

SOURCES AND DISTRIBUTION OF METAL CONTAMINATION IN SURFICIAL SEDIMENTS OF SYDNEY HARBOUR, NOVA SCOTIA

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Geochemical studies in Sydney Harbour indicate that its sediments are contaminated to varying degrees with 'pollution' metals such as As, Cd, Hg and Pb. Results based on the analyses of 119 surface sediment samples show that above background concentrations of Ag, As, Bi, Cd, Cu, Hg, Mo, P, Pb, Sb, and Zn occur in the sandy muds and muds adjacent to the urban and industrial development on the east side of the South Arm and the Sydney River estuary. The distributions of these metals are more strongly controlled by the individual anthropogenic sources of the metals than by the natural depositional patterns. Flocculation and deposition of anthropogenic material in the immediate vicinity of the sources is of greater importance than the more general dispersal, flocculation and settling of fine grained material in the harbour. Organic matter, which is a significant component of many of these inputs, plays an important role in the sequestering and settling of the metals close to the sources. The distributions of Al, Ba, Co, Cr, Fe, Li, Ni, Sr, Ti and V, on the other hand, are controlled by the dispersal, flocculation, settling and resuspension of fine grained aluminosilicate-bearing sediments in response to natural depositional conditions.

Il ressort d'études de géochimie réalisées dans le port de Sydney que les sédiments du port sont contaminés à divers degrés par des métaux polluants comme As, Cd, Hg et Pb. Les résultats des analyses de 119 échantillons de sédiments superficiels dénotent la présence de concentrations de Ag, As, Bi, Cd, Cu, Hg, Mo, P, Pb, S et Zn supérieures aux teneurs naturelles dans les vases et les boues sableuses adjacentes aux aménagements urbains et industriels situés sur la rive est du bras sud et dans l'estuaire de la rivière Sydney. La répartition de ces métaux est déterminée par la source anthropique de chacun davantage que par les régimes naturels de sédimentation. La floculation et le dépôt de matières anthropiques dans les environs immédiats des sources revêtent plus d'importance que le processus général de dispersion, de floculation et de sédimentation des matières à grain fin dans le port. Les matières organiques, qui représentent une importante composante d'un bon nombre de ces apports, jouent un grand rôle dans la séquestration et la sédimentation des métaux à proximité des sources. Par ailleurs, la répartition de Al, Ba, Co, Cr, Fe, Li, Ni, Sr, Ti et V est régie par la dispersion, la floculation, la sédimentation et la remise en suspension des sédiments à grain fin contenant de l'aluminosilicate en fonction des conditions naturelles de sédimentation.

INTRODUCTION

In coastal areas adjacent to population centres and industrial activities, sediments are a major repository for metal contamination, and a potential source for subsequent remobilization of these metals. Sydney Harbour lo-

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cated on the northeast coast of Cape Breton Island in Nova Scotia, Canada is an example of a harbour subject to sedimentary metal contamination resulting from urbanization and industrial activities surrounding the harbour.

Sydney (with a population of 24,000 according to the 2001 census) is the second largest city in Nova Scotia and approximately 50,000 people live in the area surrounding Sydney Harbour. The main point-sources of waste to the harbour have historically been extensive shipping activity, domestic and industrial raw sewage which enters through numerous discharges, and the Sydney Steel Corporation (Sysco) steel foundry operations including coal-coking (terminated in the 1980s) and steel manufacture. The steel mill and coke oven effluent drained into Coke Oven Brook and the Sydney Tar Ponds. The Tar Ponds are an area at the mouth of the freshwater portion of Muggah Creek which is separated from the estuarine portion of Muggah Creek by a causeway. The Tar Ponds are highly enriched in polyaromatic hydrocarbons and metals and continue to release contaminated effluent to the estuarine portion of Muggah Creek (Stewart & White 2001). A major engineering project is now underway for the containment and/or removal of the contaminated materials from the Coke Ovens site, Coke Oven Brook, the Tar Ponds and Muggah Creek. PWGSC (2005) describes the extent of this project including requirements for environmental monitoring.

Sydney Harbour is a Y-shaped estuary comprising an outer harbour, the North West Arm (axial length 8.1 km, width 2.6 km) and the South Arm (axial length 10.7 km, width 2.2 km) which connects to Sydney River. The total surface area of the harbour is 52 km² with a volume of 5.17×10^8 m³ and a maximum depth of 19 m (Gregory et al. 1993). The tides are semi-diurnal with amplitudes of 0.9 m, tidal volume of 4.79×10^7 m³, and peak tidal current speeds of 0.05 m/s. Flushing time is on the order of 140 hours. Current meter observations show that the residual circulation is estuarine with net outflow in a very shallow surface layer and net inflow at greater depth (Petrie et al. 2001). Studies of metal and PAH contamination of Sydney Harbour sediments from the 1980s to early 1990s are summarized by Vandermeulen (1989) and Stewart and White (2001). These studies show highly elevated concentrations of Cd, Cu, Pb and Zn at a small number of stations in the estuarine part of Muggah Creek, and generally higher levels of these metals in the Sydney River estuary and the central part of the South Arm than in the rest of the harbour.

In our study, surficial sediment samples were collected from 119 sites throughout Sydney Harbour to establish the geochemical factors controlling the accumulation and dispersal of the metals in the harbour. This study is a component of an extensive assessment of contaminant distributions and biological effects in the harbour that was funded by the Toxic Substance Research Initiative (TSRI) of Health Canada (see Lee (2002) for summary of results of this project). The description of metal distributions in surficial sediments presented in this paper should provide a valuable reference point for on-going monitoring and final assessment of the success of the recently

initiated Tar Ponds clean-up.

METHODS

Surficial sediment samples were collected at 94 sites using a 0.1 m² Eckman grab, hand-deployed from a Boston Whaler, in October 1999. The top 1 cm of the grab was sub-sampled using a modified 10 ml plastic syringe. The sediment sub-samples were placed in 25 ml plastic Bitran bags to be analyzed for water content and grain size. A second 50 ml sub-sample, for trace metal analysis, was taken from the top 1cm of the sediment using a plastic spoon, placed in 125 ml plastic specimen containers, and stored at -15°C. All samples were returned to the laboratory for processing. A second set of 30 sediment samples was collected at the same time from the CCGS Navicula for trace metal analysis (no grain size measurements) using similar techniques, for a total of 124 samples.

Salinity and temperature profiles were obtained at or adjacent to 54 of the stations using a Seabird 25 CTD. The station locations are shown in Fig 1. Station and sample information for the Boston Whaler samples and a complete listing of grain size results are available (Stewart et al. 2001).

The disaggregated inorganic grain size (DIGS) of each of the Boston

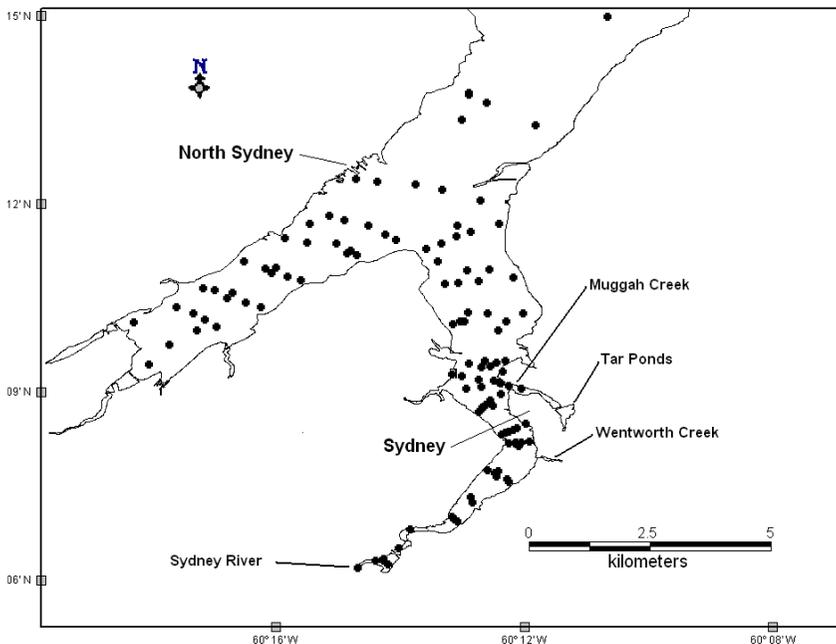


Fig 1 Map of harbour showing sampling locations and geographic locations mentioned in the text.

Whaler samples was determined by electro-particle sizing techniques described by Milligan and Kranck (1991). Sediment samples were placed in 20 ml Pyrex beakers, weighed wet, air-dried, and subsequently re-weighed. The samples were then digested in an excess of 35% H_2O_2 , weighed again, re-suspended in 1% NaCl, and finally disaggregated with a sapphire tipped sonic probe. The DIGS distributions were determined using the Coulter Multisizer IIe over a size range from 0.87 to 500 μm . Percentage weight of the sediment was calculated using a specific gravity of 2.65 kg/m^3 to convert sediment volume to weight, which was then normalized to total sediment weight in the size range analyzed. Diameters are reported as the midpoint of the size class based on a $1/5 \phi$ interval (i.e. the diameter doubles every 5 channels).

All sediment samples for metal analysis were dried at 58°C prior to homogenization with a mortar and pestle. Samples were analyzed by Chemex Labs (Toronto, Ont.) for Ag, Al, As, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hg, Li, Mo, Mn, Ni, P, Sb, Sr, Ti, U and V, and Zn. Samples except for mercury were triple acid digested ($HF/HCl/HNO_3$) and analyzed by a combination of Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) and Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Mercury (Hg) was determined using sulphuric acid digestion and a cold vapour atomic absorption technique. NRCC-certified marine sediment reference materials (MESS-2, PACS-2) were included in the analysis to ensure quality control. Readily oxidizable organic carbon content was determined for 49 of the Boston Whaler samples (35 from the South Arm and 14 from the North West Arm and outer Harbour) by the Walkley-Black method adopted and modified by Jackson (1958). This method differentiates humus matter from extraneous sources of organic carbon such as graphite and coal. For the determination of total organic carbon, the Navicula samples were washed with dilute HCl at 60°C to remove carbonates, dried at 80°C and analysed with a LECO carbon analyser.

Lithium normalization procedures (Loring 1990, 1991) were used to compensate for the effect of grain-size and mineralogical variability on the metal distributions. Factor analyses were also used to establish the geochemical factors controlling the accumulation and dispersal of the metals. For this study, the principal factor (correlation) matrices were rotated to produce normal varimax orthogonal solutions. Since organic matter is also an important carrier of metals in coastal environments, the factor analysis and discussions of metal carriers and dispersal factors was based on the subset of samples from the South Arm ($n=35$), the North West Arm and outer harbour ($n=14$) for which the readily oxidizable organic matter data were available. Maps showing metal distributions were generated using Map Info Vertical Mapper using natural neighbour interpolation.

RESULTS

Sediment distribution and characteristics

The depositional history of the sediment can be determined through the analysis of the DIGS (Kranck et al. 1996a, b). The inorganic fraction of the sediment can be divided into the three components from which it was formed: material settled as flocs, material settled from suspension with no subsequent re-working (termed one-round), and material that has been re-worked, usually under high energy conditions, and has become well-sorted. The DIGS analysis from Sydney Harbour indicated mainly floc-deposited and single-grain sediment for most of the Harbour with well-sorted, high-energy sediments located at the mouth. The average percentages of the sediment, by weight, that were $<64 \mu\text{m}$ and $<5 \mu\text{m}$ are listed in Table 1 for the sediments from Sydney River and the six subdivisions of the harbour identified in earlier studies (Stewart & White 2001). The $<64 \mu\text{m}$ represents

Table 1 Grain size and organic carbon data for sediments from the seven harbour areas.

	$< 5 \mu\text{m}$ (wt %)*	$< 64 \mu\text{m}$ (wt %)*	Organic C (wt %)*	Organic C (wt %) +
River	33.0 \pm 9.5 (n=7)	90.3 \pm 10.0 (n=7)	9.29 \pm 0.94 (n=4)	
Estuary	37.7 \pm 11.9 (n=20)	91.1 \pm 21.0 (n=20)	6.97 \pm 2.62 (n=14)	8.05 \pm 1.06 (n=2)
Central South Arm	34.3 \pm 12.1 (n=15)	85.9 \pm 25.4 (n=15)	7.57 \pm 3.47 (n=13)	9.15 \pm 3.4 (n=10)
Outer South Arm	35.2 \pm 12.3 (n=9)	91.8 \pm 21.4 (n=9)	4.38 \pm 1.67 (n=2)	4.49 \pm 1.24 (n=7)
North West Arm	33.4 \pm 9.7 (n=21)	91.2 \pm 18.6 (n=21)	4.34 \pm 1.59 (n=10)	3.02 \pm 1.43 (n=6)
Central harbour	25.6 \pm 5.3 (n=15)	94.8 \pm 7.6 (n=15)	3.37 \pm 0.51 (n=5)	
Outer harbour	14.6 \pm 25.2 (n=4)	38.8 \pm 43.3 (n=4)		2.97 \pm 1.62 (n=4)

* samples from Boston Whaler survey.

+ samples from Navicula survey.

the silt + clay size fraction of the sediments that has been used to correlate trace metal concentration with fine sediment concentrations (Loring et al. 1998). The $<5 \mu\text{m}$ fraction represents the very fine particulate fraction of the sediment that is associated with floc deposition. Sediments that had $>90\%$ silt + clay ($<64 \mu\text{m}$) content predominated in all areas except the outer harbour with the fraction of very fine-grained ($<5 \mu\text{m}$) material decreasing from 30-40% in the South and North West Arms to 25% in the central harbour and 15% in the outer harbour. Carbon content of the sediments decreased from 7-9% in the South Arm to approximately 3% in the central and outer harbour.

Estimations of the critical erosion shear stresses, based on DIGS data,

were made using the expression of Wiberg and Smith (1987). Areas of low shear stress corresponded to regions dominated by floc deposition. The distribution of critical erosion shear stress indicated that Sydney Harbour is dominated by fine sediment deposited as flocs. This is important because trace metals and other contaminants are primarily associated with fine particulate matter in suspension (Muller 1996). Previous studies have shown that dredging operations can increase particle flux (Kranck & Milligan 1989). Dredging in depositional areas such as Sydney Harbour would release pore water and easily solubilized metals to the water column but also has the potential to enhance the flux of trace metals to the sediment through increased flocculation.

Abundance and distribution of trace metals

Table 2 summarizes the average metal concentrations and standard deviations (SDs) for surficial sediments (0-1 cm) in Sydney River and the six subdivisions of the harbour identified in earlier studies (Stewart & White 2001). The results were similar to those of the earlier studies summarized in Stewart and White for the few metals (Cd, Cu, Hg, Pb and Zn) for which comparisons could be made, except for Hg where the maximum values seen in the estuary and central South Arm were clearly lower than those reported earlier.

Table 3 compares the mean concentrations of metals in Sydney Harbour and its two major arms with those found in sediments from Country, Halifax, Lunenburg and Shelburne harbours on mainland Nova Scotia. The overall average concentrations of As and Co in Sydney Harbour were slightly higher than those of the other harbours. Cadmium concentrations were higher than those of Country and Shelburne Harbours, but lower than those from Lunenburg and Halifax harbours. Chromium values were similar to Country Harbour, lower than Lunenburg and Halifax harbours, but higher than those from Shelburne Harbour. Mercury concentrations were higher than those from Country and Shelburne harbours, but lower than those found in the other harbours listed in Table 3. Nickel values were lower than those found in Lunenburg and Shelburne Harbours. Lead concentrations were higher than those found in all Harbours except Halifax Harbour. Antimony and V values were higher than those found in Country, Lunenburg and Shelburne harbours; and Zn values were higher than those found in Country, Lunenburg and Shelburne harbours, but lower than those found in Halifax Harbour. The concentrations of Ag, As, Bi, Cd, Cu, Hg, Mo, Pb, Sb and Zn were significantly higher (student t test, $p < 0.05$) in the more developed and industrialized South Arm of Sydney Harbour than in the North West Arm and outer harbour. The concentrations of metals such as Cd, Cu, Pb and Zn were similar to those found in other developed harbours such as Halifax and Lunenburg. In the North West Arm and outer Sydney Harbour, concentrations of the metals were more like those in the less developed Country and Shelburne harbours.

Most (71 to 80%) of the samples from the South Arm (Sydney River, estuary

Table 2 Metal distributions in seven harbour areas (mean \pm standard deviation, mg/kg except wt % as indicated)

	River n=7	Estuary n=22	Cent. S. Arm n=25	Outer S. Arm n=15	N. W. Arm n=27	Central Hrbr n=16	Outer Hrbr n=6
Ag	0.81 \pm 0.26	1.50 \pm 0.74	1.64 \pm 1.56	0.86 \pm 0.26	0.67 \pm 0.25	0.63 \pm 0.13	0.21 \pm 0.09
Al (%)	5.04 \pm 0.71	5.90 \pm 1.19	6.13 \pm 1.54	7.08 \pm 0.81	7.21 \pm 1.16	7.08 \pm 0.90	3.69 \pm 0.98
As	16.4 \pm 6.5	20.6 \pm 8.0	26.2 \pm 11.2	21.1 \pm 8.1	15.7 \pm 5.3	14.5 \pm 2.9	14.4 \pm 2.6
Ba	266 \pm 11	336 \pm 70	361 \pm 88	424 \pm 66	437 \pm 57	459 \pm 42	362 \pm 48
Bi	0.50 \pm 0.19	0.84 \pm 0.39	0.92 \pm 0.59	0.66 \pm 0.34	0.39 \pm 0.14	0.35 \pm 0.12	0.11 \pm 0.04
Ca (%)	1.90 \pm 1.67	0.84 \pm 0.36	0.79 \pm 0.56	0.65 \pm 0.34	0.71 \pm 0.22	0.68 \pm 0.15	0.59 \pm 0.15
Cd	0.89 \pm 0.31	0.86 \pm 0.38	1.25 \pm 0.72	0.63 \pm 0.41	0.45 \pm 0.13	0.26 \pm 0.08	0.06 \pm 0.06
Co	10.3 \pm 1.6	12.4 \pm 2.9	12.5 \pm 2.6	14.0 \pm 0.9	13.5 \pm 2.1	14.1 \pm 1.3	7.8 \pm 1.9
Cr	44.7 \pm 9.6	59.0 \pm 13.7	71.3 \pm 18.7	72.5 \pm 7.3	64.4 \pm 14.0	65.1 \pm 9.6	28.6 \pm 10.8
Cu	39.4 \pm 14.9	69.5 \pm 30.2	81.3 \pm 67.4	42.8 \pm 15.1	34.0 \pm 11.7	30.9 \pm 7.0	10.4 \pm 4.9
Fe (%)	3.08 \pm 0.61	3.80 \pm 0.90	4.52 \pm 1.18	4.55 \pm 0.83	3.76 \pm 0.71	3.87 \pm 0.56	2.19 \pm 0.42
Hg	0.11 \pm 0.07	0.18 \pm 0.11	0.33 \pm 0.34	0.10 \pm 0.07	0.04 \pm 0.02	0.10 \pm 0.28	0.02 \pm 0.01
K (%)	1.58 \pm 0.21	1.74 \pm 0.32	1.78 \pm 0.45	1.97 \pm 0.23	2.05 \pm 0.30	1.94 \pm 0.28	1.07 \pm 0.14
Li	43.9 \pm 9.2	51.3 \pm 11.5	51.3 \pm 12.2	55.6 \pm 7.4	57.7 \pm 11.9	53.9 \pm 6.7	25.7 \pm 9.7
Mg (%)	0.97 \pm 0.23	1.15 \pm 0.24	1.18 \pm 0.23	1.10 \pm 0.14	1.17 \pm 0.20	1.00 \pm 0.17	0.45 \pm 0.15
Mn	396 \pm 74	410 \pm 114	417 \pm 78	449 \pm 82	457 \pm 126	584 \pm 71	652 \pm 89
Mo	4.1 \pm 1.6	7.0 \pm 3.1	8.3 \pm 3.6	2.8 \pm 2.9	4.4 \pm 1.7	2.9 \pm 1.4	1.0 \pm 0.8
Ni	20.8 \pm 3.8	27.9 \pm 7.4	30.2 \pm 6.7	32.6 \pm 2.5	29.7 \pm 5.9	30.3 \pm 3.6	13.2 \pm 5.1

Table 2 Continued

	River n=7	Estuary n=22	Cent. S. Arm n=25	Outer S. Arm n=15	N. W. Arm n=27	Central Hrbr n=16	Outer Hrbr n=6
P (%)	0.10±0.03	0.09±0.02	0.11±0.06	0.10±0.03	0.09±0.02	0.08±0.02	0.05±0.01
Pb	85±27	161±78	201±124	110±52	71±31	50±19	18±5
Sb	0.91±0.16	1.66±0.70	1.94±0.87	1.52±0.51	1.07±0.34	1.27±0.72	0.60±0.24
Sr	145±36	122±25	159±160	129±12	133±15	136±16	100±26
Ti (%)	0.22±0.02	0.24±0.05	0.24±0.06	0.28±0.03	0.30±0.05	0.31±0.03	0.17±0.05
Tl	0.60±0.07	0.70±0.16	0.80±0.22	0.71±0.12	0.71±0.11	0.61±0.08	0.31±0.07
U	2.97±0.60	3.82±0.96	3.84±1.06	3.77±0.63	3.59±0.73	3.20±0.48	1.72±0.61
V	79±11	104±24	114±28	128±18	116±22	110±18	50±14
Zn	173±41	237±91	316±156	201±88	139±36	115±32	50±16

Table 3 Comparison of metal concentrations (mg/kg) in Sydney Harbour with those in other Nova Scotia inlets

	n	As	Cd	Co	Cr	Cu	Hg	Li	Mn	Mo	Ni	Pb	Sb	U	V	Zn
Sydney Harbour	118	19.6	0.71	13	63	51	0.15	52	459	5.6	29	118	1.4	3.6	109	200
Sydney – Outer harbour & N W Arm	42	15.9	0.37	13	60	31	0.07	53	506	3.7	28	61	1.0	3.3	106	125
Sydney – South Arm	76	21.6	0.90	13	65	62	0.20	52	433	6.7	29	150	1.6	3.7	111	242
Country Harbour*	28	14.7	0.41	8	59	18	0.05	49	486	3	21	25	0.51	2	67	70
Halifax Harbour^	250		0.81		85	91	0.92	54	663		142	160				226
Lunenburg Harbour*	14	14.1	1.31	8	83	58	0.22	55	612	9	27	42	0.7	3.6	81	159
Shelburne Harbour*	23	13.7	0.48	7	28	16	0.06	33	625	3	45	29	0.53	2.3	43	45

* Loring et al. (1996) ^ Buckley and Winters (1992)

and central and outer South Arm) had concentrations of Ag, Bi, Cd, Cu, Pb and Zn that were above background concentrations. For As, Hg, Mo and Sb the percentages of samples greater than background were somewhat less (53-64%) whilst for Co, Cr, Ni and V, they were <30%. Background metal-Li relationships for Sydney Harbour were established using the samples from the North West Arm and outer harbour (Loring 1990, 1991). Two samples that were obviously contaminated with a number of metals were excluded from this analysis, all the rest of the North West Arm and outer Harbour samples were assumed to represent background conditions. The relationships between metals and Li are illustrated in Fig 2 with one example from each of the three groups of metals identified above. Comparison of the concentrations in this part of Sydney Harbour to concentrations (and metal-Li relationships) in other relatively pristine harbours such as Country Harbour, St. Mary's Estuary, Petpeswick Inlet and Pubnico Harbour suggested that this was not an unreasonable assumption except in the case of Pb, where concentrations normalized for grain size were approximately twice those in the reference harbours. For As and Hg, good relationships to Li could not be established for the North West Arm/outer harbour subset, so background concentrations of 20 mg/kg for As and 0.10 mg/kg for Hg were estimated based on more general comparisons to the literature for pristine areas (Loring et al. 1996).

The highest concentrations of Ag, As, Bi, Cd, Cu, Hg, Mo, P, Pb, Sb, and Zn occurred in the sandy muds and muds adjacent to the urban and industrial development on the east side of the central South Arm and into the Sydney River estuary. Fig 3 shows that the highest concentrations of Ag occurred in an extensive area of the eastern shore just south of Wentworth Creek and at a more intense 'hot spot' at the mouth of Muggah Creek. The Cu distribution was very similar. High concentrations of Pb (Fig 4) occurred along the axis and eastern side of the South Arm with the highest concentrations off the mouth of Muggah Creek and off the central part of the City of Sydney. The Zn distribution was very similar. High average Hg levels (and large standard deviations) in the central South Arm and the central harbour (Table 2) were the result of three samples (two in the central South Arm at the mouth of Muggah Creek and one off North Sydney) with very high concentrations of Hg (>1 mg/kg). Otherwise Hg concentrations were not particularly high. A second group of metals that included Al, Ba, Co, Cr, Fe, K, Li, Ni, Th, Ti and V had their highest concentrations in the outer South Arm, the North West Arm and the central harbour. The distributions of these metals, as illustrated by the distribution of Ni (Fig 5), more closely followed the pattern shown for shear stress and the deposition of fine sediments.

Surface sediment metal carriers and dispersal factors

In general, the trace metals have been introduced into these sediments as constituents of, or in association with, solid inorganic and organic particles supplied from natural and anthropogenic sources or precipitates from solution. Provenance, mineralogy, grain-size, depositional conditions,

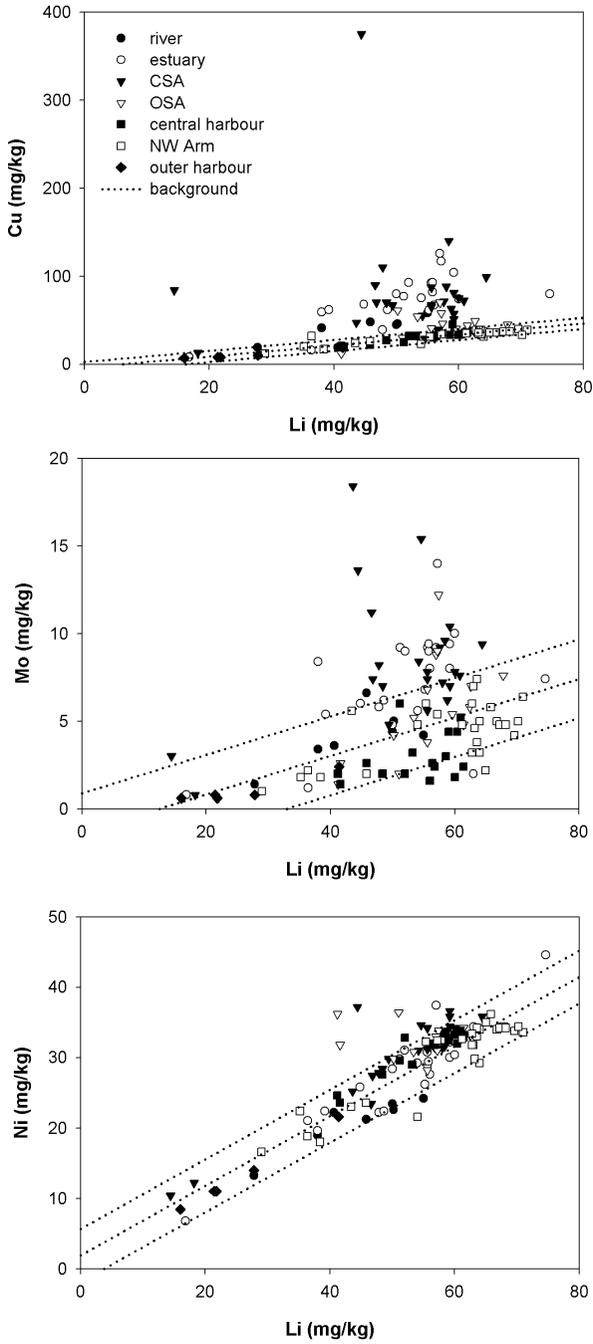


Fig 2 Cu, Mo and Ni vs. Li plots. The dotted lines represent the Metal:Li regression line and 95% confidence band for data from the North West Arm and outer harbour.

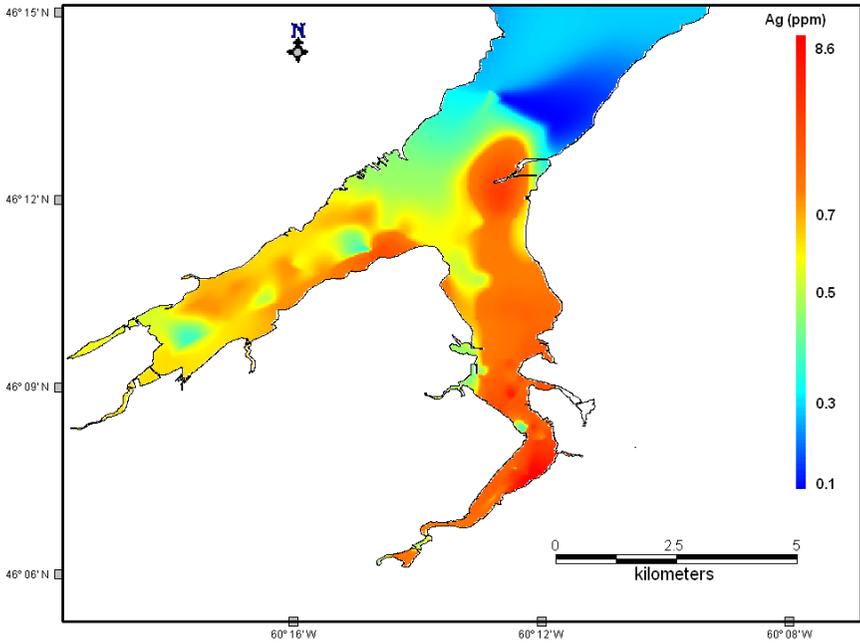


Fig 3 Ag distribution (mg/kg) in surficial sediments of Sydney Harbour.

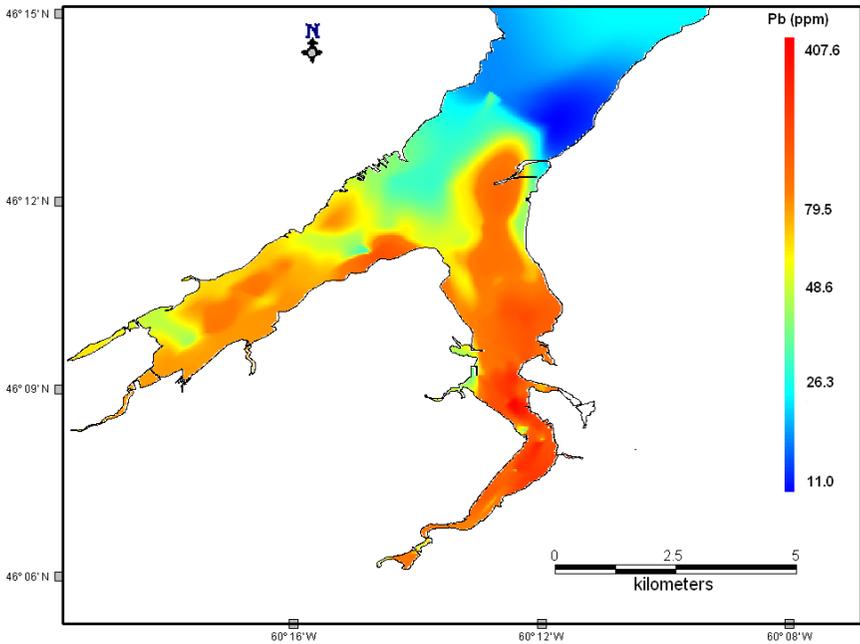


Fig 4 Pb distribution (mg/kg) in surficial sediments of Sydney Harbour.

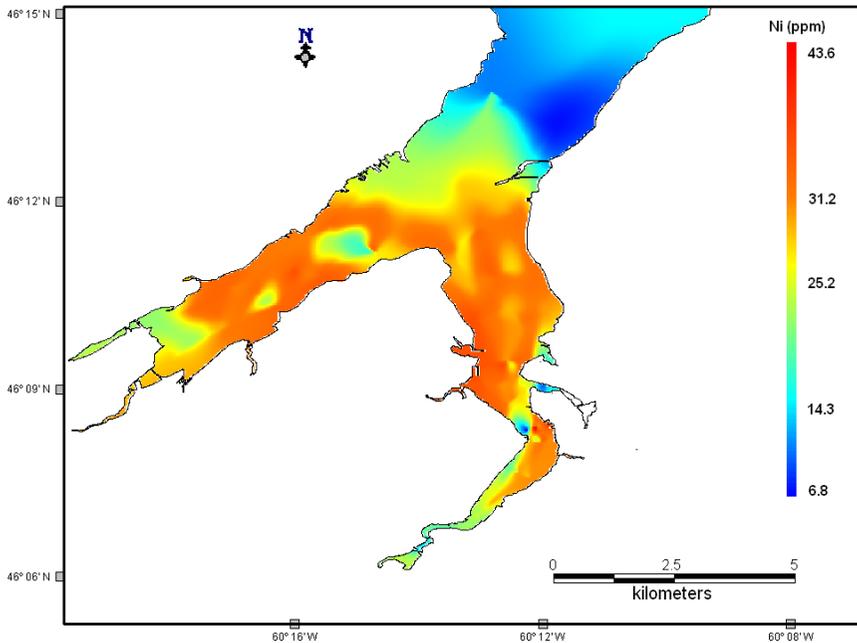


Fig 5 Ni distribution (mg/kg) in surficial sediments of Sydney Harbour.

and anthropogenic inputs therefore determine the trace metal chemical composition of the sediments. Since organic matter is also an important carrier of metals in coastal environments, the discussions on metal carriers and dispersal factors are based on those samples for which organic matter contents are available.

Strong ($p \leq 0.01$) positive correlations of Al, Ba, Co, Cr, Li, Mn, Ni, Sr, Ti and V, with the $<64 \mu\text{m}$ size fraction suggested that carriers of these metals were predominantly enriched in the fine-grained sediments of Sydney River and the South Arm as well as for Al, Cr, Li, Ni, Sr, Ti, and U in the North West Arm and outer harbour sediments. The strong positive covariances ($p \leq 0.01$) of the metal concentrations with Al and Li concentrations showed that Li and/or Al normalized for most of the granular and mineralogical variability of Ba, Cr, Co, Fe, Ni, Sr, Ti, U, and V (see Fig 2 for relationship between Ni and Li). The data reflect the association with and/or inclusion of these metals in the lattices of fine-grained aluminosilicate minerals such as micas, ferromagnesium silicates (pyroxenes, hornblendes) and clay minerals (illite, smectite and chlorite) that most likely constituted the bulk of the fine-grained sedimentary material. The strong covariances of Ag, Bi, Cd, Cu, Hg, Pb and Zn with the organic matter and phosphorus in the Sydney River and South Arm sediments suggested that these metals were associated with the presence of natural and anthropogenic organic matter including that derived from sewage outfalls. Arsenic covaried ($p \leq 0.01$) with Bi, Fe, Pb,

Sb, and Zn in these sediments. In the North West Arm and outer harbour sediments, Cd, Mo, and U were also closely correlated ($p \leq 0.01$) with the organic component and with phosphorus. Iron covaried ($p \leq 0.01$) with Ag, As, Bi, Cu, Hg, Pb and Zn.

Factor analyses of the two data sets established the most likely geochemical factors that control the accumulation and dispersal of metals in the Sydney River and South Arm sediments as well as those factors for the North West Arm and outer Harbour sediments.

The varimax matrix (Table 4) for Sydney River and South Arm shows that five factors account for 87% of the total problem variance. Factor 1 accounts for 32% of the total problem variance. This factor has significant positive loadings on Al, Ba, Co, Cr, Li, Ni, Sr, Ti, V, and material $<64 \mu\text{m}$. This may be identified as the sedimentation factor. It represents the accumulation of fine-grained aluminosilicates with their accompanying lattice trace metals in response to the present depositional conditions. Factor 2 accounts for 32% of the total variance and has significant loadings on organic matter and phosphorus as well as many of the chalcophile metals. It indicates that organic matter controls the abundance and distribution of Ag, Bi, Cd, Cu, Hg, P, Pb, Sb and Zn in the sediments. The inclusion of phosphorus in this factor suggests that sewage is the main source of the organic matter. Factor 3 accounts for 8.2% of the total variance. The significant loadings on Mo and U alone suggest that the small amounts of these metals behave independently. Factor 4 accounts for 8.9% of the total variance. Significant loadings of As, Pb, and Fe on this factor suggest the presence of independent As and Pb bearing Fe minerals or possibly anthropogenic Pb and As-Fe particles released from the of the Sysco coking operations control the abundance and distribution of As and Pb in the sediments. Factor 5 accounts for 6.4% of the total variance. Significant positive loadings on Ca in this factor alone suggest that the abundance and distribution of Ca in these sediments is derived from shell fragments.

The varimax matrix for the North West Arm and outer Harbour sediments shows that three factors account for 89% of the total problem variance. Factor 1 accounts for 39% of the total variance and has significant loadings on Al, Co, Cr, Fe, Li, Ni, Sr, Ti, U and V, as well as on material $<64 \mu\text{m}$. This is the sedimentation factor and represents the accumulation in response to present depositional conditions of fine-grained aluminosilicates with their accompanying lattice-bound trace metals. Factor 2 accounts for 35% of the total problem variance with significant loadings on Ag, As, Bi, Cd, Cu, Hg, Pb, Sb and Zn. This factor can be identified as the anthropogenic or contamination factor. It represents the enrichment of these metals above background levels by anthropogenic sources such as sewage discharges and past industrial activity. It is possible that these metals reside in the sediments as authigenic sulphides.

Factor 3 (15% of the total variance) has significant negative loadings on organic matter, Cd and Mo, and positive loadings on Ca and Mn. This factor most likely reflects the dilution of the Cd and Mo bearing organic matter by

Table 4 Varimax matrices for metals from Sydney River and South Arm, and North West Arm and outer harbour showing component loadings for each factor.

Factor	Sydney River and South Arm					North West Arm and outer harbour		
	1	2	3	4	5	1	2	3
OM		0.73						-0.79
<64µm	0.75					0.70		
Ag		0.97					0.94	
Al	0.96					0.99		
As				-0.82			0.76	
Ba	0.89							
Bi		0.89					0.93	
Ca					0.88			0.72
Cd		0.91					0.63	-0.71
Co	0.91					0.97		
Cr	0.75					0.95		
Cu		0.97					0.95	
Fe				-0.63		0.86		
Hg		0.71					0.98	
Li	0.81					0.94		
Mn								0.70
Mo			-0.81					-0.77
Ni	0.89					0.97		
P		0.91						
Pb		0.59		-0.6			0.96	
Sb		0.69					0.94	
Sr	0.63					0.95		
Ti	0.94					0.91		
U			-0.82			0.67		
V	0.84					0.89		
Zn		0.93					0.91	
%	31.8	31.7	8.2	8.9	6.4	39.4	35.0	15.0

OM = organic matter; <64 µm = <64 µm size fraction;
 % = % of total problem variance explained by each factor

carbonate debris in the harbour sediments.

DISCUSSION

It is clear from an inspection of Table 2 and the factor analysis that the distributions of the majority of the metals can be described by one of two patterns. The distributions for the first group (those in factor 1 of the factor analyses) were controlled by the dispersal, flocculation, settling and resuspension of fine grained sediments. The estimation of critical erosional shear stress from the DIGS data showed that the areas of low shear stress where floc deposition occurs correspond quite closely to areas with high concentrations of these more detrital metals (as illustrated by the distribution of Ni shown in Fig 5). The correlation coefficients for the linear regressions of these metals with shear stress varied from $r = 0.4$ to $r = 0.6$, all of which

are significant at $P < 0.01$.

The second group of metals (those in factor 2 of the factor analysis) contained the potentially toxic metals such as As, Cd, Hg and Pb that are generally the focus of environmental concerns. For these elements, the distributions were more controlled by the individual anthropogenic sources of the metals than by the depositional patterns in the harbour. For the input from these sources, flocculation and deposition of the anthropogenic material in the immediate vicinity of the sources was more important than the more general dispersal, flocculation and settling of fine grained material in the harbour. Organic matter, which was a significant component of inputs such as sewage discharges, played an important role in the sequestering and settling of the metals close to the sources. Surprisingly, there was no evidence to indicate that runoff and/or discharge from the Tar Ponds made a dominant contribution to the concentration of potentially toxic metals such as As or Cd in the sediments of South Arm.

There was not a single common source for all these anthropogenic metal inputs. The distribution seen for Ag (Fig 3) and Cu ($r = 0.955$ for the correlation between Ag and Cu) with highest concentrations in the area off and to the south of Wentworth Creek and off the mouth of Muggah Creek were entirely consistent with the fact that the largest sewage and storm water discharges to Sydney Harbour were into these two areas. The 'hot spot' near Wentworth Creek should be a more or less purely sewage signal as there were no other major sources in this area, but the one off Muggah Creek reflected sewage inputs, inputs from the Sydney Tar Ponds and/or other industrial inputs from the central core of Sydney or the International Piers area just to the north of Muggah Creek. The distributions seen for Pb (Fig 4) and Zn ($r = 0.929$ for the correlation between Pb and Zn) with the highest concentrations off and to the south of Muggah Creek reflected the relatively greater importance of these additional sources for Pb and Zn compared to Ag and Cu. Observations (summarized in Stewart and White (2001)) of very high concentrations of As, Cd, Cr, Cu, Pb, Hg and Zn in sediments from the central part of Muggah Creek indicated that the Tar Ponds were an important source of the metals in Muggah Creek, but even within Muggah Creek, differences in distributions of PAHs and metals suggested that the Tar Ponds were not the only source for metals.

Ernst et al. (1999) observed that concentrations of a number of metals, most notably Cu, Pb and Zn, were higher in sediments to the south of Muggah Creek than to the north. This is consistent with our observations as illustrated by the Pb distribution (Fig 3). They concluded that these observations indicated that "Muggah Creek was not the only, and may not even be the most important, source of metals in Sydney Harbour". Our data confirmed the importance of other sources, most notably the contribution from the sewage sources in the Wentworth Creek area for Ag and Cu. We should point out, however, that the estuarine circulation pattern in the harbour will transport particulate matter and metals introduced into the deeper waters, or particulate matter and associated metals that settle

out of the surface layer, in a net inward (southward) direction. Because the net transport of the deeper layer of this estuarine circulation is inward, contaminants introduced into Muggah Creek could be transported to the south and contribute to the elevated levels seen in the sediments in the central South Arm south of Muggah Creek.

CONCLUSIONS

Sydney Harbour provides an excellent example of sedimentary metal contamination resulting from adjacent urban and industrial activities. Sedimentary geochemical and particle dynamic studies of the Y-shaped Sydney Harbour indicated that its surficial sediments were contaminated to varying degrees with Ag, As, Bi, Cd, Cu, Hg, Mo, P, Pb, Sb and Zn. The concentrations of these metals were significantly higher (student t test, $p < 0.05$) in the more developed and industrialized South Arm than in the North West Arm and outer Sydney Harbour with elevated concentrations in the sandy muds and muds adjacent to the urban and industrial development on the east side of the South Arm and the Sydney River estuary. The concentrations of metals such as Cd, Cu, Pb and Zn were similar to those found in other developed harbours in Nova Scotia such as Halifax and Lunenburg. In the North West Arm and outer Sydney Harbour concentrations of the metals were more like those in the less developed Country and Shelburne harbours.

The distributions of most of the metals can be described by one of two patterns viz. natural and anthropogenic. The distributions of Al, Ba, Co, Cr, Fe, Li, Ni, Sr, Ti and V were controlled by the dispersal, flocculation, settling and resuspension of fine-grained aluminosilicate bearing sediments in response to the natural depositional conditions. The distributions of the potentially toxic metals, such as As, Cd, Hg and Pb, that are generally the focus for environmental concerns, were more controlled by the individual anthropogenic sources of the metals than by the depositional patterns in the harbour. For the inputs from these sources, flocculation and deposition of the anthropogenic material in the immediate vicinity of the sources was more important than the more general dispersal, flocculation and settling of fine-grained material in the harbour. Organic matter, which was a significant component of many of these inputs, played an important role in the sequestering and settling of the metals such as Ag and Hg close to their sources. Sewage and storm water runoff appeared to be the most important source of metallic contaminants to the surficial sediments but other sources, including runoff from the Tar Ponds, contributed to the observed distributions. There is also some suggestion from the data that deposition of Pb and As-rich particles derived from coking activity could have contributed to levels of these metals in the North West Arm and the outer harbour.

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