spain, Trinidad	3	1.5	0.3		6.5				1.6		102
Izmir Bay, Turkey	4		0.04	0.2	1.0				4.3	44	6.0
Yangtze River estuary, China	5	0.1	0.3								1.7
Hudson Raritan estuary, NY	6	12	5.4	Bd	3.5	1.5	Bd	0.4	Bd	353	259
		Bd-34	Bd-19	Bd	Bd-14	Bd-13	Bd	Bd-6.3	Bd	6–1973	1–921
San Diego, USA	6	4.8	Bd	Bd	Bd	Bd	Bd	Bd	Bd	94	13
		Bd-473	Bd-3.2	Bd-0.4	Bd-6.3	Bd-0.8	Bd-4.5	Bd-1.4	Bd	Bd-1987	Bd-291
Tampa Bay, USA	6	17		5.1	2.6	1.5	4.7	1.0	10	262	107
		Bd-473		Bd-157	Bd-19	Bd-21	Bd-214	Bd-25	Bd-392	0.9–8338	Bd-3802

Bd = below detection. Single values are mean concentrations.
References: 1 in Birch and Taylor, 2000a, 2000b; 2 Akhil and Sujatha, 2014;3 Barakat et al., 2013; 4 Mohammed et al., 2011; 5 Pazi et al., 2011; 6 in house data.

other restricted localities, but are associated with current and historical stormwater discharge in the upper reaches of Iron Cove, Hen and Chicken Bay and Rose Bay.

4.4. Magnitude of anthropogenic change

The choice of which statistical or empirical method to use for determining the magnitude of anthropogenic change depends on the characteristics of the ecosystem being assessed. Statistical approaches identify two sub-populations within a data set separating pristine from contaminated data, however in Sydney estuary all samples are modified and establishing a threshold (background concentration) separating natural from anthropogenic material is not possible using statistical methods (King, 2004). This problem may be apparent for many of the large, older harbours of the world.

Empirical methods employed to determine background concentrations using pristine fluvial samples discharged to the estuary and other potential source material, i.e. catchment soils and shales, proved to be inappropriate. The major lithology in Sydney estuary catchment (Hawkesbury Sandstone) contains twice the Zn concentration of global sandstone, a third of global shale and half the level of local estuarine sediments (King, 2004). Fluvial sediments entering the estuary (Shulkins, 1994; Fanous, 1996) and catchment soils (Birch et al., 2010; Hodge, 2002) are several orders more elevated in Cu, Pb and Zn than the lowest concentrations (background) observed in Sydney estuary sediments due mainly to stormwater sourced from a highly urbanized catchment (Snowdon and Birch, 2004; Birch and Rochford, 2010) and could not be used to determine pristine levels (King, 2004). These results will undoubtedly be repeated in other highly urbanised and industrial catchments.

In Sydney estuary, the most appropriate approach to establish background metal concentrations is by obtaining sediment deposited prior to European settlement. Background metal concentrations have been taken from dated (12) and undated sedimentary cores ($n = 109$) retrieved from all parts of the estuary demonstrating continuous deposition and an absence of re-mobilisation by chemical, physical and biological mechanisms (Taylor et al., 2004). Even in estuaries with some pristine areas, sedimentary cores have the advantage of providing temporal information, including the date of onset of contamination, sedimentation and relaxation rates. Sedimentary cores are considered highly advisable in the assessment of estuarine condition (Maher et al., 1999).

Background metal concentrations vary spatially and are not valid for regional assessments due to changes in geology and vary between different biogeographic provinces. A large range in pre-settlement metal concentrations was determined by coring in 38 estuaries over 600 km of coastline of central New South Wales (Table S1) (Birch et al., 2016). However, background metal concentrations are reasonably consistent across estuaries the size of the Sydney waterway (30 km long, 4 km wide) and have been determined to be 10 ± 2 μg/g, 33 ± 3 μg/g and 47 ± 4 μg/g for Cu, Pb and Zn, respectively (Birch et al., 2013).

In the current work a simple, quick and pragmatic, but scientifically sound methodology of estimating anthropogenic influence has been adopted, i.e. metal enrichment. To negate the effects of variable grain size, sample and background data have been size-normalised (<62.5 μm). This approach has been previously used successfully for local (Rubio et al., 2000; Birch and Taylor, 2004; Birch et al., 2008a) and regional assessment of human impact (Birch et al., 2016). A unique map of metal enrichment (Pb) in sediments of Sydney estuary is provided in Fig. 3B for the entire estuary.

Maximum enrichment for Sydney estuary is >100 times for Cu, Pb and Zn (Table 6), whereas mean enrichment for these metals are 12, 14 and 15, respectively. The concentration of at least one metal exceeds background values in all parts of the estuary (Birch and Taylor, 2002a,

Table 5

Polycyclic Aromatic Hydrocarbons (PAHs) in sediments of Sydney estuary and other Australian and global harbour estuaries.

	Reference	Na	2-M	Acy	Ace	Fl	Phe	An	Flt	Py	BaAn	Ch	Bapy	Daph
Australian harbour estuaries														
Sydney estuary	1	289	190	509	79	138	1311	469	3034	3520	1607	1615	2292	290
		1–13,187	Bd-10,056	1–13,072	Bd-1300	Bd-2356	2–26,263	1–5810	3–60,361	4–64,682	7–29,201	3–26,128	3–45,323	Bd-4216
Port Kembla	1	16		1.4	0.5	1.5	5.6	1.6	4.6	4.4	2.5	2.5	3.2	0.5
Townsville Harbour, Australia[a]	2					1400	4.2	1	na	4500	1700	1500	2600	1500
Herron Island, Great Barrier Reef[b]	3						<0.1	<0.1	<0.1	<0.01	<0.01	<0.01	<0.01	<0.01
Gladstone Harbour	3									270	180		820	
Brisbane Harbour	3						110–1490	30–390	340–2340	320–2260	120–890	190–970	170–1060	
Greenwick Bay	3								4509	4970			757	
Georges River	3						84–700	25–643	20–1713	6–2096	93–1503	73–774	5–1999	717–5674
Tomago River	3						8	7	8	4	2		0.2	0.1
Hawkesbury River	4	12	8.7	9.1	4.7	6.8	53.2	13	155	160	80	90	92	16
		2.5–24	2.5–20	2.5–38	2.5–19	2.5–30	2.5–156	2.5–41	2.5–517	2.5–483	2.5–253	2.5–290	2.5–300	2.5–57
International harbour estuaries														
Gulf of Mexico	5	21	1.5	2.6	13	5.2	13	1.8	5.2	6.8	2.0	2.2	8.4	na
Offshire Malaysia	6	31	22	29	29	22	15	26	24	21	37	48	28	50
Zhoushau Archipelago, China	7	0.5		0.04	0.3	0.3	1.6	0.3	1.4	2.3	1.1	2.2	1.1	0.2
Xianghau Harbour China	7	0.7		0.1	6.4	0.4	2.7	0.5	5.4	6.3	5.1	7.6	5.1	0.9
Capiberibe estuary Brazil	8	21		3.5	1	11	37	14	62	91	29	59	24	12
Yangpu Bay, China	9	579		33	53	101	390	54	245	339	175	220	175	75
Hudson Raritan estuary, NY	10	796	618	567	1553	1523	5736	2790	4604	5773	2595	2508	2819	270
		1–17,414	1–15,557	1–12,915	Bd-56,338	Bd-54,209	Bd-194,343	Bd-89,366	Bd-108,236	Bd-143,232	Bd-59,298	Bd-60,331	Bd-54,862	Bd-4534
San Diego, USA	10	9.2	10.8	14.9	18.6	46	318	260	721	661	326	515	499	78
(all minimums are Bd)		632	644	416	774	416	10,700	13,600	12,500	13,800	4710	8040	5410	810

All values in µg/kg. Single values are mean concentrations.

References: 1 This work and unpublished data, 2 Haynes and Johnson, 2000; 3 Maher and Aislabie, 1992; 4 Hornsby Shire Council, 2013;5 Ruiz-Fernández et al., 2015; 6 Masood et al., 2016; 7 Zang et al., 2015; 8 Maciel et al., 2015; 9 Li et al., 2015; 10 in house data.

Abbreviations: Na = napthalene, M2 = 2-methylnaphthalene, Acy = acenaphthylene, Ac = acenaphthene, Fl = fluorene, Phe = phenanthrene, An = anthracene, Flt = fluoranthene, Py = pyrene, BaAn = benzo(a)anthracene, Ch = chrysene, BaPy = benzo(a)pyrene, DaPh = dibenz(ah)anthracene.

[a] Maximum for the GBR, Townsville Harbour.

[b] Pristine area.

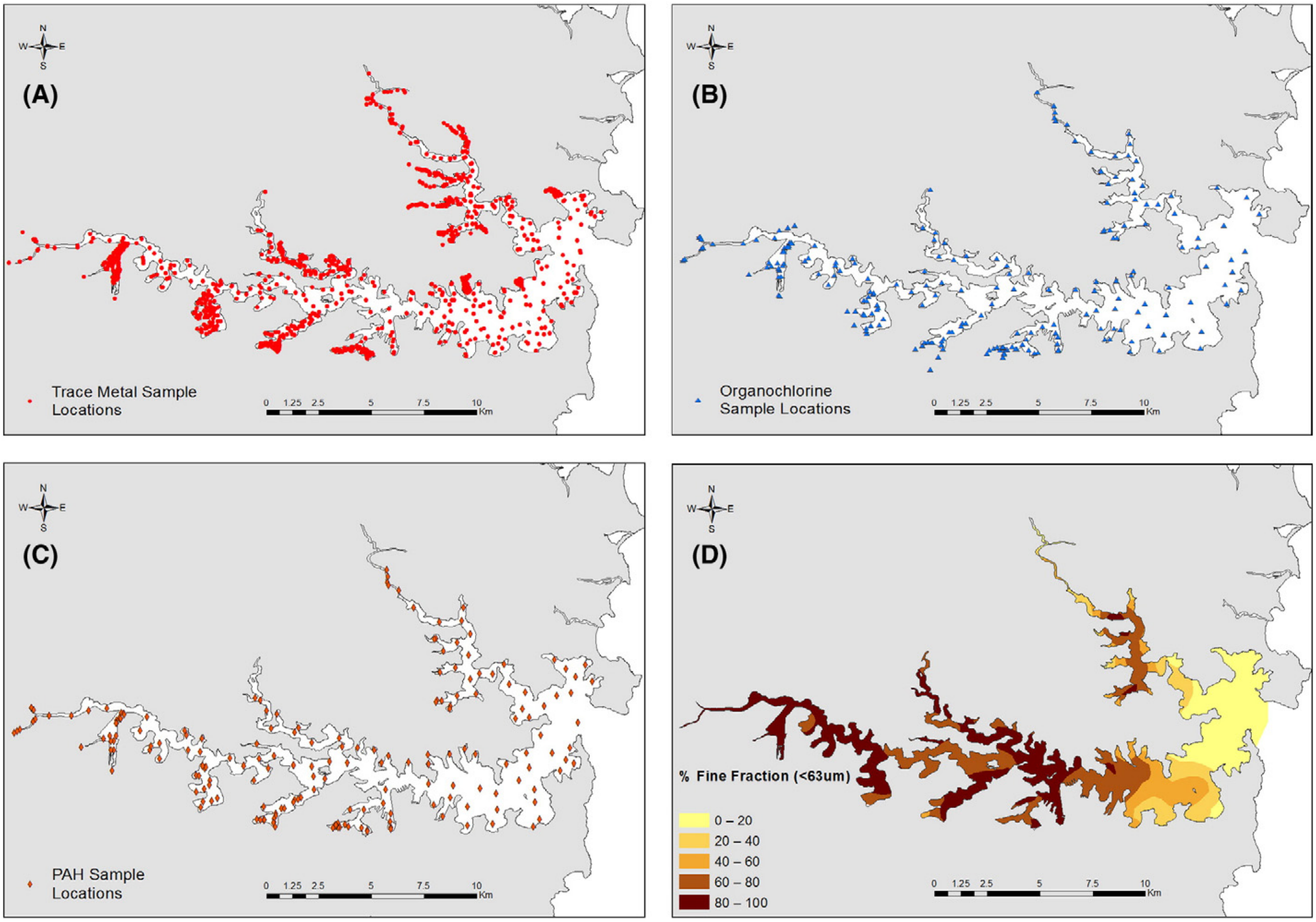

Fig. 2. Distribution of surficial sediment samples. (A) for metals; (B) for organochlorine compounds (OCs); (C) for polycyclic aromatic hydrocarbons (PAHs); (D) distribution of fine sediment (<63 μm).

2002b, 2002c). Copper is spatially the most widely enriched metal and sediment in the upper and middle estuary is enriched >10 times in this metal and in the lower estuary enrichment is greater than five times. The highest Cu enrichment is in sediments of Hen and Chicken Bay (>50 times) and the greatest Pb enrichment (>50 times) is in sediments of Blackwattle/Rozelle Bay, Iron Cove and some embayments of western Middle Harbour. Zinc enrichment is spatially less wide spread than Cu and Pb, however enrichment is >10 times in the upper estuary.

A suite of three metals (Cu, Pb and Zn) was combined into a Mean Enrichment Quotient (MEQ), whereby each metal is normalised to its background concentration and the total is divided by three to make a more integrated assessment of anthropogenic change (Brady et al., 2015) (Fig. 3). The MEQ is >10 times for sediment in the upper and middle estuary and >5 times for the lower estuary.

4.5. Biologic risk posed by sedimentary contaminants

An initial screening process for assessing estuarine condition requires a basic approach using easily acquired data, which is inexpensive to acquire and easily interpreted (Belin et al., 2014). The method requiring the least complex computation based on a SQG, either of effects or no effects data, is the most appropriate for initial assessments of large, impacted harbor/estuaries. The NOAA effects-based approach was used to assess risk of adverse biological effects in Sydney estuary sediments using the quotient approach (MERMQ) and the distribution of samples exceeding ERLS and ERMs.

Copper, Pb and Zn are the contaminants of most concern in sediments of Sydney estuary and areas of the waterway with sediment exceeding ERM concentrations for these metals represented approximately 2, 50, and 36% of the estuary, respectively (Birch and Taylor, 2002a, 2002b, 2002c). Sediment in the entire estuary, except a small area near the entrance, exceeded ERL concentrations for at least one metal. The risk of adverse effects due to sedimentary Pb is given in Fig. 3D.

Organochlorine pesticides exceeded ERM concentrations in sediment over extensive parts of Sydney estuary, including the seaward area, however sediments in only a small proportion of the waterway exhibit PCB concentrations above ERM values. Sediments in most of the upper and middle estuary, including Middle Harbour, has at least one OC, or PAH concentration exceeding ERM values.

The risk of adverse biological effects for the four major contaminant classes (metals, OCs, PAHs and PCBs) and for all contaminant types combined are presented in Fig. 4 (see Table 1 for individual chemicals included in each contaminant class). The MERMQ for metals is widespread and highest in the upper parts of embayments in the central estuary and is the contaminant posing the most biological risk. Sediments mantling Iron Cove, Hen and Chicken and Homebush Bays are high risk for OCs, whereas most adverse risk for total PAHs is in restricted parts of the central and upper estuary. The MERMQ for all contaminant classes combined was used to classify the estuary into 'risk areas' (Long et al., 2000). Sediments in the highest risk class (IV) are located mainly in embayments of the central estuary (Iron Cove, Rozelle Bay)

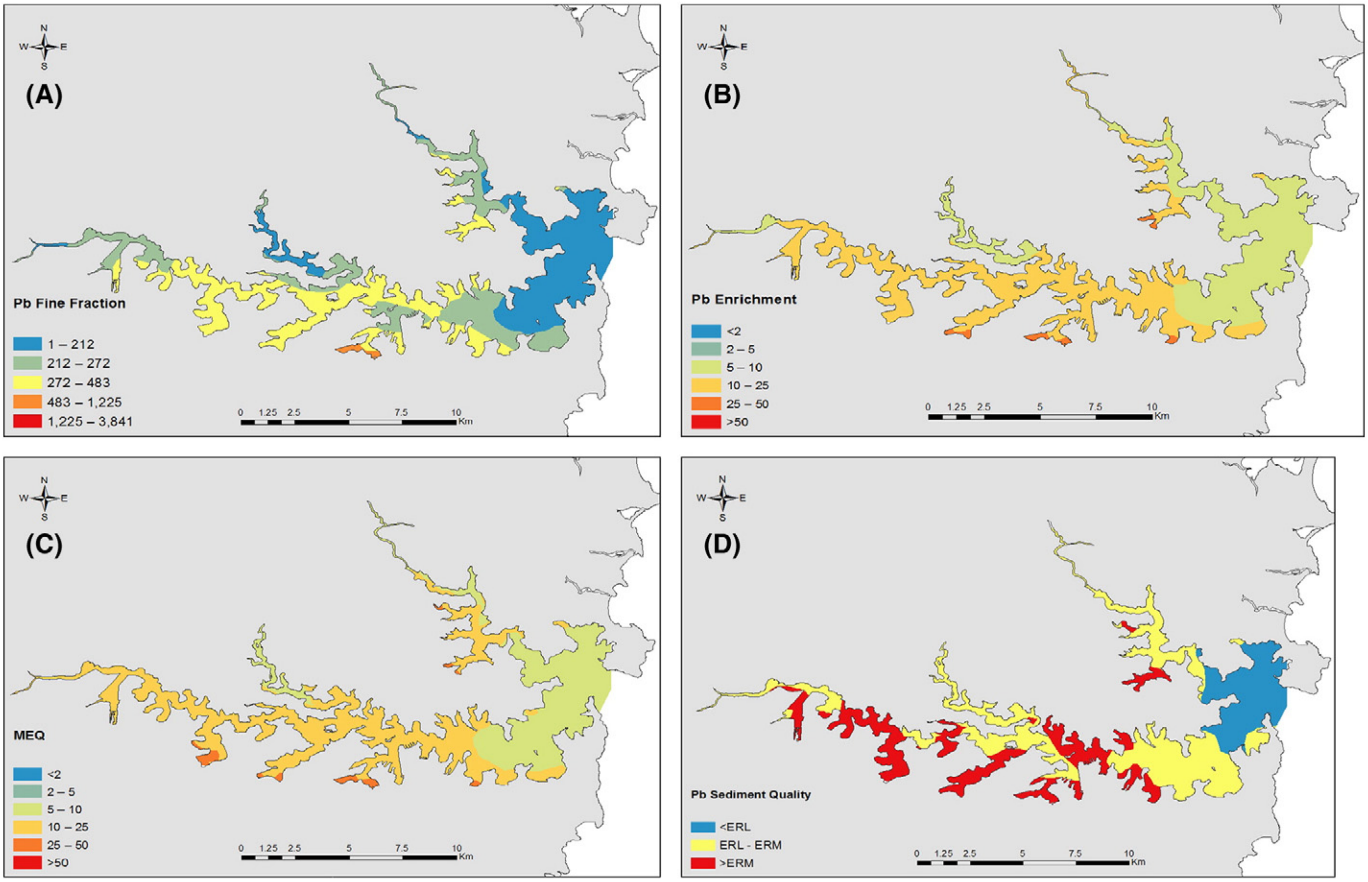

Fig. 3. Distribution of Pb in surficial sediments in Sydney estuary. (A) in fine (<62.5 μm) sediment; (B) as times of Pb enrichment over background; (C) mean enrichment quotient (MEQ) for three metals (Cu, Pb and Zn), and (D) as sedimentary risk for Pb. ERL - effects range low; ERM – effects range median.

(Fig. 4D) and moderate risk sediments (class III) mantle the Parramatta River and the central estuary (Homebush Bay, Iron Cove, Five Dock, Rozelle/Blackwattle Bays). Sediments with slight risk (class II) of adverse effects are located in the main channel of the central and lower estuary, Lane Cove and Middle Harbour, whereas the mouth of the harbour is mantled in sediment with minimal, or no risk (class I). Sediments with high, moderate, slight and minimal risk comprise 19%, 54%, 25% and 2% of the estuary, respectively (Birch and Taylor, 2002a, 2002b, 2002c), which is similar in extent as that of North American estuaries (Long et al., 2000). The results of a more recent investigation (Birch et al., 2008a) where toxicology and sediment chemistry data were combined into a single WOE matrix, were similar spatially and in magnitude to that predicted by the MERMQ analysis.

4.6. Possible global scheme for assessing anthropogenic change and biological risk in the marine environment

A classification scheme for assessing the magnitude of anthropogenic change based on MEQ and biological risk founded on MERMQ, which are well established in the literature (Birch and Olmos, 2008; Mashiatullah et al., 2013; Long et al., 1998; Birch and Taylor, 2002a, 2002b, 2002c) are presented in Table 6A. These categories may well be adopted as a global scheme for comparing marine environments as the information on which the classifications are based require data that are generally available, or easily and inexpensively acquired.

This scheme applied to Sydney estuary (Table 6B) demonstrates that this waterway is highly enriched/modified by anthropogenic activities (Class IV MEQ>5) and bottom sediments pose a moderate risk to benthic communities (Class III MERMQ 0.5–1.5).

5. Conclusions

An assessment scheme providing a simple, pragmatic, yet scientifically sound determination of estuarine sediment quality is outlined in the current work. The scheme provides two important pieces of information on which the status of estuarine sediment may be judged, i.e. the magnitude of contamination, which is the human-induced deviation from the pristine condition and sediment quality, i.e. the risk of adverse effect posed by sedimentary contaminants to benthic populations. These two types of data are very different and should not be confused, or combined as they define vastly different attributes of the ecosystem and are based on different data and guidelines/references.

The extent of contamination and anthropogenic change has been estimated by expressing surficial sediment metal concentrations as enrichment. Background metal concentrations were obtained from the pre-European settlement section of dated sedimentary cores. Enrichment for three metals (Cu, Pb and Zn) was combined into a Mean Enrichment Quotient (MEQ) for a more integrated assessment of human-induced change. Surficial mapping of enrichment provided a unique spatial depiction of the magnitude of human-induced change for the entire estuary. The risk of possible biological stress due to sedimentary contaminants was assessed using SQGs for a suite of metallic and organic chemicals for which guidelines are available.

An initial, sediment-based environmental assessment of the kind described in the current work identifies high-risk regions of the study area and highlights chemicals of most concern helping to focus future more comprehensive investigations reducing cost, effort and time. A weight of evidence and hierarchical approach should be applied to the

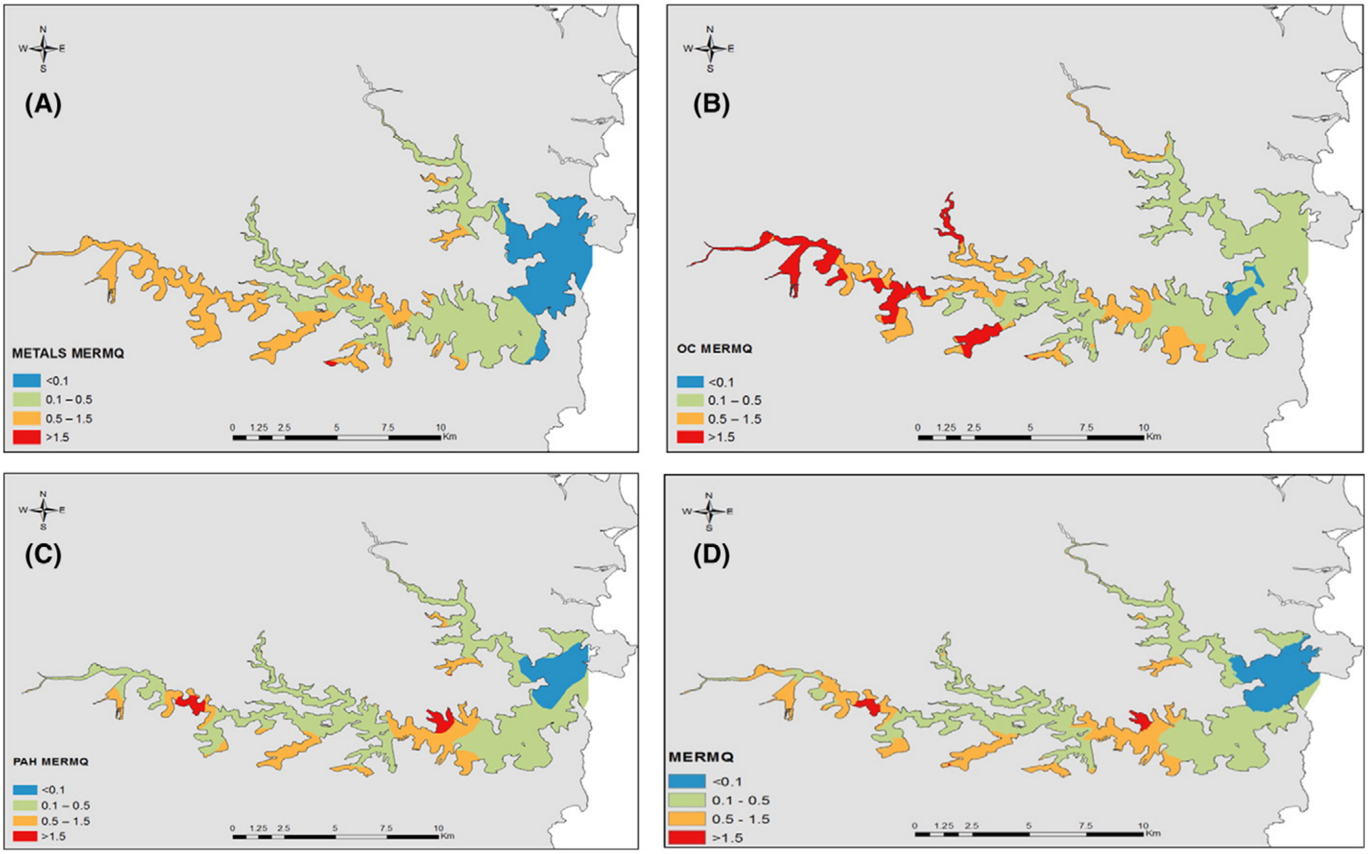

Fig. 4. Distribution of mean effects range median quotients (MERMQ). (A) for metals; (B) for organochlorine compounds (OCs); (C) for polycyclic aromatic hydrocarbons (PAHs); (D) for metals + OCs + PAHs + PCBs. MERMQ <0.1 minimal risk of adverse effects; 0.1–0.5 slight risk; 0.5–1.5 moderate risk; >1.5 high risk.

assessment of estuaries so that limited resources can be used most effectively. Sedimentary metal indicators provide a suite of powerful tools for management and governance of coastal water bodies, which is often not fully appreciated, or utilised.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marpolbul.2017.01.013.

Table 6
A. Suggested classes of anthropogenic change and biological risk.
B. Classes of anthropogenic change and biological risk for Sydney estuary sediments.

Magnitude of anthropogenic change (MEQ)			Biological risk posed by sedimentary contaminants (MERMQ)		
Class	Enrichment/Modification	MEQ	Class	Risk	MERMQ
IV	Highly enriched	>5	IV	High risk	>1.5
III	Moderately enriched	3–5	III	Moderate risk	0.5–1.5
II	Slightly enriched	1.5–3	II	Slight risk	0.1–0.5
I	Not enriched	<1.5	I	Minimal risk	<0.1

Magnitude of anthropogenic change (MEQ)			Biological risk posed by sedimentary contaminants (MERMQ)		
Class	Enrichment/Modification	MEQ	Class	Risk	MERMQ
IV	Cu	21	III	Metals	0.57
IV	Pb	14	III	OCs	0.52
IV	Zn	15	III	PAHs	0.59
IV	MEQ	17	III	PCBs	0.61
			III	Combined	0.58

MEQ - mean enrichment quotient for Cu, Pb and Zn; MERMQ - mean effects range median quotient; OCs- organochlorine compounds; PAHs-polycyclic aromatic hydrocarbons; PCBs-polychlorinated biphenyls.

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