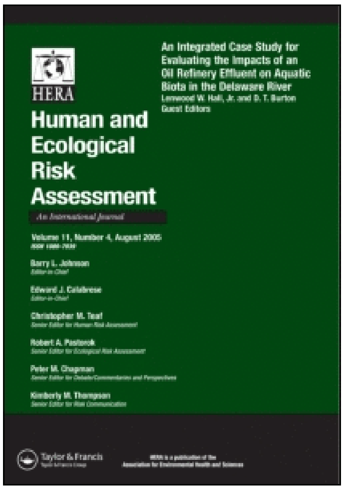

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Probabilistic Risk Assessment and Risk Mapping of Sediment Metals in Sydney Harbour Embayments

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ABSTRACT

Sediment metal concentrations in embayments of Sydney Harbour, acquired from the literature and from samples collected for this study, were used to generate contaminant probability density distributions using AQUARISK. The sediment metal concentrations often exceeded Australia's interim sediment quality guidelines. Similarly, estuarine spiked sediment toxicity test literature provided adverse biotic effects concentration data to generate species sensitivity distributions using AQUARISK. Although the harbor is subject to other inorganic and organic contamination, we have used sediment metals to demonstrate an approach for ecological risk mapping and environmental management prioritization. Sufficient spiked sediment toxicity test data were found for only three metals—Cd, Cu, and Zn—and some tests were likely to overestimate toxicity. The estimates of the hazardous concentration to 5% of species (the 50th percentile of the 95% species protection level) were 5, 12, and 40 mg/kg DW of total sediment metal for Cd, Cu, and Zn, respectively. These values were generally low when compared with the interim sediment quality guidelines due to the overestimation of toxic effects in the literature data. The parameters for the species sensitivity distributions have been combined with the measured sediment metal concentrations in Homebush Bay to generate risk maps of the estimated species impact for each metal as well as for all three metals collectively assuming proportional additivity. This has demonstrated the utility of comparing contaminants on a consistent scale—ecological risk.

Key Words: probabilistic ecological risk assessment, metals, sediments, Precautionary Principle, risk mapping.

INTRODUCTION

Sydney Harbour (Port Jackson) has a highly urbanized and industrialized catchment that has resulted in areas with high concentrations of metallic and organic

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Table 1. Australian interim sediment quality guideline values for selected metals (mg/kg DW, ex Table 3.5.1, ANZECC/ARMCANZ 2000).

Metal	ISQG-Low	ISQG-High
Cadmium	1.5	10
Copper	65	270
Lead	50	220
Zinc	200	410

contaminants (Birch and Taylor 1999; Birch and Taylor 2000) often exceeding Australia's interim sediment quality guideline values (ISQGs; ANZECC/ARMCANZ 2000, Table 1). Despite recent reductions in contaminant inputs, questions arise as to how much of a risk the elevated concentrations pose to biota within the harbor and which of the readily identifiable contaminants pose the greatest risk. A study on Sydney Harbour sediments suggested that metals, in particular Cu, Pb, and Zn, may be the predominant cause of sediment toxicity based on a correlation analysis between sediment contaminant concentrations and toxicity in standard laboratory tests (amphipod survival and reburial and sea urchin fertilization) (McCready *et al.* 2006a). Metals also provide a good example of risk assessment methodologies.

In this study, we have used species sensitivity distributions (SSDs) to establish cause–effect relationships (Posthuma *et al.* 2001) between sediment Cd, Cu, and Zn and toxicity. Similarly, probability density distributions (PDDs) of published sediment contaminant concentrations within the harbor, together with data acquired in this study, have been compiled and compared with the interim sediment quality guideline values. The contaminant distributions are also compared with the SSDs to generate individual and cumulative risk maps for Homebush Bay using the ecological risk assessment model, AQUARISK (Twining *et al.* 2005).

For sediment quality assessments there are a number of factors that make a simplistic use of spiked sediment toxicity test results as input to SSD analyses sub-optimal. These factors have recently been highlighted in a review by Simpson and Batley (2007 and citations therein). The principal issues of concern are that firstly, the toxicant bioaccumulation pathway may be dominated by the water uptake pathway if the sediment spiking has resulted in metal concentrations in the pore or overlying water that are many times greater than found in contaminated sediments in the field. In this situation, the toxicity test is more a measure of aquatic toxicity rather than sediment toxicity. Secondly, test organism(s) and the sedimentary substrate quality (mud, sand, gravel, organic contents; pore water pH; sulphide, Fe, and Mn phases and redox potential; *etc.*) used in the sediment toxicity test should be similar to those in the environment under consideration of risk. Upcoming guidelines will specify minimum requirements for sediment toxicity testing and will also recommend consideration of developing exposure-effects models and biotic ligand models in their interpretation (Simpson and Batley 2007). These new models will be focused on using the bioavailable fraction of the contaminant in the sediment as the best measure of concern. Spiked sediment toxicity tests to date typically provide an overestimate of toxicity that can be considered precautionary for risk assessment purposes.

When the improved models and testing procedures are in place and generating information from targeted experiments and field observations, the data generated will still best be applied to evaluate risks at the habitat or ecosystem level of environmental complexity using the SSD approach demonstrated in this article. As well as providing a means to bring together relevant data across a range of species, the SSD approach has the advantage of normalizing all contaminants onto a common assessment scale, probabilistic risk. This means that contaminants can be ranked for effective environmental management prioritization. It is also then possible to combine the outputs for individual contaminants to generate an overall risk map of the affected area (Traas *et al.* 2001).

METHODS

Study Site

Sydney Harbour (Port Jackson) is a drowned valley estuary, grouped with other types as tide-dominated estuaries (Roy *et al.* 2001). The embayments for which data were selected occur approximately 10–20 km from the ocean entrance. These represent parts of the estuary geomorphologically known as the central mud basin, dominated by organic-rich mud and muddy sand, and fluvial deltas at the heads of embayments (with sandy mud and muddy sand), although these zonations are not well defined in Sydney Harbour (Mesley 2004, after Roy 1984).

Sydney Harbour Sediment Metal Concentration Data

Metal concentrations in Sydney Harbour sediments were compiled into a database from published results (MacFarlane *et al.* 2000; Taylor 2000; Simpson *et al.* 2002; MacFarlane 2002). There was sufficient evidence, such as the inclusion of analysis of standard reference materials, to indicate that the data in the references were of adequate quality. Where a publication reported sediment metal concentrations in samples from multiple depth intervals (Simpson *et al.* 2002), only the information on the surface sample was included. Similarly, only the most recent sample was included if samples from the same locations at different times were reported (MacFarlane 2002). To conform to the other sediment contaminant data and the spiked sediment toxicity test (SSTT) data, the values from Taylor (2000) were converted to total sediment metal concentration from metal concentration in the mud fraction (<63 μm) using the percentage mud for each sediment sample. This assumes that the metal contribution from the coarse fraction of the sediment is zero, which is generally a reasonable assumption due to the much greater metal binding capacity of the fine fraction. Some sediments in Sydney Harbour contain coarse hydrocarbon particles, that most likely originate from coal burning power stations, and that have high concentrations of metals (Birch and Taylor 1999; Simpson *et al.* 2002). However, it could reasonably be assumed that the metals associated with these particles are not bioavailable, particularly given the length of time since coal-fired power generation in the harbor ceased in 1984. Where a metal was below the analytical detection limit, a value of half the detection limit was used in the calculation. A summary of the total metal concentration (mg/kg DW) data in each embayment is given in Table 2.

Table 2. Summary of sediment metal concentrations (mg/kg DW) in embayments of Sydney Harbour. All are total concentrations from the literature except for the data from Homebush Bay, which comprise total (TM) and acid-soluble metals (ASM) for sediments sampled in this study.

Metal	Cd					Cu					Pb					Zn				
Bay	Max	Min	Mean	Med	n	Max	Min	Mean	Med	n	Max	Min	Mean	Med	n	Max	Min	Mean	Med	n
Hen and Chicken Bay	2.05	0.30	0.83	0.78	31	766	98	332	288	31	546	136	311	291	31	989	300	681	702	31
Homebush Bay—ASM	3.25	0.07	1.06	0.76	29	111	21	52	43	28	489	72	152	119	29	652	33	302	257	29
Homebush Bay—TM	3.61	0.04	1.16	0.92	29	214	39	93	85	29	490	63	171	135	29	993	83	454	403	29
Iron Cove	5.34	0.05	1.92	1.51	30	328	62	212	225	30	815	150	474	459	30	1460	290	864	835	30
Long Bay	7.58	0.08	1.12	0.82	21	276	19	177	205	26	581	39	305	308	26	822	60	487	542	27
Rozelle Bay	4.14	0.05	1.06	0.37	22	359	34	157	126	22	956	45	364	243	22	1660	128	617	410	22
Sailors Bay	2.61	0.01	1.07	1.03	24	381	1	100	81	52	565	4	181	213	52	756	1	273	290	52

To supplement the dataset and provide a risk map case study, sediment samples (n = 29) were collected from Homebush Bay and adjacent intertidal areas in Powells and Haslams Creeks in October and November 2006. A stratified sampling protocol was applied along two longitudinal transects following the major axis of the bay and one transverse transect at its widest point as well as a number of edge samples within the intertidal zone. The sampling was constrained by either navigation depth or ease of access from the shore but was designed to encompass the known major contaminant inputs as well as provide a reasonable geographic spread for mapping purposes. A gravity corer with a polycarbonate tube was used to sample the sediment to a depth of 10 cm. Sediment cores were removed and sub-sampled on site for the 0–2 cm and 2–10 cm depth intervals, stored in clean plastic zip-lock bags or acid-washed HDPE containers and refrigerated below 4°C.

For total metals (TM) analysis, each wet sediment sample was homogenized and a 1 g aliquot placed in a Teflon vessel. Two ml of concentrated HNO_3, 0.1 ml concentrated HF, and 2 ml of Milli-Q water were added to the wet sample. The sample was then capped and placed in an ultrasonic bath for 160 minutes at 60°C. For acid-soluble metals (ASM) analysis, each wet sediment sample was homogenized and then a 1 g aliquot was placed in a Teflon™ vessel. Fifty mL of 0.6M HCl acid was added to the wet sample, and the sample was then capped and shaken for 60 minutes. The samples were centrifuged and the supernatant separated for analysis.

After extraction, the digests were diluted to volume according to standard procedures (Simpson *et al.* 2005) for analysis using either a HP4500 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) or a Vista Simultaneous Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES). Reagent blanks, 2 random duplicate samples and 2–3 Standard Reference Material (SRM) samples (MESS-2) were included in each analytical batch of 15 samples and processed identically to the samples. To meet quality control criteria, the analytical results for the SRM sample must be within ±20% of the value for each metal established by the National Institute of Standards and Technology. These requirements were met for all batches of samples analyzed. The metal concentration was expressed on a dry weight basis and corrected using the recovery value of the SRM.

Marine Spiked Sediment Toxicity Test Data

The literature was reviewed for marine SSTTs of metals and a database compiled. There were only sufficient SSTT data to construct SSDs for Cu, Cd, and Zn. Most tests were laboratory assays although some data were from field colonisation tests of spiked sediments. From the full set, data were accepted for the risk analysis on the basis of the following criteria:

1. As recommended in ANZECC/ARMCANZ (2000, 8.4.5vii), only tests that reported ecologically relevant effects that impact population level processes such as survival, growth or reproduction were included. Behavioural effects, for example, emergence and reburial, and other non-crucial criteria, for example, root-shoot ratio and height of mangroves, were not included;

2. There were insufficient data to construct a database of no-effects (NOEC) results. Hence, the endpoints used included LOECs and other effect concentrations (*e.g.*, EC_{10}, LC_{50}) that will be less precautionary;
3. When a study reported multiple endpoints for a particular species, only the most sensitive was included in the database. If there were multiple values for the same species, across all references, the geometric mean of those values was determined. The single, derived value for that species was then used in the database to ensure each species received equal weighting in the species sensitivity distribution (ANZECC/ARMCANZ 2000; Wheeler *et al.* 2002). For example, for Spionid annelids adversely affected by Zn a geometric mean of 1020 mg/kg DW, based on five LOEC values reported in the literature, was the single value used for this species;
4. In one study (Simpson 2005) Cu toxicity data were derived for sediments with a range of textures (sand through to silt). The data for a silty sediment with medium Fe and total organic carbon content and a K_d of 5×10^4 was chosen as being most representative of Sydney Harbour embayment sediments. The LC_{50} value from the sediment with 25% fine fraction from Correia and Costa (2000) was used.

The final sets of SSTT data used in the analyses are given in Table 3. The complete database, including data rejected using the aforementioned criteria, is available from the authors.

Probabilistic Ecological Risk Assessment

The sediment metal concentration data in Sydney Harbour embayments were initially screened by comparison with the Australian ISQG-low and -high values (Table 1), a Tier 1 risk analysis using AQUARISK (Twining *et al.* 2005). A more detailed probabilistic analysis was then performed on each metal by fitting cumulative probability density functions using log-normal and Burr Type III distributions (ANZECC/ARMCANZ 2000; Shao 2000) to both the concentration and effect data. The Kolmogorov-Smirnov test was used to assess the goodness-of-fit of the derived PDDs. Once the distribution parameters and their uncertainties were evaluated, critical values were also derived from the log-normal or Burr Type III SSDs for comparison with the ISQGs. These values were the median hazardous concentration affecting n% of species ($HC_{n;50}$) and the 95% lower confidence limit ($HC_{n;95}$).

AQUARISK estimated the degree to which the contaminant data are likely to exceed the ISQG values and the critical values determined from the SSD. AQUARISK was used to convolute the two distributions (*i.e.*, PDD and SSD) for each metal and embayment to determine the probability and extent that overlaps occur. This evaluated the percentage of species likely to be adversely affected by the contaminant concentrations.

Finally, the required reduction in the median contaminant concentrations to achieve acceptable risk was estimated using AQUARISK. This was in terms of the exceedence probability of the various criteria as well as the percentage of biotic species likely to be affected.

Table 3. Spiked sediment toxicity test data used to construct SSD for Cd, Cu, and Zn.

Metal	Organism	Effect	Endpoint	Test duration	Sediment metal concentration (mg/kg DW)	Reference
Cd	*Amphiascus tenuiremis*	Mortality	LC_{50}	96 h	35*	Green *et al.* (1993); Cited in Hagopian-Schlekat *et al.* (2001)
	Arenicola marina	Mortality	LC_{50}	10 d	35	Bat and Raffaelli (1998)
	Corophium volutator	Mortality	LC_{50}	10 d	14.4	Bat and Raffaelli (1998)
	Cylindotheca closterium	Growth	EC_{50}	72 h	79	Moreno-Garrido *et al.* (2003)
	Paracorophium excavatum	Mortality	LC_{10}	10 d	10.6	Hickey and Roper (1992)
	Pontoporeia affiniis	Mortality	LOEC	446 d	11	Sundelin (1984) cited in Long and Morgan (1990)
	Rhepoxynius abronius	Mortality	LC_{50}	10 d	10*	Kemp *et al.* (1986); Mearns *et al.* (1986); Robinson *et al.* (1988); Swartz *et al.* (1985)
	Ruditapes philippinarum	Mortality	LC_{50}	48 h	4.5	Shin *et al.* (2002)
Cu	*Amphiascus tenuiremis*	Mortality	LC_{50}	96 h	282	Hagopian-Schlekat *et al.* (2001)
	Arenicola marina	Mortality	LC_{50}	10 d	20	Bat and Raffaelli (1998)
	Avicennia marina	Biomass	EC_{50}	6 months	380	MacFarlane and Burchett (2002)
	Boccardia proboscidea	Mortality	LC_{50}	14 d	350	Cited in McPherson and Chapman (2000), reported LC_{50} range 303–384 mg/kg
	Cylindotheca closterium	Growth	EC_{50}	72 h	26	Moreno-Garrido *et al.* (2003)
	Gammarus locusta	Mortality	LC_{50}	10 d	159	Correia and Costa (2000)
	Kandelia candel	Leaf weight	LOEC	3 months	125	Chiu *et al.* (1995)
	Leptocheirus plumulosus	Growth	IC_{25}	28 d	70	Cited in McPherson and Chapman (2000), reported IC_{25} range 56–93 mg/kg
	Macomona liliana	Mortality	LC_{10}	10 d	10.5	Roper and Hickey (1994)
	Neanthes arenaceodentata	Weight	IC_{25}	28 d	56	Cited in McPherson and Chapman (2000)
	Paracorophium excavatum	Mortality	LC_{50}	10 d	55	Marsden and Wong (2001)
	Polydora cornuta	Growth	IC_{25}	14 d	132	Cited in McPherson and Chapman (2000)
	Nematodes	Abundance	LOEC	2 months	794	Austen and McEvoy (1997)

(Continued on next page)

Table 3. Spiked sediment toxicity test data used to construct SSD for Cd, Cu, and Zn. *(Continued)*

Metal	Organism	Effect	Endpoint	Test duration	Sediment metal concentration (mg/kg DW)	Reference
	Entomoneis punctulata	Growth	LC_{50}	10 d	850	Cited in Simpson (2005)
	Corophium colo	Mortality	LC_{50}	10 d	4100	Cited in Simpson (2005)
	Corophium insidiosum	Mortality	LC_{50}	10 d	1500	Cited in Simpson (2005)
	Melita plumulosa	Mortality	LC_{50}	10 d	1300	Cited in Simpson (2005)
	Mysella anomala	Mortality	LC_{50}	10 d	3700	Cited in Simpson (2005)
	Tellina deltoidalis	Mortality	LC_{50}	10 d	1020	Cited in Simpson (2005)
	Soletellina alba	Mortality	LC_{50}	10 d	1000	Cited in Simpson (2005)
	Australonereis ehlersi	Mortality	LC_{50}	10 d	1150	Cited in Simpson (2005)
	Nephtys australiensis	Mortality	LC_{50}	10 d	2000	Cited in Simpson (2005)
Zn	*Amphiascus tenuiremis*	Mortality	LC_{50}	96 h	671	Hagopian-Schlekat *et al.* (2001)
	Arenicola marina	Mortality	LC_{50}	10 d	50	Bat and Raffaelli (1998)
	Avicennia marina	Biomass	EC_{50}	6 months	392	MacFarlane and Burchett (2002)
	Corophium volutator	Survival	LC_{50}	10 d	32	Bat and Raffaelli (1998)
	Kandelia candel	Leaf weight	LOEC	3 months	250	Chiu *et al.* (1995)
	Rhepoxynius abronius	Mortality	LC_{10}	10 d	158	Swartz *et al.* (1988)
	Tellina deltoidalis	Mortality	LOEC	10 d	3900	King *et al.* (2004)
	Spionids	Abundance	LOEC	7–9 d	1020*	Watzin and Roscigno (1997)
	Capitellids	Abundance	LOEC	7–9 d	2230*	Watzin and Roscigno (1997)
	Syllids	Abundance	LOEC	7–9 d	3038*	Watzin and Roscigno (1997)
	Bivalves	Abundance	LOEC	7–9 d	8145	Watzin and Roscigno (1997)
	Gastropods	Abundance	LOEC	7–9 d	3128*	Watzin and Roscigno (1997)
	Harpacticoids	Abundance	LOEC	7–9 d	1636*	Watzin and Roscigno (1997)
	Ostracods	Abundance	LOEC	7–9 d	1636*	Watzin and Roscigno (1997)
	Nematodes	Abundance	LOEC	7–9 d; 2 months	1331*	Watzin and Roscigno (1997); Austen and McEvoy (1997)
	Turbellarians	Abundance	LOEC	7–9 d	1849*	Watzin and Roscigno (1997)

*Indicates a geometric mean was used.

Risk Mapping

The Homebush Bay sediment analyses were used to generate maps of Cd, Cu, Zn, and Pb sediment concentrations using Surfer®. Because the concentration data were irregularly spaced we chose to use Kriging, a flexible geostatistical gridding method, to produce interpolated metal concentrations at nodal points on a fine grid encompassing the bay. Parameters for describing risk-concentration distributions from the AQUARISK modeling and the measured metal concentrations were also used to calculate a risk estimate (% species likely to be adversely affected) for each metal using the cumulative distribution function of the Burr Type III distribution:

$$y_i = 1/[1 + (b/x_i)^c]^k \tag{1}$$

where y_i is the estimated proportion of species likely to be adversely affected by the metal; x_i is the interpolated metal concentration at any individual node; and b, c, and k are the parameters of the Burr Type III distribution for each metal derived using AQUARISK. The risks for the three metal concentrations were combined assuming proportional additivity according to the equation:

$$\text{Total risk} = y_{Cu} + y_{Cd}(1 - y_{Cu}) + y_{Zn}(y_{Cu} + y_{Cd}(1 - y_{Cu})) \tag{2}$$

where y_{Cu}, y_{Cd}, and y_{Zn} are the estimates of the proportions of species likely to be affected by Cu, Cd, and Zn (respectively) at that node. While synergistic and antagonistic effects are understood to occur, proportional additivity is a reasonable first estimate when considering multiple contaminants from a single class (Warne and Hawker 1995), in this case heavy metals.

RESULTS

The total metal concentration data in embayments of Sydney Harbour, together with our results for total and acid soluble metals in Homebush Bay, are summarized in Table 2. Only embayments for which there were at least 20 measurements are included. The ISQG-Low value (Table 1) is exceeded for each metal in all bays. The ISQG-High value for Cd is not exceeded in any bay. The ISQG-High value for Cu is exceeded in all bays except Homebush Bay. The ISQG-High values for Pb and Zn are exceeded in all bays. The variations between embayments can be attributed to both the size of Sydney Harbour and the diversity of catchment land uses over the past two centuries. Changing patterns of urbanization and industrialization over that period have resulted in various contaminant influxes to different parts of the harbor (Taylor *et al.* 2004).

The cumulative probability distributions for Cd, Cu, and Zn sediment concentrations were generated for each embayment. Those for Homebush Bay (ASM) are shown in Figure 1 as an example. These PDDs were used for later comparison with the SSDs derived from the SSTT data. The Kolmogorov-Smirnov test showed that, for the large majority of comparisons across all metals and embayments, the Burr Type III distributions fit the data better than the log-normal. In some data sets, neither distribution provided a reasonable fit for the data ($p < .7$), mostly due to the occurrence of polymodal data distributions. As a consequence, further probabilistic risk analyses of Cd in Iron Cove and of all metals in Sailors Bay were discontinued.

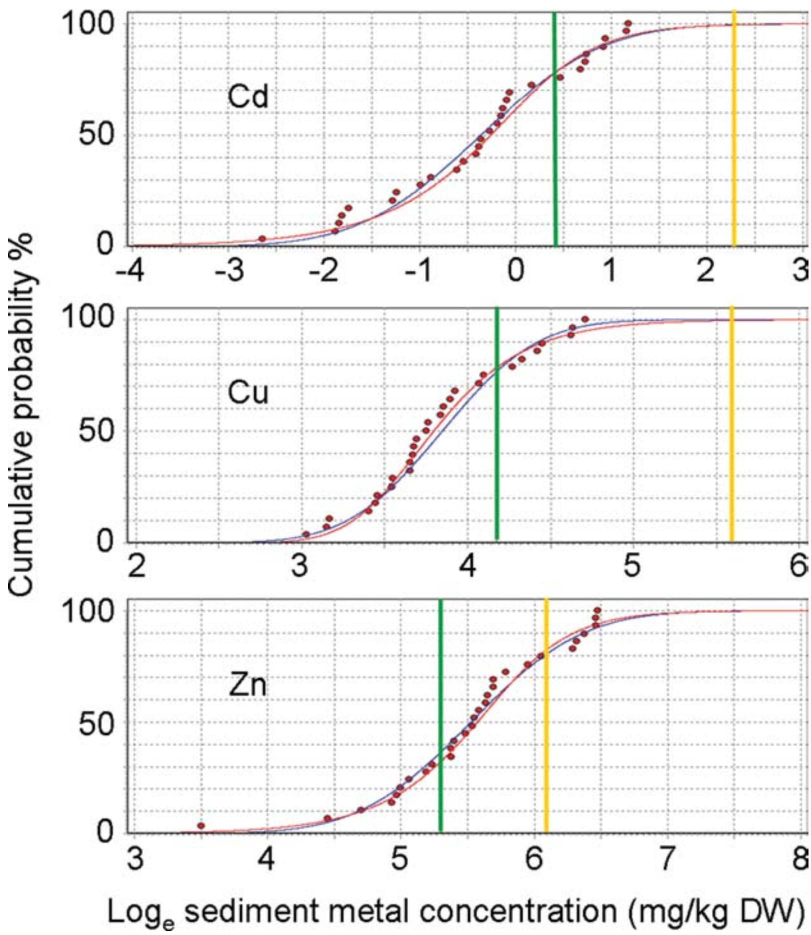


Figure 1. Fitted cumulative probability distributions of acid soluble metal (ASM) sediment concentrations of Cd, Cu, and Zn (in mg/kg DW) in Homebush Bay using log-normal (blue) and Burr Type III (red) functions. The vertical lines indicate the ISQG-low (green) and ISQG-high (yellow) values.

Using the Burr Type III distributions, AQUARISK estimated the probabilities that sediment metal concentrations in any sample from each of the bays would exceed the ISQG values as well as the degree of remediation required in order to achieve acceptable levels of exceedence (Table 4). Note that the target concentrations for any metal vary between embayments. The larger the range of the contaminant concentrations, the lower the median target in that site. This is a consequence of AQUARISK accounting for the spread of the contaminant probability distribution in each site. AQUARISK assumes that the spread of the contaminant concentrations does not decrease if the overall contamination levels are reduced by any remedial action. This assumption was made to ensure a precautionary outcome. In practical terms, identification and remediation of the more highly contaminated zones

Table 4. Current probability of exceeding ISQG values and the proportional reductions and median target concentrations required for each metal to achieve a 5% or less probability of exceeding the guideline values, derived from AQUARISK.

Metal	Cd						Cu						Pb						Zn					
	ISQG low			ISQG high			ISQG low			ISQG high			ISQG low			ISQG high			ISQG low			ISQG high		
Bay	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	C
Hen and Chicken Bay	0.05	nil	0.8	0.00	nil	5.1	0.99	91	24	0.50	64	100	0.98	90	29	0.81	57	130	1.00	81	130	0.96	61	260
Homebush Bay—ASM	0.22	58	0.3	0.00	nil	1.9	0.23	34	31	0.00	nil	130	0.98	83	23	0.15	24	100	0.63	73	68	0.23	45	140
Homebush Bay—TM	0.26	63	0.3	0.01	nil	2.0	0.73	62	32	0.00	nil	130	0.98	85	22	0.22	54	95	0.91	79	84	0.48	87	170
Iron Cove	d			d			1.00	82	36	0.20	25	150	1.00	94	27	0.97	74	120	1.00	87	110	0.97	73	220
Long Bay	0.20	50	0.4	0.00	nil	2.5	0.91	85	23	0.19	38	95	1.00	93	20	0.65	67	90	0.90	82	76	0.53	64	160
Rozelle Bay	0.20	63	0.2	0.01	nil	1.2	0.83	83	21	0.13	31	88	0.97	95	12	0.58	79	54	0.89	87	62	0.59	74	130

[a]The likelihood that sediment concentrations in the embayment will exceed the ISQG. A value of 1 meaning 100%.
[b]The percentage reduction in overall contaminant concentrations within the embayment to achieve no more than a 5% chance of exceeding the ISQG.
[c]The median sediment metal target concentration (mg/kg DW) to achieve no more than a 5% chance of exceeding the ISQG.
[d]Not evaluated due to poor PDD fitting.

Table 5. AQUARISK estimates, based on Burr Type III SSDs, of the hazardous concentrations of metals in sediments (mg/kg DW) likely to affect up to 5, 10, 25 or 50% of species (50% confidence limit). The 95% lower confidence limit of the 5% effect level is also given.

Hazard	$HC^{a}_{5;50}$	$HC^{b}_{5;95}$	$HC^{c}_{10;50}$	$HC^{d}_{25;50}$	$HC^{e}_{50;50}$
Cd (n = 8)	5.0	3.2	6.3	9.7	15
Cu (n = 22)	12	2.3	29	120	460
Zn (n = 16)	40	9.0	110	430	1300

[a]50% confidence limit of the metal concentration estimated to be hazardous to 5% of species (*i.e.*, the 95% species protection concentration).
[b]95% lower confidence limit 95% species protection concentration.
[c]50% confidence limit of the 90% species protection concentration.
[d]50% confidence limit of the 75% species protection concentration.
[e]50% confidence limit of the 50% species protection concentration.

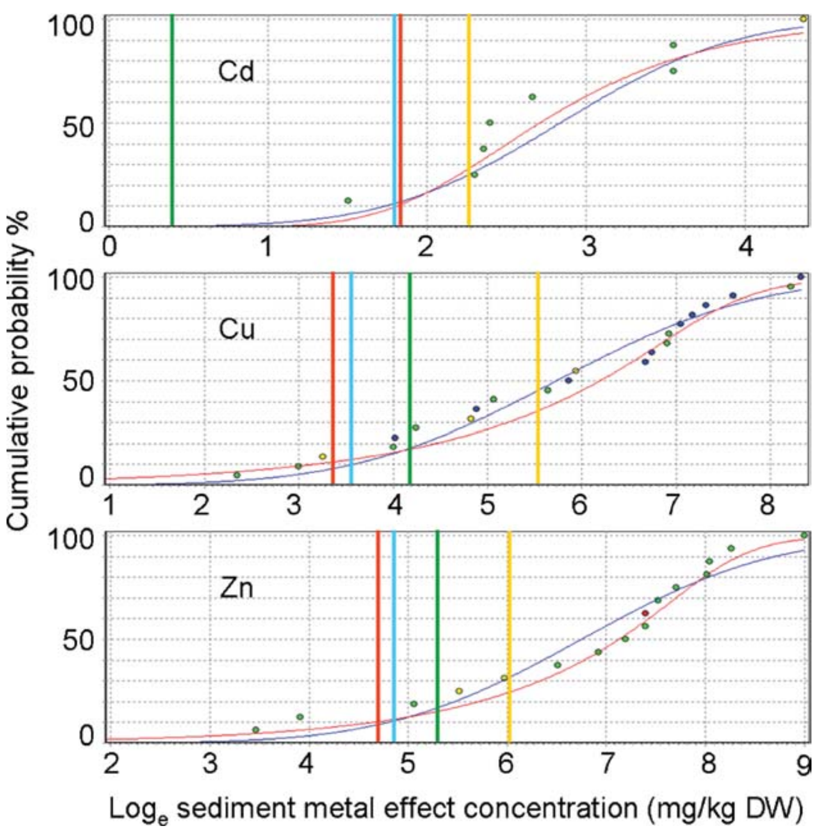


Figure 2. Cumulative species sensitivity distributions for sediment metal contaminants (Cd, Cu, and Zn; in mg/kg DW). The vertical lines indicate either the ISQG values (low—green, high—yellow) or the 50% confidence limit of the 10% species effect level (90% species protection) for the log-normal (blue) and Burr Type III (red) functions.

Table 6. Percentage of species likely to be adversely affected by the sediment concentrations of Cd, Cu, and Zn (calculated using Burr Type III distributions) and the proportional reductions and median target concentrations required to achieve no more than 5% species impact due to that metal within each embayment (calculated using log-normal distributions).

	% Species affected[a]			% Reduction required[b]			Median target concentration[b] (mg/kg DW)		
Bay	Cd	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn
Hen and Chicken Bay	0	48	44	Nil	94	90	3.3	16	67
Homebush Bay—ASM	1	14	23	Nil	64	79	1.9	17	67
Homebush Bay—TM	1	23	32	Nil	80	86	1.9	17	57
Iron Cove	c	40	49	c	91	93	c	17	61
Long Bay	1	35	34	Nil	90	87	2.2	15	55
Rozelle Bay	1	31	37	Nil	88	89	1.4	15	51

[a]Calculated using Burr Type III probability density distributions.
[b]Calculated using log-normal probability density distributions.
[c]Not evaluated due to poor PDD fitting.

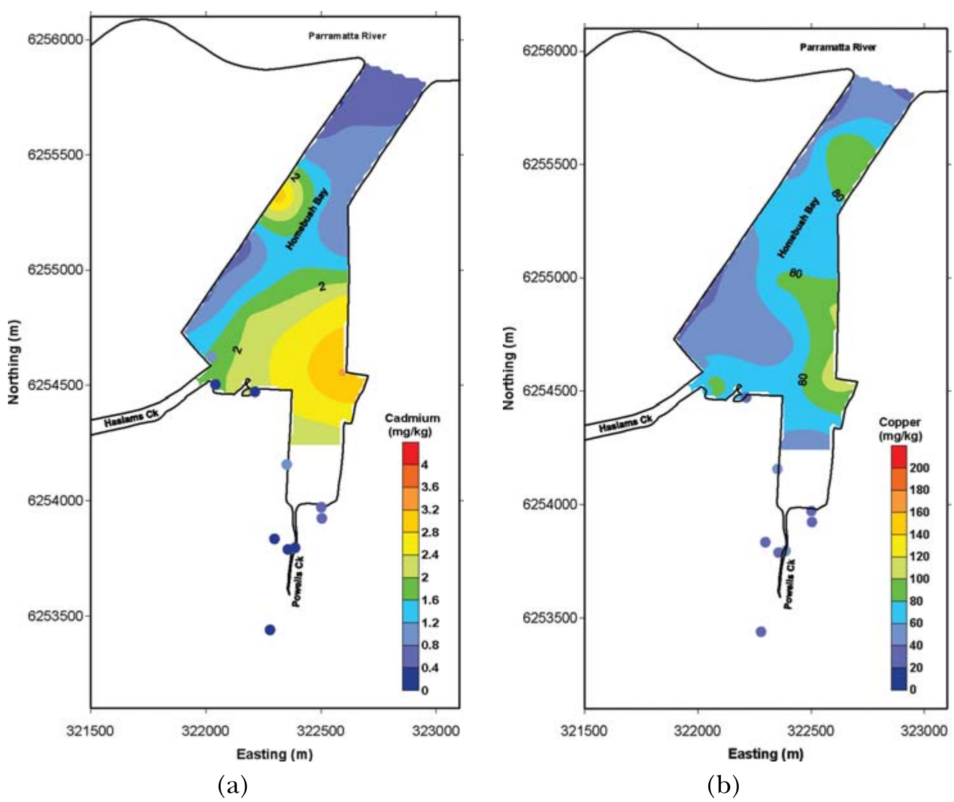
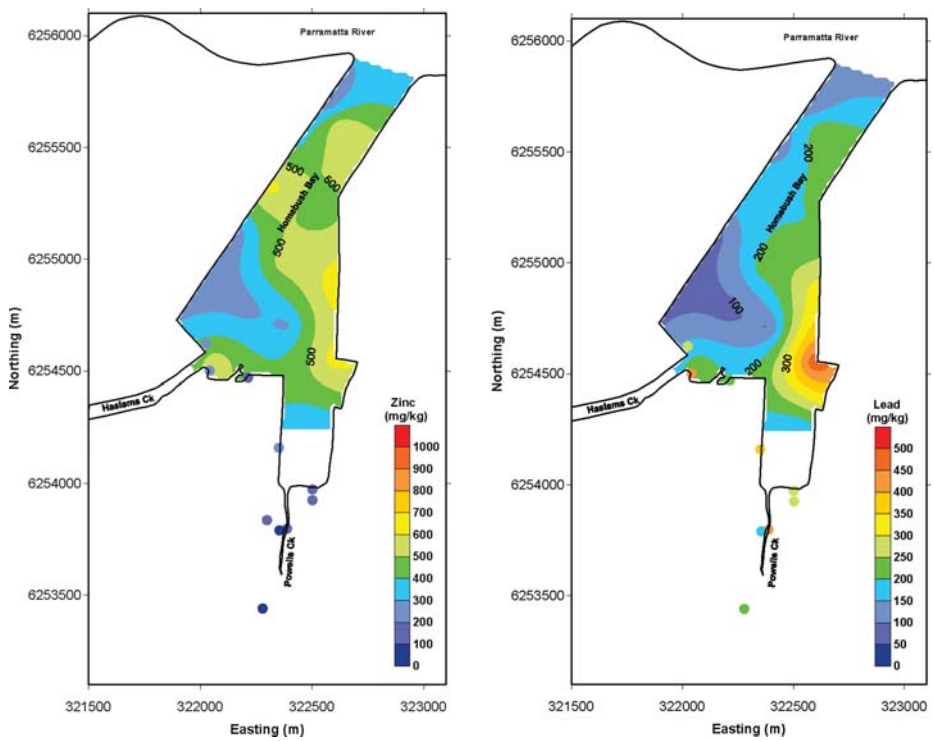


Figure 3. Maps of acid soluble metal concentrations (mg/kg DW) of Cd, Cu, Zn, and Pb in sediments of Homebush Bay. *(Continued)*



(c) (d)

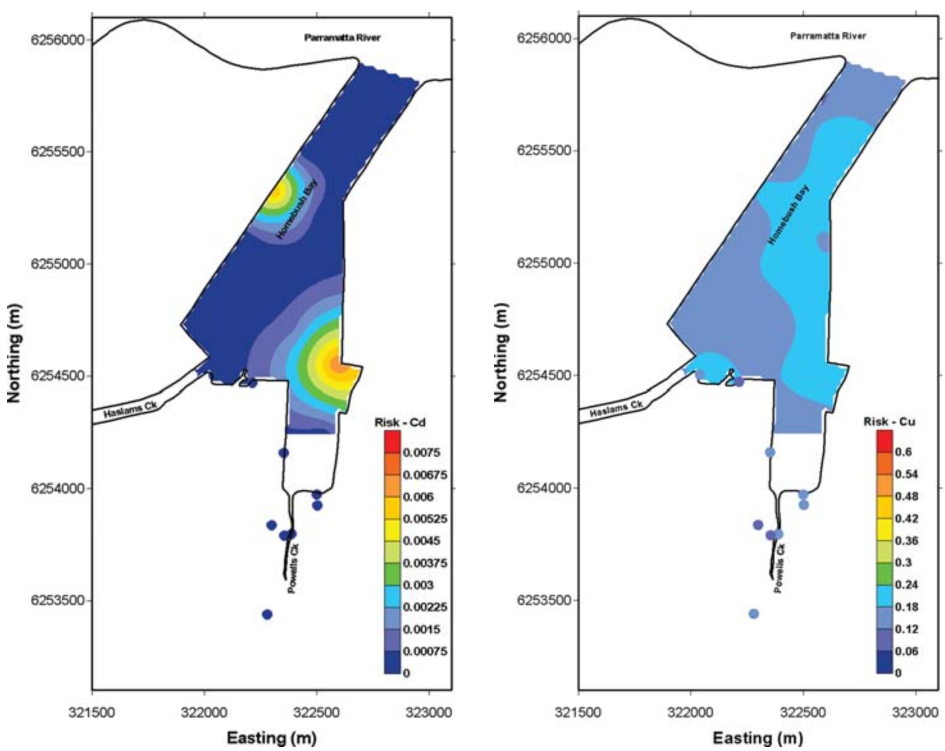
Figure 3. (Continued).

within the embayment will reduce the spread of contaminant concentrations. A subsequent, revised risk assessment for the bay as a whole will give greater median target concentrations, which are possibly more achievable and realistic in terms of remediation.

The cumulative probability distributions of the species sensitivity generated from the SSTT data for Cd, Cu, and Zn are shown in Figure 2. For these SSDs the Kolmogorov-Smirnov test indicated that both the log-normal and Burr Type III distributions fit the data ($p > .7$) for Cd and Cu and only the Burr Type III fit the Zn data, hence the Burr Type III distributions were used to evaluate criteria for metal concentrations likely to affect 5% or more of the species (Table 5). The values for the 50th percentile of the concentrations estimated to adversely affect 5%, 10%, 25%, and 50% of species, and the 95% lower confidence limit of the 5% effect level are reported. The confidence limits reflect the uncertainty in the fits of the SSDs and the variability of the data. The $HC_{5;95}$ value is up to 5.2 times lower than the $HC_{5;50}$ value (for Cu).

In Table 6 is shown the percentage of species likely to be adversely affected by each metal in each embayment. These were assessed using the Monte Carlo simulation within AQUARISK (Twining *et al.* 2005) to convolute the SSD and PDD for each metal in each bay. Similarly, using the log-normal SSDs and PDDs (AQUARISK cannot make these assessments using the Burr Type III distributions due to computational difficulties, Twining *et al.* 2005), and assuming that any remedial activity will reduce all measures of metal contamination similarly, the proportional reduction in each of the sediment metal concentrations required to achieve a target of 95% species protection (*i.e.*, a 5% effect level) within the embayment was estimated (Table 6). As with the remedial targets for acceptable exceedence of the ISQG, the variability in the remedial targets for acceptable species impact is due to the spread of the PDD for the metal within that embayment. In line with the Precautionary Principle, the method assumes that the best measure of the spread of the contaminant data, the standard deviation of the log-transformed mean, does not decline as the overall contaminant load is reduced by the chosen remediation method. The approach considers each metal independently rather than jointly. Nonetheless, it does provide a scale for the degree of improvement required for the system as a whole.

The concentrations of metals measured in Homebush Bay sediments as part of this study were mapped using Surfer® as shown in Figure 3. The contouring was confined to areas of the embayment that were below the Mean High Water (MHW) elevation. Samples collected above this height in the adjacent mangroves and salt marshes were plotted as measured concentrations but not used in the gridding process. The



(a) (b)

Figure 4. Maps of risk to biota (proportion of species affected) from acid soluble Cd, Cu, Zn, and the three metals combined, in sediments of Homebush Bay. Note the expanded scale for Cd due to its relatively lower risk. *(Continued)*

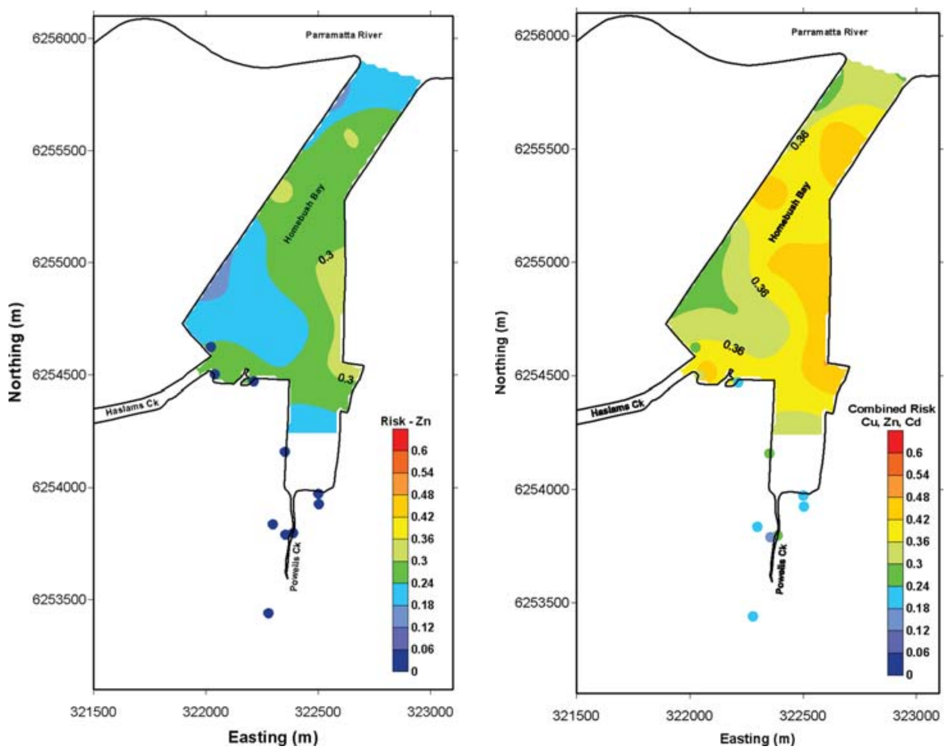


Figure 4. (Continued).

parameters used to describe the Burr Type III distributions of the SSDs for each metal were also used, together with the actual and interpolated sediment metal concentrations, to provide a risk map for each metal in Homebush Bay [Eq. (1)] as well as a combined risk for the three metals considered simultaneously and assuming proportional additivity of risk that is a reasonable approximation for multiple contaminants [Eq. (2); Figure 4; Warne and Hawker 1995].

DISCUSSION

Data Limitations

The sediment metal concentrations used in this study were assumed to be randomly representative of the embayments being assessed. However, the reported values were for samples collected to suit the needs of the original authors rather than for the purposes of quantitative probabilistic risk assessment. They were not commonly collected using a randomized sampling strategy but often focused on areas of known contamination without characterizing the whole site. Hence there are biases in any sampling data and subsequent analyses due to these pragmatic decisions. The data were also assumed to represent the sediments that most Sydney Harbour sediment biota were likely to inhabit but this assumes a relatively high degree of sedimentary homogeneity, which is unlikely to exist naturally. For example, the physico-chemical nature of sediments within mangroves, and the communities they support, is substantially different to that in adjacent salt marshes, seagrass beds, or un-vegetated zones. Although a targeted or more refined sampling program can attempt to overcome the difficulties, these problems will always exist when attempting to representatively sample any natural system at scales relevant to economically effective environmental management. Given the on-going need to use pragmatically compromised field data for future risk assessments, the approach applied in this study is recognized as not ideal but can be considered to be a practical example.

The results of poor distribution fitting for Sailors Bay sediment metals raised an issue of concern for probabilistic risk analysis, that of substantially polymodal contaminant concentration distributions. This can often occur, for example, where a plume of contamination has entered an embayment and is not evenly distributed or where "hots spots" have developed under conditions of poor mixing. This problem may be overcome by improved sampling as discussed earlier. However, it may also be possible, and eventually more economic, to improve curve fitting procedures to better convert the available data to probabilistic distributions. A variety of distribution forms have been used to describe concentration and effects data over the period of development of probabilistic risk analysis methodologies (Posthuma *et al.* 2001) and development is likely to continue. In AQUARISK some data are better fitted by the Burr Type III distribution, which allows for more flexibility than the log-normal distribution. However, the Sailors Bay data are beyond that capacity and are currently untenable for risk extrapolations.

The use of effects data rather than no-effects data was not precautionary but necessary, due to the relative lack of NOEC values and the implicit biases warned against by the interim sediment quality guidelines (ANZECC/ARMCANZ 2000) based on their prior investigation of the available data. To check the potential effect of this selection, the limited numbers of available NOECs were subsequently included in the analyses, as additional values or to replace equivalent effects data; to compare with the results obtained earlier using only effects data. The decrease in the mean values of the SSTT data for Cu and Zn were only 14% and 18%, respectively, and Cd actually increased by 2% as one of the added NOECs was a high value for an additional species (40 mg/kg DW for the polychaete *Nereis virens*; Olla *et al.* 1988).

The use of mixed endpoints (LOECs, EC_{50}s, LC_{50}s, *etc.*) in the SSDs is also an issue for discussion. The studies used in our evaluation usually did not report a full range of endpoints for a species and the raw data were not available for recalculation to a common endpoint. Factors have been used to convert different endpoints to a NOEC in deriving the water quality guidelines (ANZECC/ARMCANZ 2000, Section 8.3.2.2). However, similar conversion factors have not been validated for sediment toxicity tests and their arbitrary use would introduce an additional source of uncertainty in the risk analyses. In our assessment, we always used the most restrictive endpoint reported for a particular species, which will tend to provide a conservative risk analysis. It is important to include as many species as possible in SSDs, rather than excluding any species due to a lack of particular endpoint, in order to increase the representativeness of the SSD to the biological community. The interpretation of the derived HC_n values based on mixed endpoints is that the concentration is harmful to a degree that is related to the endpoints used. In our examples the Cd value is primarily based on LC_{50} data (but includes some more sensitive endpoints) and hence at the $HC_{5:50}$ approximately 5% of species would be expected to show 50% (or less) mortality.

The decision to exclude behavioral and other data not directly related to survivorship from the SSDs was based on the assumption that these factors would not prevent the occurrence of the organism in the environment. Although the relative performance of the organisms may be depressed, they could still persist and hence contribute to the ecological structure and function of the system in question. In contrast, a recent review by Fleeger *et al.* (2003) summarized a wide range of indirect responses, including impacts on keystone species leading to functional deficiencies in the affected ecosystem, trophic cascade effects from impairment of sensitive species on tolerant species, and additional contaminant exposure pathways via bioaccumulation and trophic transfer. Inclusion of the available non-crucial or indirect effects data would have produced lower acceptability criteria and increased estimates of risk.

Although a range of genera (macrophytes, algae, annelids, molluscs [both bivalves and gastropods], and crustaceans) were included in the SSD analyses, there were some major groups missing (notably bony fish) and the balance between trophic levels was poor. It has been estimated that 64% will be primary producers in a simple 3-level food chain (Forbes and Callow 2002). The Australian Water Quality guidelines (ANZECC/ARMCANZ 2000) recommend that the data used for such an assessment should comprise at least five species across four taxonomic groups. These criteria were achieved for the three metals included. Additionally, the range of species included and the effects measured are ecologically relevant to an estuarine environment and hence can be considered reasonable at this stage.

Despite a comprehensive search being undertaken, sufficient SSTT data were found for only three metals. Even those were constrained by data quality and will need to be assessed further in the light of the upcoming recommended protocols (Simpson and Batley 2007). The paucity of SSTT data on Pb in particular was both surprising and unfortunate in relation to this assessment. Lead is known to be a contaminant of concern in Sydney Harbour sediments (McCready *et al.* 2006a) and is generally regarded as a common toxic metal. This lack highlights the need to undertake more tests for a range of organic and inorganic contaminants, across a variety of species representative of the key functional and structural components of ecosystems and the scope of potential environmental conditions, to provide adequate data for reliably predictive modeling of environmental risk. This agrees with an earlier critical appraisal of the SSD methodology by Forbes and Calow (2002) who concluded that, although the approach did provide a better estimate of community effects thresholds, it was adversely influenced by inadequate data and subject to unpredictable shifts in derived thresholds depending on data selection.

The lack of effects data on other toxic contaminants in Sydney Harbour also constrains the overall risk analysis reported here. The cumulative risk assessment will undoubtedly increase with the inclusion of other contaminants. Nonetheless, this article is designed to describe a methodology and in that case it is fit for purpose.

Comparisons with other results

The SSD approach typically uses a 5% effect level as a reasonable basis for setting acceptability criteria in moderately impacted ecosystems (*e.g.*, ANZECC/ARMCANZ 2000). When the median 5% effect values ($HC_{5;50}$) and their lower 95% confidence limits ($HC_{5;95}$) (Table 5) are compared with the Australian ISQG values (Table 1) the derived values for Cd fall between the High and Low guidelines but the values for Cu and Zn are substantially lower (up to a factor of 28 comparing the $HC_{5;95}$ with the ISQG-Low for Cu). The current interim guidelines were evaluated for Sydney Harbour using matched chemical and toxicological data by McCready *et al.* (2006b) and found to be reasonable. Similarly, the derived HC values (Table 5) also need to be considered against estimated background sediment metal concentrations in Sydney Harbour. The mean background concentrations of Cd, Cu, and Zn in Sydney Harbour are 2, 10, and 47 mg/kg (in the mud fraction) with ranges of <1–2.5, 4–28, and 18–123, respectively (Irvine and Birch 1998), although the bioavailable fraction will be less. The $HC_{5;95}$ values for Cu and Zn are below mean background concentrations.

The low estimates derived from the SSDs are, in part, a consequence of the inherent uncertainty and variability of the SSTT data but are primarily due to the overestimated toxicity of sediment metals in the SSTT data, as discussed previously. These observations reinforce the need to undertake new and better testing under revised experimental protocols as recommended (Simpson and Batley 2007) but do not detract from the SSD approach. As an example, Simpson (2005) used SSDs to derive $HC_{5;50}$ values for Cu of 993, 378 and 42.5 mg/kg for sediments with K_d values of 10^5, 10^4, and 10^3, respectively. These experiments were carried out using protocols similar to those likely to be recommended under conditions where the toxicants were much less bioavailable and, consequently they provide higher estimates than our value and are of the same order as the ISQGs.

Leung *et al.* (2005) also used a SSD approach to derive sediment quality criteria based on field data of contaminant loadings and benthic community structure, as distinct from laboratory ecotoxicology studies. Their result for a HC_5 for Cd was 0.014 mg/kg, much lower than our value of 5.0 (3.2–95% lower limit) mg/kg and the ISQG-low value of 1.5 mg/kg. This was ascribed in part to a sensitive species bias, a consequence of their data mining process. Correcting for this, using the ratio of sensitive species applied versus all species sampled in the field, derived a probable effects level (PEL- approximately equivalent to a HC_{10} in this study) of 0.129 mg/kg, still low compared to our HC_{10} value of 6.3 mg/kg (Table 5) and the ISQG-low value (Table 1). One other explanation postulated was that the organisms and sediments tested were from a substantially different habitat both biologically and physicochemically, at an average of 185 m depth, than the estuarine studies used elsewhere. The types of organisms reported in Leung *et al.* (2005) are similar to those found in estuarine systems but the species are different. In addition, Leung also suggests synergism with co-contaminants and that the sensitivity of organisms to metals appears to be increased in the presence of PAHs. This reinforces the need for more site and/or ecosystem specific data.

Given the high probability (certainty in some cases) that the ISQG criteria are exceeded by the current levels of sediment metals in Sydney Harbour (Table 4), the proportion of species likely to be adversely affected (Table 6) may seem incongruously low (although it does go as high as 40% for Zn alone). One obvious reason is the existence of tolerant organisms, including those that are able to take advantage of disturbed systems. Stark (1998) found significantly different assemblages in polluted and unpolluted estuaries near Sydney with greater abundances of capitellids, spionids, nerieids, and bivalves in the more contaminated bays. Another reason is that AQUARISK convolutes the proportion of species likely to be affected at (relatively) low concentrations with the likelihood that those concentrations will occur. The resultant estimates of adverse species impact thus tend to be lower than the simpler estimate of the likelihood that a specific value will be exceeded. Although there is currently no direct evidence in support of the species impact estimates we have derived for Sydney Harbour embayments, the same approach has been validated at freshwater sites affected by metals in acid rock drainage elsewhere (Brown *et al.* 2000; Twining *et al.* 2000). These examples showed that AQUARISK estimates were close to, but slightly over, real measures of species decline indicating a precise and accurate, but appropriately precautionary, outcome. The added advantage of this approach is that it links environmental engineering remediation targets directly to ecological goals (species impacts) rather than to chemical criteria (metal concentrations).

Risk maps

The contaminant concentration maps of Homebush Bay (Figure 3), show distinct regions and potential sources of contamination that differ for the four separate metals and, as such, are useful in their own right. However, they do not give any indication of whether the levels of contamination are of concern or which metals are more significant contributors to ecosystem impact. In this sense, the risk maps (Figure 4) are more useful to environmental managers. The risk maps have the added advantage of imaging each of the contaminants on the same scale. It is apparent from Figure 4 that, of the three metals assessed in Homebush Bay, Zn is of most concern and that remediation strategies that are most successful coping with Zn would be the preferred options. The maps also clearly identify the geographic locations where remedial action would be most likely to have the greatest improvement in terms of species recovery. These are also the sites that should be focused on for further sampling to better define the problem, to assess remedial options and generate revised targets as discussed earlier.

Assuming proportional additivity, Cu, Zn, and Cd alone are likely to have adversely affected more than 60% of sediment-dependent species in restricted areas of Homebush Bay (Figure 4). This compares to the average total risk of 35% (derived using individual risks given in Table 6) for the bay when considered as a whole and hence shows the advantage of using a risk mapping approach. The cumulative risk estimated on the total metal concentrations in sediment increased to 48% although the better estimate of bioavailability based on the ASM is likely to be the more reliable.

Estimates across the embayments for total risk from the 3 metals range from the 35–48% estimated in Homebush Bay to as high as 71% in Hen and Chicken Bay (from Table 6). It is apparent that ecological risk estimates and mapping can also be used to rank and prioritize remedial activity in different embayments. There are issues relating to the simplistic assumption of proportional additivity applied here that ignores synergism and antagonism, commonly known to occur with metals.

The approach has been shown to be somewhat problematic for other contaminants such as pesticides (George *et al.* 2003), but more workable for non-specific narcotic toxicants (Warne and Hawker 1995). Our approach for multiple heavy metal impacts on aquatic biota has been validated in freshwater systems (Brown *et al.* 2000; Twining *et al.* 2000).

Despite this, given the multitude of additional organic and inorganic contaminants present in this system, it is commonly assumed that the current diversity in Sydney Harbour is greatly reduced from pre-industrial levels. Contaminant impacts are in addition to other factors affecting diversity and abundance. For example, Lindegarth and Underwood (2002) showed that the adverse effects of metal addition to sediments in the Sydney region were less clear than the influence of habitat disturbance.

CONCLUSIONS

The authors acknowledge that a paucity of site- and species-specific ecotoxicological data exists to support SSD risk analyses in general and that more could be acquired to refine the assessment for Sydney Harbour in particular. However, this probabilistic study and numerous papers cited in our references support the contention that elevated sediment metals in embayments of Sydney Harbour pose an ecological risk.

Although we understand that heavy metal bioaccumulation and toxicity can be extreme and highly variable (*e.g.*, see review by Rainbow 2002) we do not anticipate that animals inhabiting Sydney Harbour will be substantially more or less sensitive to contaminated sediments than those species used in the tests applied to this assessment (although there is mounting evidence to suggest that populations exposed to contaminated systems in the long term may acquire tolerance by a variety of mechanisms, *e.g.*, Gale *et al.* 2003; Klerks and Lentz 1998). However, care must be taken to ensure that species and substrates used in future toxicity testing are suited to the ecosystem being evaluated. The example using deep sea organisms (Leung *et al.* 2005) is evidence of not being able to compare SSD results between different marine ecosystems.

This article has also demonstrated the useful application of the SSD approach, combined with probabilistic assessment of contaminant concentrations, to undertaking environmental management based on ecological risk assessment and mapping procedures. The release of improved protocols for undertaking sediment toxicity assays will help to provide the much needed data to improve this form of assessment in future.

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