HEAVY METAL DISTRIBUTIONS IN THE WATERS OF SYDNEY HARBOUR, NOVA SCOTIA

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Four surveys of total Hg and dissolved Cd, Cu, Fe, Mn, Ni, Pb and Zn concentrations in Sydney Harbour waters were conducted between 1999 and 2001. Suspended particulate matter samples were analysed for Cd, Cu, Fe, Mn, Ni, Pb, Zn and 22 other metals. The measurements were made to establish environmental context for toxicological studies, provide ground-truthing data for water quality modelling, and investigate estuarine geochemistry of heavy metals in a harbour subject to significant anthropogenic input. Despite the long history of metal contamination in Sydney Harbour, metal concentrations are almost all below water quality guidelines for estuarine or marine waters. The distributions of total Hg and dissolved Cu, Fe and Mn show that freshwater inputs are important contributors of these metals to the harbour. For Cu, Fe and Mn, additional inputs to the central part of South Arm are evident from the metal vs. salinity relationships. Particulate Cd, Cr, Cu, Pb, Mn, Ag and Zn distributions also show evidence of inputs in the central part of the harbour. Sewage appears to be the major, but not sole, source for these metals.

Quatre études des concentrations d'Hg total et de Cd, Cu, Fe, Mn, Ni, Pb et Zn dissous dans les eaux du port de Sydney ont été effectuées entre 1999 et 2001. On a analysé les échantillons des matières particules en suspension pour y déceler la présence éventuelle de Cd, Cu, Fe, Mn, Ni, Pb, Zn et 22 autres métaux. Les mesures obtenues visaient à établir le contexte environnemental des observations toxicologiques, à fournir des données de vérification pour la modélisation sur la qualité de l'eau et à étudier la géochimie estuarienne des métaux lourds dans un port soumis à apport anthropique important. Malgré les longs antécédents de contamination par les métaux dans le port de Sydney, les teneurs en métaux sont presque toutes inférieures aux concentrations indiquées dans les recommandations sur la qualité des eaux estuariennes ou marines. Il ressort de la répartition des concentrations d'Hg total et de Cu, Fe et Mn dissous que les apports en eau douce comptent pour beaucoup dans la présence de ces métaux au sein du port. Pour ce qui est des concentrations de Cu, Fe et Mn, la relation entre les métaux et la salinité met en évidence des apports supplémentaires dans la partie centrale du bras sud. La répartition des particules de Cd, Cr, Cu, Pb, Mn, Ag et Zn reflète aussi des apports dans la partie centrale du port. Les eaux usées semblent être la principale, mais non l'unique, source de ces métaux.

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INTRODUCTION

Wastes discharged from the Sydney Steel Plant and associated coke ovens to the Sydney Tar Ponds from the 1890s until the 1980s included very high concentrations of various hydrocarbon components and a number of heavy metals including Cu, Pb, Hg and Zn. Runoff and leachate from the Tar Ponds enters Sydney Harbour via Muggah Creek, a small tidal arm of the harbour. Numerous other discharges, including ~20,000 m^3/day of storm water and domestic and industrial sewage, enter the harbour from various locations including ~8,000 m^3/day into Muggah Creek (CBCL 1999). Contamination of harbour sediments and biota from the combination of these sources was initially assessed in the early 1980s (Matheson et al. 1983) and has been reassessed several times since, most recently by Ernst et al. (1999) and Stewart and White (2001). High levels of polyaromatic hydrocarbons (PAHs) and heavy metals were found in both sediments and biota. PAH contamination of lobster (Sirota et al 1984) resulted in an on-going closure of the commercial lobster fishery in the South Arm of Sydney Harbour commencing in 1982.

We measured water column concentrations of suspended particulate matter, nutrients, and dissolved and particulate heavy metals in Sydney Harbour on four occasions between October 1999 and May 2001 as part of an extensive reassessment of environmental contamination and biological effects in Sydney Harbour. This study is the most comprehensive assess-ment of chemical contamination of the water column to date. Previous assessments had focussed almost entirely on contamination of sediments and biota. Our study had three main objectives: to establish the contaminant reference levels for toxicological studies that were being made as part of an overall environmental assessment; to provide ground-truthing data for water quality modelling that was also being done as part of the assessment; and to investigate estuarine geochemistry of heavy metals in a harbour subject to significant anthropogenic chemical inputs. The results provide a timely assessment of environmental conditions prior to the commencement of a major Tar Ponds clean-up (PWGSC 2005).

METHODS

Water samples were collected from one of two small Canadian Coast Guard ships. In October 1999, October 2000 and May 2001 the samples were collected from the CCGS *Navicula* and in July 2000, from the CCGS *Earl Grey*. They were collected with 5 litre General Oceanics lever action Niskin bottles (Teflon-coated PVC) hung on a stainless steel hydrowire and tripped with Teflon messengers. Water samples were collected at surface and mid-depth from 9 to 16 stations on the surveys (Fig 1). Sampling for each of the surveys was spread over 1-3 days and not aligned with the state of the tide or other environmental factors. Conductivity and temperature were recorded at each station with a Seabird 25 CTD.

Two litre samples for heavy metal analysis were drawn from each sampler and filtered in a portable clean bench through pre-cleaned and tared 0.4 micron Nuclepore filters into cleaned 2 litre polyethylene sample storage bottles. When the Nuclepore filter clogged, the volume filtered was recorded and the remaining water filtered with a clean 0.4 µm Aquaprep filter. The Nuclepore filters were rinsed with 100 ml of Milli-Q water to remove salt and air dried in the portable clean bench. The filtered water samples were acidified in the BIO clean lab with 1.0 ml of Seastar sub-boiling distilled HNO_3 per litre. The Nuclepore filters were reweighed in the clean lab for gravimetric determination of suspended particulate matter (SPM) concentrations and stored at room temperature until processed for particulate metal analysis. Unfiltered water samples for total mercury analysis were drawn from the samplers into acid cleaned, 500 ml Teflon bottles and preserved with 1 ml of 0.2N BrCl in the clean bench. Unfiltered samples for salinity and nutrient analysis were also collected; the nutrient samples were stored frozen.

The water samples for Cd, Cu, Fe, Pb, Ni and Zn analyses were first heated in an oven at 60°C for a minimum of 12 hours. The metals were then extracted using an APDC/DDDC Freon extraction procedure and back extracted into HNO_3 (Dalziel et al., 1989). The extracted samples were analysed using graphite furnace atomic absorption spectrophotometry with Zeeman background correction. Manganese was analysed by direct injection into the spectrophotometer. All analytical steps were conducted in our clean room using our normal QA/QC protocols, including analysis of National Research Council of Canada (NRCC) certified reference materials (CRMs).

Samples for total Hg analysis were first heated to 60°C for 24 hours to ensure complete oxidation to Hg^{2+}. A 250ml of sample plus 0.5mL of $NH_2OH \cdot HCl$ and 1ml of $SnCl_2$ were added to a gas purging reaction vessel and the Hg^0 purged from the vessel onto an Au trap with N_2 for 30 min. After drying, the Hg on the Au trap was analysed by cold vapour atomic fluorescence spectrophotometry.

Filters for particulate metal analysis were digested in our clean lab with 2ml of Seastar HNO_3 and 1ml of HF in precleaned Loran Teflon digestion bombs and heated in a microwave oven for 45 sec. The samples were taken to dryness after digestion and redissolved in 20ml of 2% HNO_3 for analysis by inductively coupled plasma mass spectrometry (ICPMS) at a contract lab (RPC, Fredericton, NB). Filter blanks and 2-6 mg samples of NRCC BCSS-1 sediment CRM were digested and analysed using the same protocols.

RESULTS

Results from the 1999 survey are summarized in Table 1 as average concentrations in surface (1 m) and deep samples (5-15 m) for 4 regions of the harbour going from the Sydney River estuary (SRE), through the most intensely developed Central South Arm of Sydney Harbour (CSA), to the

Table 1 Average (arithmetic mean) concentrations for the October 1999 survey.

Sampling Depth	SRE 1 m	SRE 5-8 m	CSA 1 m	CSA 10-14 m	OSA 1 m	OSA 10-15 m	OH 1 m	OH 9-12 m	NWA 1 m	NWA 6-10 m
Salinity	23.76	28.50	28.43	28.67	27.88	29.06	28.47	29.33	27.86	28.73
Cd_d (ng/l)	14	19	23	24	22	23	24	32	22	25
Cu_d (µg/l)	0.63	0.42	0.51	0.43	0.55	0.33	0.44	0.33	0.48	0.42
Fe_d (µg/l)	14.8	2.87	3.22	2.91	3.40	1.45	1.67	1.14	2.67	1.78
Mn_d (µg/l)	16.7	8.4	11.0	7.6	6.4	3.9	4.8	4.1	4.8	4.0
Ni_d (µg/l)	0.46	0.36	0.57	0.38	0.42	0.31	0.36	0.45	0.45	0.45
Pb_d (ng/l)	27	13	41	21	28	23	27	17	42	26
Zn_d (µg/l)	0.64	0.34	1.88	1.50	1.30	0.56	0.42	0.32	0.90	0.51
Hg_t (ng/l)	0.77	0.53	0.51	0.36	0.34	0.56	0.43	0.25	0.43	0.24
NO_3 (µM)	2.60	0.35	0.60	0.62	0.88	0.71	0.69	0.80	0.88	0.78
NO_2 (µM)	0.25	0.11	0.24	0.22	0.20	0.18	0.19	0.16	0.17	0.20
NH_3 (µM)	5.25	2.27	3.62	3.15	2.74	2.24	1.90	1.60	1.91	2.18
HPO_4 (µM)	1.07	0.60	1.24	1.17	1.07	0.93	0.94	0.68	0.99	0.96
SiO_2 (µM)	10.40	2.54	4.41	3.95	4.59	3.61	3.72	3.02	4.10	3.67
SPM (mg/l)	1.58	1.52	1.25	1.27	1.46	1.69	2.44	4.19	1.44	1.56
Al_p (%)	5.9	5.7	2.7	3.6	5.2	8.0	8.8	11.0	4.6	6.9
Cd_p (µg/g)	0.72	1.24	1.18	0.92	0.60	0.66	0.72	0.59	0.74	0.75
Cu_p (µg/g)	107	49	78	48	66	43	63	37	48	41
Fe_p (%)	7.4	6.1	3.3	3.1	5.1	6.2	6.8	7.1	4.3	6.0
Pb_p (µg/g)	131	95	125	92	98	66	72	42	77	85
Li_p (µg/g)	42	39	34	36	43	61	57	65	31	52
Mn_p (mg/g)	4.8	6.5	4.4	3.8	4.5	2.9	2.8	1.3	3.9	4.5
Ni_p (µg/g)	29	27	29	28	32	38	41	36	26	33
Ag_p (µg/g)	0.64	0.52	0.79	0.71	0.43	0.41	0.51	0.41	0.28	0.22
Zn_p (µg/g)	289	175	342	177	188	159	137	127	165	140

SRE=Sydney River estuary, CSA=central South Arm, OSA=outer South Arm, OH=outer harbour, NWA=North West Arm.

Outer South Arm (OSA) and the Outer Harbour (OH), as well as the North West Arm (NWA) (see Fig 1 for the boundaries of these regions). Muggah Creek discharges into the CSA.
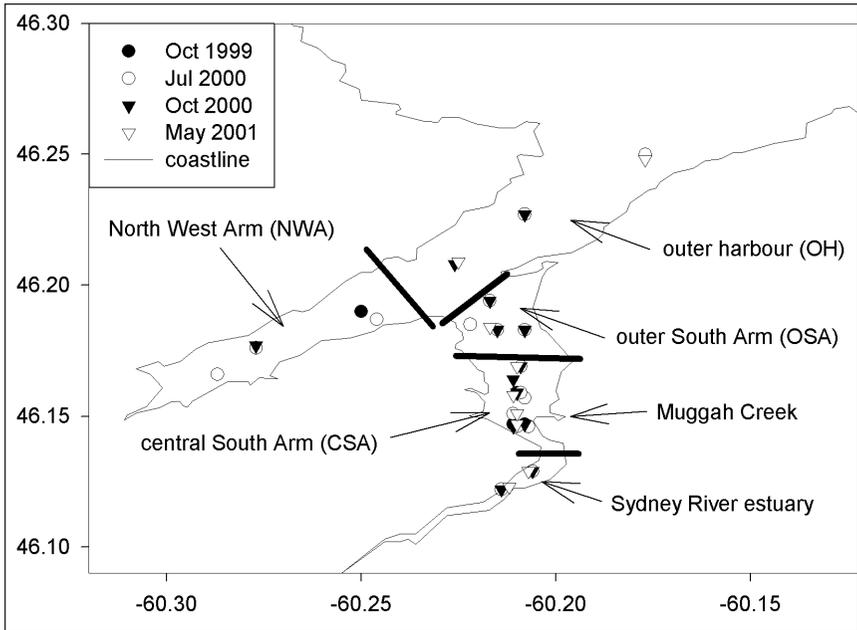

Fig 1   Map of Sydney Harbour, N.S. showing station locations and sub-region boundaries.

The salinity data in Table 1 indicated a weak estuarine pattern – salinities increased with depth in each box, and increased in both the surface and deep layers from the estuary to the outer harbour. Physical oceanographic studies showed that the general circulation pattern in Sydney Harbour was estuarine although large pulses of water into and out of the harbour (seiches) frequently overwhelmed the estuarine circulation (Petrie et al. 2001). The dissolved metal and nutrient results showed some stronger gradients, notably for Fe, Mn, NH_3 and SiO_2. The numbers of stations for each harbour region were very small (2 for SRE and OH, 4 for OSA and 5 for CSA) so it is difficult to get a good estimate of the precision of each of the arithmetic means. Based on estimates for harbour regions with larger numbers of samples, it would appear that one standard deviation precisions of the means were approximately 10-30% for Cd, Cu and Ni and 30-50% for Fe, Mn, Pb and Zn. The metal content of the particulate matter showed less variability. Particulate metal concentrations are expressed as weight of metal per gram of SPM, concentrations per litre of water can be calculated

by multiplying the metal content of the SPM by the SPM concentration. The calculations show that the particulate Cd, Cu and Ni only contributed a small percentage of the total metal concentration, but for Mn and Zn, dissolved and particulate metal concentrations were approximately equal. For Fe and Pb, the particulate dominated.

The results for the July 2000 survey are shown in Table 2. In this case the horizontal gradients in salinity were weaker, although all areas showed an increase in salinity with depth. Concentrations of the nutrients were lower than in the 1999 survey. All of these observations were consistent with lower freshwater inputs and greater biological activity that would be expected in July. One interesting difference between the October 1999 and July 2000 surveys was that concentrations of Fe, Mn, Zn and all five nutrients in July 2000 increased with depth in the CSA and OSA. Increases with depth were not evident in October 1999 except for NO_3^-. A multivariate analysis of the nutrient and metal data for these two cruises using salinity and depth as variables showed that there was a significant negative correlation ($P<0.05$) with salinity for Cu, Fe, Mn, Hg, SiO_2, NO_3^-, NH_3 and NO_2^- in the 1999 data but a positive correlation with depth only for NO_3^-. Cu and Pb showed a significant negative correlation with depth. In July 2000, there was a negative correlation with salinity only for Mn and Si, but a positive correlation with depth for Fe, Mn, SiO_2, HPO_4^{2-}, NO_3^- and NO_2^-.

The October 2000 survey (Table 3) shows virtually uniform salinities throughout the harbour, i.e. very little stratification or horizontal gradient. Freshwater input to the harbour at the time of this survey was very low, so metal concentrations in the harbour should more clearly reflect anthropogenic inputs, but concentrations in the CSA and OSA were relatively low and not significantly elevated compared to the other surveys.

The final survey in May 2001 was conducted at a time of much higher freshwater input. The results (Table 4) show much greater vertical and horizontal gradients in salinity as well as higher concentrations of Fe and especially Mn in the estuary surface samples. Despite the greater freshwater inputs, concentration increases with depth in CSA and OSA are evident for Mn, NH_3 and HPO_4^{2-}. The multivariate analysis shows significant ($P<0.05$) negative correlation with salinity for Cd, Cu, Fe, Mn, Hg, SiO_2, NO_3^- and NH_3, and positive correlations with depth for Mn, HPO_4^{2-}, NO_3^- and NH_3.

DISCUSSION

The first objective of this study was to establish the contaminant exposure levels and assess the potential toxicity of water column metals in Sydney Harbour. There are very few Canadian environmental guidelines or regulations for the concentrations of heavy metals in estuarine or marine waters. The only marine water quality guideline for protection of aquatic life given in the Canadian Council of Ministers of the Environment (CCME 2001) Environmental Quality Guidelines for the metals described in this paper is the limit of 0.12 µg/l for Cd. The guideline refers to total Cd in the water,

Table 2 Average (arithmetic mean) concentrations for the July 2000 survey.

Sampling Depth	SRE 1 m	SRE 5-9 m	CSA 1 m	CSA 10-15 m	OSA 1 m	OSA 12-17 m	OH 1 m	OH 10-14 m	NWA 1 m	NWA 7-9 m
Salinity	27.54	29.29	29.62	30.09	29.68	30.16	29.89	30.10	29.59	29.97
Cd_d (ng/l)	19	23	24	23	29	25	22	14	30	29
Cu_d (µg/l)	0.54	0.47	0.41	0.33	0.51	0.29	0.34	0.25	0.32	0.29
Fe_d (µg/l)	3.33	2.59	2.04	4.28	1.88	3.99	0.75	0.71	3.72	2.47
Mn_d (µg/l)	11.8	10.3	7.1	9.3	6.9	9.5	3.7	2.6	6.3	6.9
Ni_d (µg/l)	0.35	0.33	0.36	0.31	0.33	0.31	0.30	0.29	0.27	0.32
Pb_d (ng/l)	8	8	15	10	8	8	12	12	13	8
Zn_d (µg/l)	0.68	1.13	1.61	1.31	0.88	1.17	0.36	0.35	0.45	0.43
Hg_d (ng/l)	0.36	0.35	0.48	0.42	0.28	0.41	0.25	0.21	0.23	0.21
NO_3 (µM)	0.19	0.13	0.22	0.42	0.06	0.25	0.08	0.10	0.11	0.25
NO_2 (µM)	0.11	0.10	0.12	0.17	0.08	0.13	0.10	0.10	0.08	0.12
NH_3 (µM)	0.32	0.34	0.65	1.02	0.60	0.84	0.10	0.10	0.48	0.65
HPO_4 (µM)	0.90	0.72	0.74	1.02	0.58	1.01	0.55	0.54	0.62	0.81
SiO_2 (µM)	8.20	5.19	4.41	6.73	3.23	6.48	2.08	2.73	2.98	4.97
SPM (mg/l)	1.60	1.09	1.32	1.97	1.67	1.06	0.69	0.79	0.90	1.54
Al_p (%)	1.8	1.8	2.2	2.4	1.7	3.5	3.3	4.2	2.4	2.3
Cd_p (µg/g)	1.52	1.87	1.43	0.93	1.24	1.45	1.54	1.16	1.27	0.78
Cu_p (µg/g)	56	45	52	33	33	29	42	37	19	26
Fe_p (%)	3.5	3.9	3.1	5.0	1.6	4.5	2.4	2.7	2.1	2.6
Pb_p (µg/g)	89	94	100	83	55	74	62	38	68	47
Li_p (µg/g)	16	16	18	20	15	29	28	36	21	22
Mn_p (mg/g)	5.3	5.8	2.9	2.7	2.7	2.2	2.9	2.0	3.2	2.1
Ni_p (µg/g)	83	11	14	9	16	32	32	35	12	31
Ag_p (µg/g)	1.13	0.89	0.64	0.45	0.31	0.42	0.29	0.26	0.36	0.29
Zn_p (µg/g)	234	198	149	148	110	155	94	112	99	117

SRE=Sydney River estuary, CSA=central South Arm, OSA=outer South Arm, OH=outer harbour, NWA=North West Arm.

Table 3 Average (arithmetic mean) concentrations for the October 2000 survey.

Sampling Depth	SRE 1 m	SRE 5-9 m	CSA 1 m	CSA 12-16 m	OSA 1 m	OSA 15-16 m	OH 1 m	OH 11-15 m	NWA 1 m	NWA 11 m
Salinity	28.99	29.04	29.03	29.20	29.19	29.20	29.05	29.16	29.18	19.19
Cd_d (ng/l)	19	20	24	20	16	20	22	18	21	16
Cu_d (µg/l)	0.67	0.47	0.55	0.36	0.45	0.34	0.47	0.36	0.37	0.33
Fe_d (µg/l)	2.50	2.73	2.77	3.42	1.94	2.68	1.71	1.65	1.43	1.85
Mn_d (µg/l)	5.62	5.06	5.7	5.4	2.5	4.3	2.05	2.91	1.8	2.4
Ni_d (µg/l)	0.26	0.24	0.29	0.27	0.28	0.26	0.28	0.27	0.27	0.26
Pb_d (ng/l)	34	19	33	18	10	7	26	13	11	5
Zn_d (µg/l)	1.58	1.01	0.98	0.76	0.98	0.58	0.80	0.45	0.25	0.18
Hg_t (ng/l)	0.56	0.62	0.53	0.40	0.45	0.38	0.45	0.39		
NO_3 (µM)	0.81	0.78	0.69	0.52	0.46	0.46	0.21	0.22	0.19	0.31
NO_2 (µM)	0.33	0.36	0.28	0.29	0.25	0.25	0.17	0.17	0.19	0.24
NH_3 (µM)	3.07	3.35	2.71	3.36	1.48	2.06	0.54	0.46	0.40	1.18
HPO_4 (µM)	1.36	1.54	1.53	1.29	1.35	1.13	0.69	0.82	1.03	1.11
SiO_2 (µM)	7.25	6.96	7.22	7.16	6.74	7.09	3.72	4.16	5.83	6.50
SPM (mg/l)	1.69	1.78	1.03	0.89	0.82	0.85	0.89	1.32	1.62	0.55
Al_p (%)	2.2	2.3	1.8	2.8	2.3	3.9	2.9	3.2	1.8	3.3
Cd_p (µg/g)	0.92	1.05	0.96	1.50	1.15	2.50	1.02	0.56	0.76	0.80
Cu_p (µg/g)	186	87	66	53	53	68	100	31	28	32
Fe_p (%)	3.1	3.1	3.3	3.9	3.4	4.0	2.2	2.6	1.7	3.0
Pb_p (µg/g)	142	134	121	102	98	84	68	42	54	68
Li_p (µg/g)	21	23	16	25	21	33	25	29	16	31
Mn_p (mg/g)	8.4	8.7	10.1	9.3	10.9	8.9	3.5	4.0	4.7	6.4
Ni_p (µg/g)	24	21	47	41	37	27	48	48	14	23
Ag_p (µg/g)	1.35	1.44	0.79	0.90	0.74	0.92	0.53	0.45	0.29	0.58
Zn_p (µg/g)	223	238	568	315	174	241	84	104	63	89

SRE=Sydney River estuary, CSA=central South Arm, OSA=outer South Arm, OH=outer harbour, NWA=North West Arm.

Table 4   Average (arithmetic mean) concentrations for the May 2001 survey.

Sampling Depth	SRE 1 m	SRE 7-9 m	CSA 1 m	CSA 10-15 m	OSA 1 m	OSA 16-17 m	OH 1 m	OH 12-14 m
Salinity	20.60	29.42	22.87	29.76	23.66	32.25	26.84	32.30
Cd_d (ng/l)	26	22	25	26	24	25	21	19
Cu_d (µg/l)	0.59	0.30	0.50	0.27	0.57	0.23	0.48	0.20
Fe_d (µg/l)	13.80	1.71	6.60	2.05	9.48	2.18	2.87	1.24
Mn_d (µg/l)	31.85	18.15	25.73	35.93	24.95	37.40	13.60	9.09
Ni_d (µg/l)	0.23	0.29	0.34	0.30	0.30	0.25	0.33	0.20
Pb_d (ng/l)	40	2	21	16	24	8	38	12
Zn_d (µg/l)	1.99	1.57	7.78	7.71	12.44	1.82	3.74	1.54
Hg_t (ng/l)	1.41	0.44	1.12	0.33	1.05	0.39	0.62	0.28
NO_3 (µM)	1.35	0.10	0.79	0.30	0.54	0.14	0.07	0.06
NO_2 (µM)	0.10	0.06	0.08	0.07	0.06	0.04	0.06	0.08
NH_3 (µM)	1.57	0.86	0.77	1.61	1.10	1.32	0.22	0.76
HPO_4 (µM)	0.23	0.33	0.19	0.56	0.14	0.49	0.29	0.42
SiO_2 (µM)	7.34	0.69	5.49	0.90	4.69	0.67	1.77	0.50
SPM (mg/l)	1.42	0.78	1.44	0.80	1.19	0.59	1.10	0.86
Al_p (%)	3.2	4.6	3.0	2.4	2.8	3.0	5.0	3.8
Cd_p (µg/g)	0.72	0.23	0.66	0.86	0.56	0.92	0.32	0.25
Cu_p (µg/g)	72	29	40	21	62	21	28	28
Fe_p (%)	3.3	3.6	3.0	2.3	3.3	2.7	3.7	2.7
Pb_p (µg/g)	42	45	41	32	60	30	48	21
Li_p (µg/g)	26	38	23	20	26	24	40	36
Mn_p (mg/g)	0.92	1.37	1.00	0.88	1.33	1.12	1.12	0.96
Ni_p (µg/g)	38	31	31	20	66	23	38	28
Ag_p (µg/g)	0.85	0.49	1.05	.40	0.96	0.12	0.93	0.58
Zn_p (µg/g)	126	113	531	313	478	133	281	127

SRE=Sydney River estuary, CSA=central South Arm, OSA=outer South Arm,
OH=outer harbour.

so we need to compare the sum of measured dissolved and particulate Cd to the guideline. The maximum total Cd concentration seen in all of our surveys was 0.061 µg/l (0.059 µg/l dissolved + 0.002 µg/l particulate), i.e. only half of the guideline concentration. Average concentrations of dissolved plus particulate Cd in Sydney Harbour (Tables 1-4) were less than 25% of the guideline.

Other jurisdictions give guidelines for some of the other metals. For example, the Australia and New Zealand Environment and Conservation Council (ANZECC 2000) gives guidelines for the protection of aquatic ecosystems that includes, at the most stringent level of protection (99% of test species), 0.7 µg/l for Cd, 0.3 µg/l for Cu, 2.2 µg/l for Pb, 0.1 µg/l for Hg, 7 µg/l for Ni and 7 µg/l for Zn. The European Union (EU) guidelines are 0.1 µg/l for Cd, 5 µg/l for Pb, 0.05 µg/l for Hg and 5 µg/l for Zn. The EU Cu guideline (0.05 µg/l) is not appropriate because it refers to free ionic Cu, not total dissolved Cu. US guideline levels are generally higher. Eighty-three percent of our samples were above the most stringent ANZECC Cu guideline, but all samples were below the ANZECC guideline for protection of 95% of test species and the US guideline. Also, it is not clear that marine

guidelines established for open coastal waters would be appropriate for the lower salinities found in estuaries. If we estimate salinity dependent estuarine guidelines based on linear interpolations between the ANZECC freshwater and marine guidelines, only 3 of the Sydney Harbour Cu samples would be above this 'guideline'. Four of the samples from the May 2001 survey exceeded the ANZECC Zn guideline of 7 µg/l, but all were below the guidelines from the US and EU, and as noted above for Cu, they would be below an estuarine guideline interpolated between the freshwater and seawater guidelines. Zn concentrations of samples from the other three surveys were all below the guidelines.

It is difficult to accurately assess the toxicity of Cu because of the difference in toxicity between ionic Cu (highly toxic) and organically complexed Cu (much less toxic). Bioavailability would also be reduced for Cu complexed to terriginous organic matter (e.g. humic and fulvic acids). Ionic Cu was used in most of the laboratory toxicity tests upon which the guidelines are based, but in estuarine and marine environments most of the Cu would be complexed. Organic complexation probably eliminates any potential Cu toxicity for the Sydney Harbour waters.

The consistency in the picture of metal distributions observed from one survey to the next bodes well for establishing the usefulness of the data presented in Tables 1-4 for meeting the second objective of the project, i.e. to provide data for ground-truthing of water quality models. It would be difficult to relate highly variable measurements of the concentrations to the monthly or seasonally averaged descriptions of water circulation and water quality that are being developed, but the data presented in the tables show relatively little variability from survey to survey and muted gradients within the surveys.

The main sources of heavy metals in Sydney Harbour are the natural freshwater input ($\sim 1 \times 10^6$ m^3/day) and the various anthropogenic inputs including outflow from the Sydney Tar Ponds and the many untreated municipal/industrial sewage/storm water discharges ($\sim 2 \times 10^4$ m^3/day). Water entering the harbour from the offshore as a result of the estuarine circulation also brings heavy metals into the harbour. Most of the natural freshwater input is from the Sydney River into the SRE. The two largest sewer inputs are $\sim 8 \times 10^3$ m^3/day into the CSA through Muggah Creek (also the point of entry for input from the Tar Ponds) and $\sim 6 \times 10^3$ m^3/day into the SRE near Wentworth Creek. The next largest sewers ($\sim 3 \times 10^3$ m^3/day at Dobsons Point and $\sim 1 \times 10^3$ m^3/day at Sydport) discharge into the CSA (CBCL 1999). The relative importance of these sources for the various dissolved metals are evident from the data presented in Table 1 and illustrated in the plots of metal concentration vs. salinity for the October 1999 survey (Fig 2). For Fe, the distribution was clearly controlled by input from the rivers, dilution with seawater within the harbour and removal by chemical precipitation, although some indication of additional inputs to the CSA was evident. For Cu, Mn, Ni, Pb and Zn inputs from both the natural and anthropogenic sources were important. The freshwater source was relatively more important for
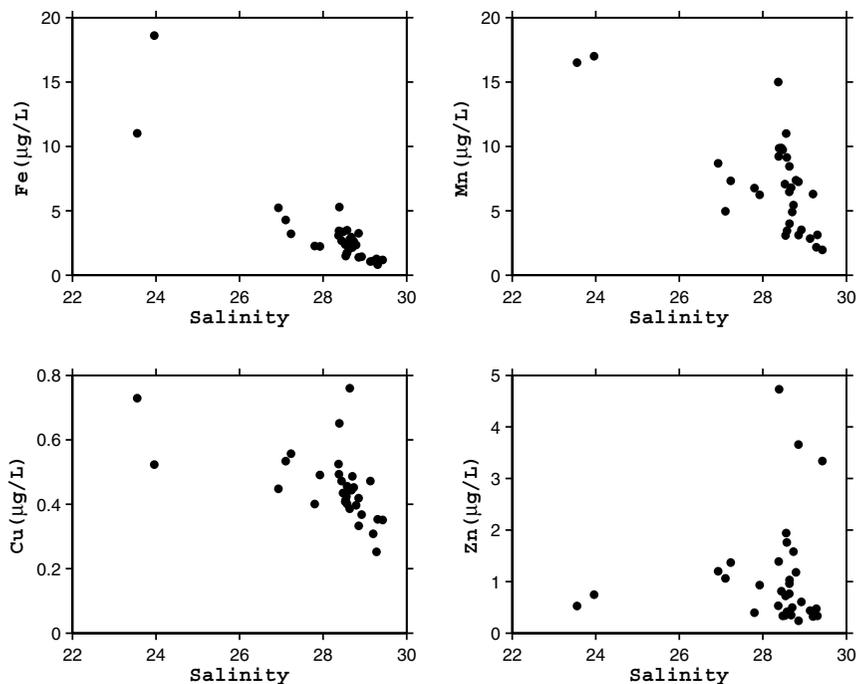
Fig 2   Metal vs. salinity relationships for the October 1999 survey.

Mn and Cu than for Ni and Pb and least important for Zn. Inputs from the two types of sources can be seen in all the plots of concentration vs. salinity where elevated concentrations in the CSA (anthropogenic inputs) were superimposed on a general decrease in concentration with salinity (natural freshwater input). For Mn and Zn, the elevated samples included CSA and OSA samples from both surface and deep layers while for Cu, Ni and Pb, the elevated concentrations were restricted to a few surface layer samples. Similar patterns were seen for the nutrients where natural freshwater inputs dominated for SiO_2 and NO_3^-, with anthropogenic sources increasingly important for NO_2^-, HPO_4^{2-} and NH_3. There is a very strong covariance of the Mn and NH_3 concentrations (r=0.881). It would appear that these two parameters are the strongest markers for the sewage input to the harbour. Data collected by Environment Canada on metals in sewage showed elevated average Mn concentrations of 248 µg/l for the Wentworth discharge and 361 µg/l for the Muggah Creek discharge (Julien 2000). Cd concentrations increased with increasing salinity, pointing to the importance of offshore waters as a source for the Cd in the harbour waters.

For the July and October 2000 surveys the observed salinity ranges were reduced but the basic metal vs. salinity relationships remained much the same. The only significant differences were that elevated concentrations were also observed in the OSA and were more restricted to the bottom

Fig 3   Combined Cu vs. salinity plot for all four surveys.

waters. These differences were also evident in the average concentra-
tions listed in Tables 1-4. The nutrients followed very similar patterns. The
absolute concentrations were reduced in the July survey presumably as
a result of biological activity but all showed the decreasing concentrations
with increasing salinity and positive anomalies for predominantly bottom
water samples for the CSA and OSA, i.e. the same pattern as seen for Fe,
Mn and Zn.

The final, more limited survey in May 2001 found a much greater range in
salinity (spring runoff), general decreases in concentrations of Cu, Fe, Mn,
NO_3^-, NH_3 and SiO_2 with increasing salinity and elevated concentrations in
bottom waters of CSA and OSA for Mn, NH_3 and HPO_4^{2-}, basically the same
pattern as seen on the other cruises. The survey to survey comparability
is sufficiently good that all the data can generally be described by single
metal salinity relationships, such as for Cu shown in Fig 3.

The four Zn results from the May 2001 survey that exceeded the ANZECC
water quality guideline were found in the CSA (1 surface and 2 deep) and
OSA (1 surface). Anomalously high Cu samples, when observed, were
always CSA or OSA surface samples. Pb anomalies also tended to be sur-
face samples, but for Fe, Mn and the nutrients, results that were above the
parameter vs. salinity regression lines were predominantly deep samples.
This distinction is interesting; surface runoff including the overflow from
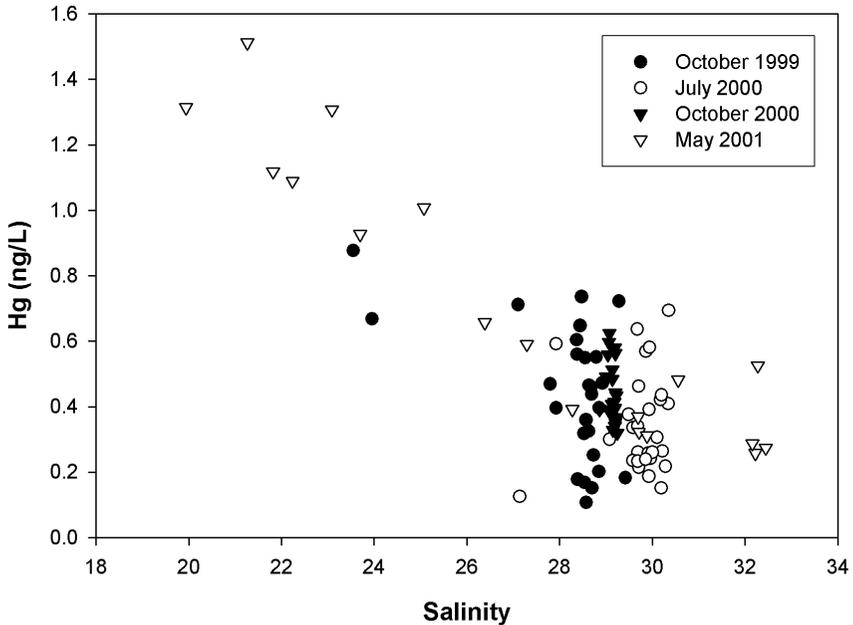the Tar Ponds is into the surface layer but sewage inputs are, initially at

Fig 4   Total mercury vs. salinity relationship for Sydney Harbour.

least, into the deep layer because the sewage discharge points are gener-
ally submerged. Discharges do not have to be very deep to be into the
deep layer because the surface layer in Sydney Harbour is very thin (~ 2
m). Buoyancy of the sewage (its salinity is much lower than the estuarine
receiving waters) should rapidly bring the dissolved sewage constituents
to the surface. The elevated dissolved metal and nutrient concentrations
in the deeper water likely resulted from the release from the sediments of
metals and nutrients from the anaerobic decomposition of organic matter
(mostly derived from sewage) in the sediments.

The total Hg distributions showed less indication than those of Cu, Pb,
Mn or Zn of additional inputs into the central part of the harbour. The Hg_t
vs. salinity plot for the May 2001 survey (Fig 4) shows an essentially linear
decrease in Hg concentration with increasing salinity, and the plot combin-
ing all the data from the four surveys shows little indication of elevated
concentrations in the CSA.

SPM concentrations in Sydney Harbour (0.5-2.0 mg/l) were generally
low compared to estuaries elsewhere (e.g. Postma 1980). As a result, the
contribution of particulates to the total metal concentrations was lower than
expected for estuaries.   The heavy metal content of the particulate matter
(Fig 5) showed a general background of inorganic particulates, with many
samples from the SRE, CSA and OSA having higher heavy metal content.
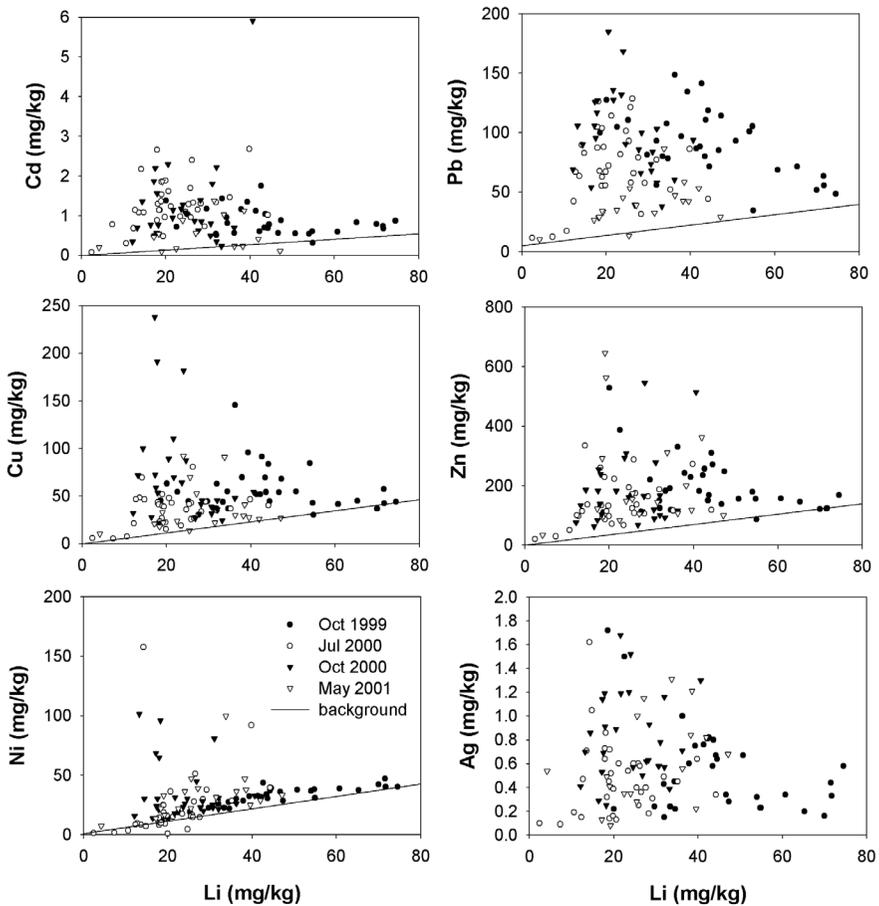Background concentrations in Fig 5 were estimated from the metal vs. Li

Fig 5   Metal vs. Li relationships for SPM samples from Sydney Harbour. Regression lines in the figure refer to background metal vs. Li relationships for unpolluted N.S. coastal sediments.

relationships found for estuarine sediments in harbours and inlets around Nova Scotia using Li as a grain-size normalizer (Loring 1990).

Ag concentrations in sediments have been shown to be good indicators of sewage input (Ravizza & Bothner 1996). In Sydney Harbour maximum sediment Ag concentrations (Loring et al. 2008) were seen adjacent to the two largest sewage discharges. Ag content of the SPM samples (Fig 5) showed a rather similar pattern to those of Cd, Cu, Pb and Zn suggesting, perhaps, a common sewage source for all these metals. Principal component analysis for the 29 elements that were determined for the 112 SPM samples from all four surveys (Table 5), however, showed grouping of Cr, Mo and Ni in one factor and Cu, Pb, Mn and Ag in another. If factor 1 (Al,

Table 5 Varimax matrix for metals in Sydney Harbour SPM (for P=0.01, r=0.241)

	1	2	3	4	5	6
Al	0.929					
Sb						-0.514
As					0.877	
Ba	0.459	0.317				0.539
Be	0.901					
Cd					0.389	
Ca	0.385		0.753			
Cr	0.257			0.829		
Co	0.708	0.405		0.283		
Cu		0.619		0.306		
Fe	0.766				0.444	
La	0.752					
Pb		0.820			0.253	
Li	0.966					
Mg			0.870			
Mn		0.798				
Mo		0.468		0.734		
Ni				0.843		
K	0.881		0.261			
Rb	0.957					
Ag		0.664			0.246	
Na	-0.344		0.862			
Sr		0.429	0.617			0.315
Tl	0.854					
Sn						0.558
Ti	0.767					-0.328
U	0.801					
V	0.517				0.771	
Zn					0.373	0.528
% of var.	30.621	11.164	9.227	8.500	7.498	5.555

Be, Co, Fe, La, Li, K, Rb, Tl, Ti and U) is an aluminosilicate mineral factor, and the Cu, Pb, Mn and Ag grouping (factor 2) is a sewage factor, then the PCA would suggest that other sources or processes are contributing significantly to the distributions of particulate Cd, Cr, Ni and Zn.

Four surveys between October 1999 and May 2001 of dissolved and particulate metals in Sydney Harbour waters provided a comprehensive assessment of metal distributions for the period immediately preceding efforts to clean up the Sydney Tar Ponds. Average concentrations observed in various parts of the harbour were almost always below water quality guidelines for estuarine or marine waters and showed relatively little variation from one survey to another. Observations within the harbour showed that inputs to the central part of South Arm modify distributions that generally reflect estuarine dilution of freshwater inputs. Sewage appeared to be the major but not sole source of inputs to the central South Arm.

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