A Novel Method for Measuring Anthropogenic Temporal and Spatial Change in Coastal Lake Environments

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Abstract
A new method for assessing temporal and spatial anthropogenic change has been applied to two large coastal lakes (Lake Macquarie and Pittwater) in New South Wales. Environmental indicators are an essential part of natural resource management and should include a wide array of biological, physical and chemical parameters, which should be assessed in a weight-of-evidence approach. Sedimentary metals have many advantages over other commonly used indicators of environmental health. Sediment-bound metals provide a simple yet effective and inexpensive indicator, which address some of the most critical issues in natural resource assessment, i. e. natural spatial and temporal variability and establishing the pristine condition. Two vintages of data (1975 and 2003 for Lake Macquarie and 1992 and 2007 for Pittwater) on surficial sediment metal (Cd, Cu, Pb and Zn) concentrations, combined with ^{210}Pb core profiles were used to determine past changes in sediment quality and to predict possible future relaxation/expansion rates for the entire area of these estuaries in response to change in anthropogenic pressures. Past and future declining sedimentary metal concentrations in the northern part of Lake Macquarie were expected due to the closure of a nearby Pb-Zn smelter, however, possible increases by up to 75% in Pb and Zn, and especially Cu, in the south of the lake to the year 2020 were surprising. Rapidly increasing Cu and Zn concentrations in surficial sediment in southern Pittwater and Careel Bay is probably related to increasing boating activity. Declining surficial sediment Pb concentrations relate to banning of vessel- and vehicular-leaded petrol. Modelled changes to 2020 indicate only Cu will exceed sediment quality guideline trigger values in this estuary. Sedimentation rates in northern Lake Macquarie were consistent at 14 mm y^{-1} over the 55-year period investigated and in southern Pittwater sedimentation rates were 16 mm y^{-1} over the last 40 years.

Introduction

The use of environmental indicators as part of natural resource management and policy making is widely recognised (Bayer *et al.*, 2008; Backer, 2008). Consensus is that a combined, tiered approach that involves a variety of environmental indicators should be applied to provide a robust and relevant assessment. A large variety of approaches exist for assessment of coastal environments, including biological (e.g. Fernandez-Torquemada *et al.*, 2008; Moreno *et al.*, 2008; Parsons *et al.*, 2008), chemical (e.g. Belpaire *et al.*, 2008; Birch & Olmos, 2008), physical (e.g. Siciliano *et al.*, 2008; Li *et al.*, 2008; LeMarie *et al.*, 2006), as well as socio-economic proxies (e.g. Mercer Clarke *et al.*, 2008). Sedimentary metals as indicators of environmental health have many advantages over other commonly used indicators. Sediment-bound metals provide a simple yet effective and inexpensive indicator, which also address one of the most critical issues, i. e. natural spatial and temporal variability (Birch &

Olmos, 2008; Nelson & Brown, 2008; Ryan *et al.*, 2008). Sediment cores have been used extensively to determine temporal change (Batley, 1987; Harrison *et al.*, 2003); however this technique provides information for the location of the core site only and fails to give spatial information unless multiple cores are taken over an extensive area. Taking multiple cores can be time consuming, difficult and expensive, and depending on the extent of the study area, a large number of cores would be required for adequate spatial resolution.

The 2003 investigation of Lake Macquarie was undertaken as part of a larger coastal ecosystem monitoring programme at the University of Sydney's Environmental Geology Group (USEGG), which, over the past 18 years, has been undertaking a systematic contaminant study of sediments in coastal lakes and rivers of adjacent catchments in New South Wales (NSW). This programme aims to provide a cost-effective, integrated and regionally consistent assessment of estuarine health and to provide baseline data against which future trends may be assessed and with which success of management strategies may be judged.

The objective of the current investigation was to describe a novel technique, which has been developed as part of the USEGG programme to provide information on temporal change in environmental condition both vertically and spatially for a large coastal lake (Lake Macquarie) on the central coast of NSW, Australia. This information was used to assess relaxation rates in response to change in anthropogenic pressure.

Lake Macquarie is a large (120km^2), shallow (max. 11m) estuary about 130 km north of Sydney on the east coast of NSW, Australia. It has an open, narrow ocean entrance with twin training breakwaters, resulting in poor tidal flushing with approximately 1% of lake volume being exchanged with ocean waters during an average tidal cycle (Batley, 1987; DNR, 2008). An essential requirement for effective management of this system was to assess temporal change in sediment metal concentrations and to determine relaxation (natural clean up) rates for the whole lake. It had long been known that sediments in the lake were highly contaminated by metals (Cd, Pb, and Zn) mainly due to industrial discharge from a Pb-Zn smelter located on the banks of Cockle Creek entering the north east of the water body (Roy and Peat, 1975; Crawford *et al.*, 1976; Spurway, 1982; Roy and Crawford, 1984; Batley, 1987). Early work by Pringle (1975) indicated abnormally high metal concentrations in water and bottom sediment in proximity to the mouth of the Creek. As a consequence, Roy and others (Crawford *et al.*, 1976; Roy and Crawford, 1984) undertook a comprehensive sampling programme, including 203 surface samples and 34 cores, across the entire lake area. This study showed the highest published concentration of Cd (max. 660 μg g^{-1}), and elevated concentrations of Cu, Pb and Zn in Cockle Creek sediments (420, 7050 and 6250 μg g^{-1}, respectively). Metal concentrations were also high in estuarine sediments in the north of the water body (max. 340, 190, 2650 and 3300 μg g^{-1}, respectively) and a strong contaminant gradient was observed from the mouth of the river southwards. The Sulphide Corporation Pty. Ltd. Pb-Zn smelter commenced operations on Cockle Creek in 1897 producing Cd, Pb, Zn and sulphuric acid and was in operation for more than a century. Waste effluent was dispersed into Cockle Creek until the 1970s when a sludge treatment work was installed (Spurway, 1982). However, even after treatment, wastewater and dumping storage piles containing metals continued to contribute contaminants to the creek and the estuary until the smelter was closed in 2003 (Willmore *et al.*, 2006).

Methods – Lake Macquarie

A novel GIS-based technique allowed the spatial extent and magnitude of change in contaminant concentrations in estuarine sediments of Lake Macquarie to be determined over time. Metal concentrations of surficial sediments taken in the lake in 1975 and again 2003 using similar field and analytical techniques enabled a spatial depiction of changed chemical conditions in the bottom environment for the entire estuary over the 28-year interval to be made. Subsurface chemical and isotope (Pb^{210}) profiles from cores in selected areas provided a detailed history of chemical change over a much longer period to be determined in calendar years.

Field and laboratory methods

The 1975 study

Samples (n=203) collected in 1975 used a pipe sampler to recover the top 5cm of surficial sediment and a wedge-shaped, stainless steel box corer to obtain subsurface samples (n=34) (max depth 100cm) (Crawford *et al.*, 1976). Surface and subsurface samples were wet sieved through a nylon 67 µm nylon mesh with deionised water and dried samples were digested using a 1:3 volume ratio of nitric:perchloric acid. Samples were heated for one hour at 120^{o}C and for a further 6 hours at 180^{o}C. After cooling, the samples were diluted with deionised water and made up to the 15 ml mark. Analyses were performed by atomic absorption spectrometry and concentrations were expressed on a dry-weight basis in micrograms per gram.

The 2003 investigation

Sediment samples (n=102) were again collected in the estuary in 2003 using a stainless steel boxcorer (Fig. 1) with locations selected according to the 1975 study (Crawford *et al.*, 1976). The upper 1cm of surface sediment was taken with a metal-free polyethylene spatula and immediately transferred to air-tight plastic bags and stored at 4° C in an ice box on board prior to laboratory analyses. Three sediment cores were taken using aluminium push corers in the mouths of major creeks discharging to the lake (Cockle and Dora Creeks), and also in the southern part of Lake Macquarie Fig. 2).

Total and size-normalised sediment was analysed for Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. Samples were size-normalised by wet sieving through a 62.5 µm nylon mesh to reduce the confounding effects of variable grainsize (Loring & Rantala 1992; Barbanti & Bothner 1993; Birch & Taylor 2000; Birch 2003). Samples were digested in aqua regia (2 ml HNO3, 2 ml HCl and 10 ml ultra-pure water 18 MO/cm), and total recoverable elements were determined using a Varian Vista-AX Inductively Coupled Plasma Optical Emission Spectrometer (ICPOES) (modification of the USEPA method 200.8 Rev.4.4: USEPA 1991).

Compatibility of the 1975 and 2003 data sets

The 4 µm difference in the size (67µm for the 1975 data and 63 µm for the 2003 survey) of the material analysed in the two studies should have negligible effect on the results of the two studies and if any, the 1975 data will be minutely lower in concentration due to the slightly larger sediment size used.

The different acid digestion (nitric:perchloric acid for the 1975 survey and *aqua regia* for the 2003 study) and the different machines (atomic absorption spectrometry for the 1975 study and ICP-OES for the 2003 investigation) used for analysis in the two studies were tested for the ability to produce compatible results. An international reference material (MAG-1, marine mud from the Gulf of Maine, United States Geological Survey, USGS) was analysed by both methods to verify that results from the two techniques were statistically similar. Means for Cd, Cu, Pb and Zn did not differ significantly according to the t-test performed ($n = 10$; $P<0.05$).

Isotope dating and spatial analysis

Twelve samples from Core 3 (Cockle Creek) were dated using the ^{210}Pb method (Goldberg, 1963; Oldfield & Appleby, 1984). Lead-210 occurs naturally as one of the radionuclides in the ^{238}U decay series (Appleby, 2001). Total ^{210}Pb activity is determined by measuring the granddaughter isotope ^{210}Po, which is assumed to be in equilibrium with ^{210}Pb, while supported ^{210}Pb is determined by measuring ^{226}Ra activity.

Two ^{210}Pb dating models are commonly used for calculating sediment rates: the CRS (constant rate of ^{210}Pb supply) and the CIC (constant initial ^{210}Pb concentration) models (Appleby & Oldfield, 1978; Appleby, 2001). The basic assumption of the CRS model is that the rate of supply of fallout ^{210}Pb to the core site is constant, reflecting the constant flux of ^{210}Pb from the atmosphere. The CIC model assumes that sediments in the core had the same initial unsupported ^{210}Pb concentration at the time the materials were deposited on the bed of the lake, regardless of differences in sedimentation rate (Walling *et al.*, 2002).

Three samples from Core 3 were analysed for the anthropogenic radioisotope ^{137}Cs, a result of atmospheric nuclear bomb testing that may be used to validate ages calculated using the ^{210}Pb dating method (Appleby, 2001). Caesium-137 is usually present in environmental samples and can be used as an independent verifier of sediment age. Sediments deposited prior to atomic testing in 1954 should not have a ^{137}Cs signature. A subsurface peak in ^{137}Cs activity identifies the year 1963 at which time atmospheric testing was at a maximum.

Spatial Analysis

The two measures used in the present work to evaluate temporal change were ‘enrichment’ and ‘sediment quality’. Enrichment is expressed as current surficial sediment metal concentrations over pre-anthropogenic (or background) concentrations and provides an assessment of human-induced change. Background levels of metals were determined by calculating mean concentration at the base of the three cores where values declined to a consistent normalised minimum. Change in sediment quality gives an evaluation in the ability of the substrate to support a health benthic population (Birch and Olmos, 2008). Sediment quality guidelines provide two concentrations – Interim Sediment Quality Guidelines Low (ISQG-Low) and Interim Sediment Quality Guidelines High (ISQG-High) (ANZECC/ARMCANZ, 2000; Simpson *et al.*, 2005). Concentrations below ISQG-Low values (65, 50, and 200 μg g^{-}

^{1} for Cu, Pb, and Zn, respectively) identify conditions where adverse biological effects would be observed rarely; concentrations equal to or greater than ISQG-Low but below ISQG-High (270, 220, and 410 µg g^{-1}, respectively) represent a range within which biological effects occur occasionally; concentrations at or above ISQG-High values represent a range above which adverse biological effects are frequent. Metal concentrations above ISQG-Low values 'trigger' advanced environmental investigations of sediments and is used in the current study as a significant yardstick for managerial targets.

ArcGIS Version 9 was used for data manipulation, display and spatial analysis of Cd, Cu, Pb and Zn for both the 1975 and 2003 datasets. Size-normalised heavy-metal spatial distributions were determined by ordinary kriging using the Geostatistical Analyst tool in ArcGIS (ESRI, 2001).

The modelled metal distributions were analysed using the Raster Calculator tool (Spatial Analyst), which allows the use of arithmetic operators for the addition, subtraction, multiplication, and division of two raster layers, numbers, or a combination of the two (ESRI, 2001). The "absolute change" (i. e. metal concentration in 2003 minus the 1975 metal concentration) and the "percentage change" (i. e. the difference or "absolute change" divided by the original value, in this case the 1975 metal concentration) were calculated for each metal.

Methods - Pittwater

Pittwater estuary, located 30 km north of Sydney, is a drowned river valley (Fig. 2) (Roy, 1980) about 10 km long and 1 km wide (17 km^2), with a maximum water depth of approximately 22 m. Pittwater catchment (~51 km^2) is highly urbanized in the south and east with some industry in the south, while the western part is a pristine park (Ku-ring-gai National Park) (WBM Oceanics Australia, 2006).

Surficial sediment metal concentrations determined in the estuary in 1992 and again in 2007 using similar field and analytical techniques enabled changes in magnitude and distribution of Cu, Pb and Zn to be made for the entire estuary over the 15-year interval. Subsurface metal profiles from cores (n=6) taken in selected areas, combined with isotope (Pb^{210}) information from one core, provided a detailed history of chemical change over a much longer period (102 years) in calendar years.

Field and laboratory methods

The 1992 study

Samples were recovered from the estuary by a diver operating from a boat in shallower areas (<18m) (n=107) and by a boxcorer in deeper waters (n=23) (Judge, 1992) in March, 1992 (Fig. 3). Containers and plastic sampling gear were soaked for 24hrs in 10% nitric acid and rinsed twice in deionised water. The upper 2cm of sediment was scrapped off the upper surface with a plastic spatula, placed in air-tight, metal-free polyethylene bags and stored on ice onboard and at 4°C in the laboratory to minimize microbiological, physical and chemical degradation.

Total and size-normalised (<62.5 µm) sediments were analysed for Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, however only Cu, Pb and Zn were considered in the present work. Samples were size normalised by wet sieving through a 62.5 µm nylon mesh to reduce the confounding effects of variable grain size (Forstner and Wittmann, 1979; Loring and Rantala, 1992, Barbanti and Bothner, 1993, Birch, 2003). Textural analysis was for mud (62.5 µm), sand (62.5-2000 µm) and gravel fractions (>2mm) and mud and total samples were digested in nitric/perchloric acid (1:1) and total recoverable elements were determined using a Perkin Elma Flame Atomic Adsorption Spectrometer (AAS) (Judge, 1992).

Precision, determined by repeated analysis of International Reference Material (MAG-1), was < 5% Relative Standard Deviation (RSD) for all metals, whereas accuracy, expressed as recoveries and established through the use of the same reference material, were between 95% (Zn) and 111% (Mn) (Judge, 1992).

As only one sample was collected at each location, small-scale spatial variance was determined for the two main sedimentary facies present in the estuary to provide an indication of intra-site variance and to validate estuary-wide distributions. Eight replicate samples taken within an area approximately 5x5m gave a variance of 5-7% RSD for muddy sediment and between 6-9% RSD for muddy sands (Birch et al., 2001) Fluvial samples were collected from Pittwater and McCarrs Creeks, the main inputs entering Pittwater (Fig 2), in 1994 (n=13), 2002 (n=12) and 2007 (n=10) using a plastic spatula, pre-cleaned with 10% HNO_3 and rinsed with deionised water. Four samples were taken within $1m^2$ at each site and combined into a single sample for analysis to reduce small-scale spatial variance due to sediment heterogeneity (Birch et al., 2000). River samples were stored the same manner as for estuarine samples.

The 2007 study

Surficial sediment samples (n=72) were taken in May, 2007 using a stainless-steel box corer. Sample density was increased in south of the estuary where contamination is most pronounced and locations were determined by GPS. The oxic, upper 2cm of sediment was collected using a plastic spoon and samples were stored in the same manner as in the 1992 survey.

Tandem short (~0.75m) (n=3) and long (~1-2m) (n=4) push cores were taken adjacent to two large marinas in the south (Royal Motor Yacht Club (RMYC) and Royal Prince Alfred Yacht Club (RPAYC)) and a the small marina in the north (Careel Bay Boat Services) as potential contaminant sources, as well as one from the least disturbed part of Pittwater in the south west (McCarrs Creek). Short cores provided a high-resolution metal profiles from the uppermost section of the core to give information on the most recent depositional history, whereas long cores were used to penetrate the pre-anthropogenic section to provide background metal concentrations.

Cores were capped and stored at 4°C prior to laboratory analysis. Short cores were extruded and sampled at 2cm intervals, while long cores were cut in half and one side sampled at 2cm intervals and the other half archived. Cores were described and logged for texture, colour and structure. Samples were collected according to observed micro-stratigraphy and stored in air-tight, metal-free polyethylene bags and stored at 4^oC.

Total (<2mm) and size-normalised (<62.5 µm) sediment was assessed for the same elements as in 1992, however samples were digested in aqua regia (2ml HNO_3, 2ml HCl, and 10ml ultra-pure water 18MΩ/cm) and analysed using a Varian Vista-AX Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (modification of the USEPA method 200.8 Rev. 4.4).

Precision, determined by repeated analysis of International Reference Material (AGAL-10), was < 5% RSD for all metals, whereas accuracy, established through the use of the same reference material and expressed as recoveries, were between 96% (Cd) and 107% (Cr). The RSD for replicated samples (n=8) from each digestion batch was 1.3%, 1.1% and 2.9% for Cu, Pb and Zn, respectively. Laboratory blanks were used to detect possible contamination during pretreatment and digestion processes and were included with each digestion batch. Metal concentrations were below detection limits for all elements ($<1\ \mu g\ g^{-1}$).

Compatibility of 1992 and 2007 vintage data

Although the 1992 survey used mainly diver-retrieved cores to obtain sediment and a boxcorer was employed to collect material in 2007, only surficial sediment (upper 2cm) was taken for analyses in both studies. Size normalization procedures were the same in both studies and the greatest differences between investigations were in the digestion medium and the type of machine used for analyses, i. e. Flame AAS in 1992 and ICP-OES in 2007 (Cook et al., 1997). The compatibility of data produced by these two approaches was tested by running multiple analyses (n=10) of an International Reference Material (MAG-1) and of a local estuarine sediment using both methods. Student t tests showed no significant differences in the two data sets ($p<0.05$).

Isotope dating and spatial analysis

Samples from Core 1 (adjacent RMYC) were dated by ^{210}Pb (Goldberg, 1963; Oldfield and Appleby, 1984). Total ^{210}Pb activity is determined by measuring the granddaughter isotope ^{210}Po, which is assumed to be in equilibrium with ^{210}Pb, whereas supported ^{210}Pb is established by measuring ^{226}Ra activity (Appleby, 2004). Two ^{210}Pb dating models were used for calculating sediment rates, i. e. the CRS (constant rate of ^{210}Pb supply) and the CIC (constant initial ^{210}Pb concentration) models (Appleby and Oldfield, 1978; Appleby, 2004). The CRS model assumes a constant flux of ^{210}Pb from the atmosphere and a regular ^{210}Pb fallout rate to the location of interest. The CIC model assumes that sediments in the core had the same initial unsupported ^{210}Pb concentration at deposition, regardless of the rate of sedimentation (Walling, et al., 2002).

Samples from Core C1 were also analysed for the anthropogenic radioisotope ^{137}Cs in an attempt to support the ^{210}Pb data. Radioisotope ^{137}Cs deposition is a result of atmospheric nuclear bomb testing and may produce a subsurface maxima in ^{137}Cs activity in the year 1963 at which time testing was most active.

ArcGIS Version 9 was used for data display, manipulation and spatial analysis. Topographic maps from Geoscience Australia covering the study area, whereas catchment boundaries were obtained from the NSW Department of Natural Resources.

Textural and metal distributions were determined by Ordinary Kriging using the Geostatistical Analyst tool in ArcGIS.

Results – Lake Macquarie

Sediment cores

Sediment cores from three selected locations showed distinct profiles for Cd, Cu, Pb and Zn. Metal concentrations in Core 1 were low and irregular throughout the sediment profile, Core 2 showed a decrease in metal concentrations with increasing depth, and Core 3 (Fig. 3) showed significantly greater metal concentrations than the other two cores and maximum concentrations for the four metals were between 25 and 75cm core depth.

Isotope dating results

The ^{210}Pb activity profiles were determined in sediment from Core 3 to achieve radiometric dating (Table 1). Studies have shown that there may be an increase in unsupported ^{210}Pb activity with an increase in the specific surface area of sediments (He & Walling, 1996; Birch *et al*., 1998). Due to varying grain size distribution in the sediment layers, the unsupported ^{210}Pb activities for sediment core from Lake Macquarie were normalised with mud content to calculate the CIC and CRS models mass accumulation rates and sediment ages. The excess or unsupported ^{210}Pb profile (plotted on a logarithmic scale) showed an overall decay profile with depth (Figures 8 & 9). Mass depth (cumulative dry mass) was used instead of true depth to account for compaction effects (Abril, 2003, Laissaoui *et al*., 2008). The ^{137}Cs activities were very low and close to the limit of detection for the instrument and were not able to be used for marking the 1960s atomic testing period. Mass accumulation rates were relatively uniform (~1.1 g cm^{-2} y^{-1}) throughout the last ~55 years according to both CIC and CRS models.

Heavy metal distribution

Maximum Cd, Cu, Pb and Zn concentrations were always highest in the 1975 sediment than in 2003. For all four metals, concentrations were highest in the north of the lake in the vicinity of Cockle Creek, with a strong decreasing gradient to the south for both vintages of data (Figs. 4 & 5).

Absolute and percentage change from 1975 to 2003

For the majority of the lake, the absolute decrease in Cd was between 0.7 and 4.3 µg g^{-1}, a decrease equivalent to 25 and 75%. In the Cockle Creek area, however, Cd decreased up to 373 µg g^{-1}, with a minimal increase visible in Cockle Bay and Dora Creek (Figs. 6 & 7). Copper concentrations increased between 11 and 68 µg g^{-1} (25 to >75% change) in most of Lake Macquarie, except in Cockle Creek and adjacent area where concentrations decreased by up to 75% (20 to 139 µg g^{-1}). Lead and Zn showed a similar decrease in concentration in Cockle Creek and Cockle Bay, i. e. up to 75% (>200 µg g^{-1}). The Dora Creek area decreased up to 25% for Pb and Zn (1 to 49 µg g^{-1}). The southern part of the lake, in the vicinity of Myuna Bay, Brightwaters and Mannering Park, increased between 25% and 75% (51 to 100 µg g^{-1}) for Zn, while Pb increased to >75% (21 to 50 µg g^{-1}).

Results - Pittwater

The spatial distributions of sediment texture and metal content for the 1992 and 2007 studies were similar and are described together.

Texture of surficial sediment

Sandy muds are confined to the central part of the estuary, while muddy sands mantle the entrance to Pittwater and the eastern and western margins of the waterway.

Metal concentrations in surficial sediments

Normalised sediment Cu, Pb and Zn have similar spatial distributions. These metals were highly enriched in the south east of Pittwater and decreased markedly towards the north. Concentrations of these metals were also moderately high in sediment along the southern coastline. In the 2007 survey, Cu, Pb and Zn concentrations declined from approximately 300, 80 and 250 µg g^{-1} in the south east to 40, 40 and 130 µg g^{-1} in the north of Pittwater, respectively.

Metal concentrations in core sediment

In all cores Co (31 µg g^{-1}), Cr (25 µg g^{-1}) and Ni (12 µg g^{-1}) remained constant down core, indicating no anthropogenic enrichment and Cd was frequently below detection (<0.1 µg g^{-1}).

Core Site 1 (short core C1; long core C2)
Cores C1 and C2, adjacent to RMYC (Fig. 2), showed the onset of contamination at 60cm sediment depth with strongly increasing concentrations for Cu, Pb and Zn in the upper section of both cores . However, within the top 10cm Cu increased considerably to the top of the core, whereas Pb and Zn increased significantly to 8cm below the water-sediment interface and then remained constant.

Core Site 2 (short core C3; long core C4)(in McCarrs Creek)
The onset of contamination was at 98cm (high sedimentation rate) and background concentrations were 11 µg g^{-1}, 22 µg g^{-1} and 47 µg g^{-1}, respectively. Copper concentrations continued to increase strongly to the top of the core (138 µg g^{-1}), whereas Pb and Zn increased only slightly from 23cm sediment depth to the sediment surface (47 µg g^{-1} and 162 µg g^{-1}, respectively).

Core Site 3 (short core C5; long core C6)(adjacent to Careel Bay Boat Services)
Onset of contamination was at 80cm sediment depth and maximum Pb and Zn concentrations were at a sediment depth of 58cm and 45cm, respectively. Above this level these metals declined slightly, but constantly to about 100 µg g^{-1} and 200 µg g^{-1}, respectively. Copper showed continuous and marked increase to the top of the core (~550 µg g^{-1}), with considerable fluctuation in the high-resolution core (C5).

Metal concentrations in fluvial sediment

Fluvial sediment samples were taken from Pittwater and McCarrs Creeks in 1994, 2002 and 2007.

Mean concentrations of all metals were considerably higher in Pittwater Creek (approximately 310 µg g^{-1}, 250 µg g^{-1} and 1400 µg g^{-1} for Cu, Pb and Zn, respectively) than in McCarrs Creek, (about 30 µg g^{-1}, 60 µg g^{-1} and 270 µg g^{-1}, for Cu, Pb and Zn, respectively). Mean metal concentrations were also higher in Pittwater Creek sediments than in estuarine sediments.

Isotope chronology

Simular to other metals (Förstner, 1978; Förstner and Wittmann, 1979; Bubb, et al., 1990), unsupported ^{210}Pb activity increases with decreasing grain size and an increase in specific surface area of a particle (He and Walling, 1996; Birch, et al., 1998). Due to the varying grain size distribution in sediment layers in the core from Pittwater, the unsupported ^{210}Pb activities were normalised (<62.5) to calculate the CIC and CRS models mass accumulation rates and sediment ages. The excess, or unsupported ^{210}Pb profile showed an overall decay profile with depth. Mass depth (cumulative dry mass) was used instead of true depth to account for compaction effects (Abril, 2003, Laissaoui *et al.*, 2008). The ^{137}Cs activities were very low, close to the limit of detection for the instrument and were not able to be used for marking the 1960s maximum atomic testing period.

Discussion – Lake Macquarie

Background concentrations

Background concentrations were calculated as 0.4 ±0.2, 8.3 ±1.7, 10.1 ±4.1 and 30.5 ±8.2 for Cd, Cu, Pb and Zn, respectively, compared to Roy and Crawford (1984) at <20, <15 and <70 µg g^{-1} for Cu, Pb and Zn, correspondingly. Present-day maximum enrichment factors (EF), established by comparing background values with 2003 vintage surficial sediment concentrations, were 600, 100, 100 and 18 times for Cd, Pb, Zn and Cu, respectively, whereas enrichment factors for 1975 sediments were 1650, 700, 205 and 50 times, respectively. All highly enriched samples were located in Cockle Creek and adjacent bay.

Interpretation of isotope dating

Independent validation of chronology is essential if a high level of confidence in isotope dating results is to be assured (Appleby, 2001). The most commonly used method of validation is the use of ^{137}Cs, although in many cases this proves to be inadequate due to downward diffusion or remobilisation of ^{137}Cs by post-depositional activity within pore waters (Appleby, 2001; Liassaoui *et al.*, 2008; Putyrskaya & Klemt, 2007) (Figs. 8 & 9). Alternative methods for validation include pollen, diatom, sediment geochemistry and historical records of catchment development and major climatic events (Appleby, 2001; Kilby & Batley, 1993; Gale *et al.*, 1995; Haworth *et al.*, 1999).

Earlier studies of sedimentation rates in Lake Macquarie varied according to the dating method used. Roy and Crawford (1984) determined sedimentation rates at approximately 1 mm y^{-1} using ^{14}C for dating shells in deep sediments (40-90 cm), which might be expected in pre-anthropogenic sediments (Kilby & Batley, 1993). Kilby & Batley (1993) established sedimentation rates in the Cockle Creek area from 5.7 mm y^{-1} in the delta to 1.1 mm y^{-1} south of Cockle Creek. These sedimentation rates were derived from geochemical profiles observed for Pb and Zn in sediment cores from the north of the lake, compared to the history of the Pb-Zn smelter in Cockle Creek (Kilby & Batley, 1993). The smelter, which started operation in 1897, was originally intended to extract Zn from ore produced elsewhere (Broken Hill, central NSW) by the electrolytic process, but this did not prove commercially viable and the works were converted to an ordinary Pb smelting works (Lake Macquarie Council, 1985). In 1922 Pb smelting was discontinued and the plant produced sulphuric acid, superphosphate and fertilisers (Lake Macquarie Council, 1985), however in 1962 the production of Pb and Zn was resumed. It may therefore be possible to use these dates in changes in operation and output as chronological markers to validate the isotope dating results.

The CIC ages, together with the Pb/Zn chronological marker, were used in the present study to extrapolate the date back to the onset of contamination in Core 3. Both the CIC and CRS methods gave similar mass accumulation rates for a 55-year period (1952-2007), i. e. approximately 1.1 g cm^{-2} y^{-1}. This is the equivalent of a sedimentation rate of 14 mm y^{-1} for the top 75 cm of Core 3. Lead and Zn concentrations in Core 3 were used to mark the start of smelter operations at approximately 97 cm. The sedimentation rate from 1897 to 1952 (i. e. between 97 and 75 cm depth in Core 3) was 4 mm y^{-1}.

Lead and Zn increased significantly over background concentrations above 97 cm of sediment depth, which was between the initial smelter operation period during 1897 and 1922. Metal concentrations increased even after the smelter closed temporarily, suggesting that metal-rich sediment deposited in the creek and upper estuary was remobilised during high-energy/precipitation events, or that the production of sulphuric acid, superphosphate and fertilisers contributed to the contamination of the lake during the period 1922-1962. It was during this period that Cu attained maximum concentrations. In 1962 the smelter resumed operation, which coincided with an increase in Pb and Zn concentrations in the sediment profile. Lead was at a maximum concentration in Core 3 in 1970, while Zn was at a maximum circa 1983. Concentrations of Cd were at a maximum during the 1990s. Lead, Cu and Zn behaved independently with depth in this sediment profile, having maxima at different periods. This was not the case in the other two cores taken in Lake Macquarie south during the present study, where Pb and Zn, in particular, followed a similar downcore pattern. The fluctuating downcore metals profile may be due to varied smelter output, or it is possible that factors affecting metal mobility in sediments, such as pH, organic matter, salinity, acid volatile sulfides and redox potential, may have affected Core 1 3??results. However, Roy and Crawford (1984) found similar results for a core taken in the Cockle Creek delta, where Pb and Zn showed independent trends in concentration with depth.

Temporal and spatial change

Highest concentrations for all metals were in Cockle Creek and Cockle Bay in both 1975 and 2003 vintage data and the overall decrease of metal concentrations was greatest in this area over this period (Fig. 10). A temporal decreasing trend is supported by previous studies in the area. Roach (2005) found that in the Cockle Bay area Pb and Cd had declined between 20-60% and 6-48% since a previous study by Batley (1987), while Cu and Zn were 35-108% and 41-91% of 1987 concentrations.

The high Cd, Pb and Zn concentrations in sediment adjacent to the mouth of Cockle Creek decreased considerably (by approximately 75%) between the 1975 and 2003 surveys, whereas Cu concentrations decreased only slightly (by about 25%). Declining concentrations of these metals in sediments in this area were to be expected with closure of the nearby Pb-Zn smelter. However, large increases (by approximately 50-75%) in Cu, Pb and Zn towards the southern part of the lake were a surprise and the source(s) of these metals are not well understood.

Changes in Cu concentrations between 1975-2003 in the north and the southwest of the lake suggest Cockle Creek and Dora Creek are possible contemporary point sources of this metal. Sediment in Myuna Bay also has high Cu concentrations, possibly due to activities in the adjacent catchment, i. e. nearby coal-fired power plant and/or urban development. Copper increased in the majority of the lake by greater than 75%, and the only area showing an improvement or decrease in concentration in this metal over this period was in the Cockle Creek and Bay areas. This assessment based on changes to surficial sediment metal concentrations is supported by evidence in the top 20-30 cms of the three sediment core profiles, i. e. Cores 1 and 2 (southern Lake Macquarie and Dora Creek) show an increase in Cu concentration, while Core 3 (Cockle Creek) shows a decrease in concentration.

Lead and Zn exhibit similar spatial and temporal trends. Surficial sediment concentrations decrease from north to south in both 1975 and 2003 surveys and distributions shows a relative improvement in the Cockle Creek and Bay areas over this period. Unexpectedly, the percentage change for both Pb and Zn show an overall increase in concentrations in the southern part of the lake. Increased concentrations of Pb and Zn in the southern part of the lake suggest that Dora Creek and possibly large coal-fired power stations located on the southern shore of Lake Macquarie may be contemporary sources of these metals. Alternatively, Pb- and Zn-enriched sediment in the north is possibly being remobilised and transported southwards.

Relaxation rates

Relaxation rates calculated for metals in Lake Macquarie indicate Cu would increase considerably if 1975 to 2003 conditions remain constant over time, with areas 10 times greater than background increasing from less than 1 km^2 in 2003 to 36 km^2 by the year 2020, particularly in the vicinity of Myuna Bay and Bright Waters (Figs. 11 & 12). The area covered by Pb concentrations over 5 and 10 times greater than background also increases steadily in the estuary. Sediment quality, however improves for all three metals in the estuary by the year 2020, the only exception being Cu in the vicinity of Myuna Bay and Bright Waters.

Relaxation rates for Cu, Pb and Zn have been estimated for the Cockle Bay area by using the age/depth vs. metal concentration relationship. Rates of relaxation, as well as a prediction of time needed for metals to reach particular enrichment and sediment quality levels, were calculated.

Relaxation rates for the Cockle Bay area are negative; i. e. metal concentrations will decrease with time, assuming current metal loadings into this area and dispersion mechanisms remain constant. Current Cu concentrations in Cockle Bay are among the highest in the estuary, however, 2003 and 1975 concentrations are below the ISQG-Low value, i. e. low risk of adverse biological effects and below trigger levels. Lead and Zn are greater than their corresponding ISQG-Low values and it would take over 100 years to reduce concentrations to below this value, assuming loading remains constant. It would take another 65 years for Cu to reach concentrations two times background at present-day input rates. Lead concentrations would decrease much faster, with two times background concentrations being reached by 2015.

A similar relaxation rate calculation was undertaken for other areas, such as Dora Creek and the southern part of the estuary using the 1975 and 2003 data (Table 5). The area where Core 1 is located shows a slight increase in Pb and Zn concentrations with time. Copper, however, increased during the 1975 and 2003 period, which is supported by the data in Core 1 profile. If Cu continues to increase at the current rate, this metal would reach concentrations 5 times greater than background by 2012 in this area. Likewise, Cu in the vicinity of Dora Creek would reach concentrations 10 times background by 2017.

Discussion - Pittwater

Background Concentrations and enrichment

Background or pre-anthropogenic metal concentrations were required to determine the onset of contamination and to estimate the magnitude of enrichment, i. e. the number of times current sediment concentrations are elevated above pristine levels. Background metal concentrations were determined by calculating the mean normalized concentration of metals displaying consistently low values towards the base of the three cores. These data were compared to mean minimum concentrations of surficial sediment from the most pristine part of the estuary and with fluvial sediment from the creek draining the National Park (McCarrs Creek) (Table 5). Cobalt and Pb concentrations of surface sediment from the most pristine part of the estuary were similar to values obtained in deep sections of the cores. Metals, except Co and Cu, were elevated in fluvial sediments taken in the National Park, indicating that the minimal vehicular traffic passing through the reserve was sufficient to influence sediment chemistry and that the normalised data were sensitive enough to detect these impacts. Considering these data from different sources, most weight was given to metal concentrations at the base of the 6 cores taken from the estuary. Background concentrations were calculated as 4, 30, 15, 3200, 52, 12, 22 and 45 $\mu g\ g^{-1}$ for Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, respectively and mean enrichment was 2, 2, 9, 1, 8, 2, 2 and 4, respectively. The background concentration for Cd was below the detection limit, enrichments for Co, Cr, and Ni were close to parity and Fe and Mn are not considered anthropogenic constituents in this locality. The present work will thus consider only Cu, Pb and Zn.

Contaminant chronology and sedimentation rates

Onset of contamination in the south east tributary of Pittwater, determined by ^{210}Pb dating, was approximately 1970s. Confidence in isotope dating is greatly enhanced by independent validation (Appleby, 2004), commonly using ^{137}Cs dating, pollen, diatom, sediment geochemistry, major climatic events and historical records of catchment development (Kilby & Batley, 1993; Gale *et al.*, 1995; Haworth *et al.*, 1999). Insufficient material precluded the use of ^{137}Cs chronological data possibly due to remobilisation of ^{137}Cs during post-depositional activity within pore waters (Appleby, 2004; Liassaoui *et al.*, 2008; Putyrskaya & Klemt, 2007). Historical records of catchment development indicated substantial residential and industrial expansion in the south east at this time and especially a significant increase in marina mooring facilities.

Sedimentation rate determined from core C1 for the top 0.6m sediment depth, i. e. anthropogenic-influenced section, was 15mm y^{-1}. No previous estimate of sedimentation rate is available for Pittwater, however in nearby (~40km away) Lake Macquarie rates varied between 1 and 14mm y^{-1} (Roy and Crawford, 1984; Kilby and Batley, 1993; Olmos and Birch, in press) and in Sydney Harbour sedimentation rates were from 8 to 27mm y^{-1} (Taylor, et al., 2004). The sedimentation rate associated with the location from which core C1 was taken was high compared to other developed catchments, especially considering the small catchment size (<5km^2).

Temporal changes in metal distributions 1992 to 2007

Copper concentrations have increased in sediments in all parts of Pittwater and particularly in the south east where maximum levels have increased from approximately 180 µg g^{-1} to 280 µg g^{-1} or about 150% in the 15 years between surveys. Lead concentrations have declined in sediment from the majority of the estuary by approximately 10 µg g^{-1} to 20 µg g^{-1} or up to 50%. Sediment Zn concentrations have increased in the southern and north eastern parts of the estuary from maximums of about 200 µg g^{-1} to approximately 250 µg g^{-1} or 125% and by 70 to 100 or approximately 75% in McCarrs Creek. Zinc concentrations in sediments in the central estuary have increased moderately by about 10 µg g^{-1} to 20 µg g^{-1} or 5-10%.

The locations of the four cores taken in the estuary were selected to verify temporal, estuary-wide changes determined by surficial sediment metal concentrations obtained in the two surveys. High-resolution, temporal data provided by fine-interval sampling (2cm slices) of the short cores supported changes in metal distributions indicated in the spatial surveys. Down-core metal profiles in core C1, taken adjacent to the RMYC, showed strongly increasing concentrations for Cu, Pb and Zn from the onset of contamination in the early 1970s to approximately 1998, at which time Pb concentrations began to decline slightly and Zn to increase marginally, whereas Cu concentrations continued to increase substantially . Sediments in upper McCarrs Creek showed slightly declining Pb concentrations at the top of the core (cores C3 &

C4) with Cu and Zn concentrations increasing rapidly towards the surface, consistent with surficial sediment metal distributions. In this area, Zn concentrations in surficial sediment were less than Cu, reflecting the lower vessel mooring density in this part of Pittwater. Sub-surface sediment (cores C5 & C6) adjacent to the marina in the north (Careel Bay Boat Services, CBBS) showed declining Pb concentrations, slightly decreasing Zn and strongly increasing Cu concentrations towards to top of the core, consistent with changes in surficial sediment concentrations between the 1992 and 2007 surveys. Strongly increasing Cu concentrations in sediments adjacent to marinas and even in relatively remote mooring areas (McCarrs Creek) up to the present day, was a feature of subsurface and surficial metal distributions in Pittwater.

Management Implications

Contamination and relaxation rates

Relaxation may be expressed as an acceptable enrichment value (current concentration relative to pre-anthropogenic level), or as an acceptable level of biological risk, i. e. the ISQG-L value (the 'trigger' value for additional environmental investigation).

In the current study, an acceptable enrichment value was two times background and the trigger concentrations are 65 $\mu g\ g^{-1}$, 50 $\mu g\ g^{-1}$ and 200 $\mu g\ g^{-1}$ for Cu, Pb and Zn, respectively. Surficial sediment Cu concentrations in 1992 were 10 times background in the south east of Pittwater decreasing to two times background in the north. By 2007 the area mantled by sediment with 10 times background had increased in the south from 0.4 km^2 to 2.3 km^2 and is projected to be 3.9 km^2 by 2020, if it is assumed that supply and dispersion will not change. Copper concentrations were above ISQG-L in 0.4 km2 in the south east and in 2007 the area had increased to 2.5 km2 and is modelled to be 4.3 km^2, but only minor (0.02 km^2) area to be greater than ISQG-H. Sediment in all of Pittwater was greater than 2 times background in 1992 for Pb and most (8.5 km^2) of the water way was less than this enrichment in 2007 and the majority (11 km^2) of the embayment is expected to be less than this value in 2020. The area of sediment less than 5 times background decreased from 0.3 km^2 to 0.1 km^2 in 2007 and almost no sediment is expected to be greater than this value by 2020. The area of sediment greater than the trigger value (ISQG-L) was small in 1992 (0.2 km^2) and is expected to be almost non-existent in 2020. Sediment in almost all of Pittwater was greater than 2 times background for Zn in 1992 and it is modelled that the area 5 times background will increase from zero in 1992 to 1.9km^2 mainly in the south east of the embayment by 2020, however, even at this date, no sediment in the water way is expected to be greater than the trigger value.

Temporal metal trends in sediments of Pittwater indicate that Cu and Zn has increased in concentration over the last 15 years and modelling suggests that this trend will continue, if no preventative strategies are enacted. However, only Cu, and a small area of Pb, exceeds the trigger value, but that this area for Cu will increase substantially, while for Pb it will decrease in time to be negligible by 2020. Therefore, the metal of most concern is Cu and the area most at risk of biological harm is the south east of Pittwater.

Contamination Sources and Dispersion

Sediment Cu, Pb and Zn concentrations increased markedly towards the south east of the estuary in an area of dense boat moorings and large marinas. However, this is also the location of discharge of metal-rich sediment from Pittwater Creek, which drains the only industrialised area of the catchment. Metal signatures were used to determine the relative magnitude of these two potential sources of contamination to the estuary. The Cu:Pb:Zn ratio for fluvial sediment in Pittwater Creek was 3:1:4 and for estuarine sediment adjacent to the marinas, the ratio was 3:2:14, illustrating distinctly different chemical signatures related to industry and marine activities. Sediments with an industrial-metals characteristic were confined to a small area off the mouth of Pittwater Creek, indicating high concentrations, but low-metal loads, which is consistent with the small area of industrialization associated with this catchment. The industrial area comprises mainly automotive activities, including motor repairing, car and truck cleaning services, brake and clutch services, panel beater and painter services, which may be the source of elevated Pb and Zn in fluvial sediment. Sediment with elevated Cu and Pb concentrations in the south east of the water way and adjacent to the southern coast is associated with high-density marine activities. Marina facilities and boating activities contribute Cu to the environment due to Cu-based anti-fouling paints used to prevent colonization of aquatic organisms on boat hulls (Turner et al., 2007). Increased sedimentary Zn, and particularly Cu concentrations, probably reflects the heightened use of marine vessels and considerable expansion of marina and swing moorings in the southern part of the estuary. Pittwater is host to one of the largest fleets of pleasure craft in Australia (ref) and caters for a large population of vessels in marinas. The decline in Pb content of sediments is consistent with other studies in the area (Taylor et al., 2004) and is probably related to the withdrawal of leaded petrol in 1986 for vehicular use and a move towards unleaded, four stroke marine engines.

Metal concentrations decrease rapidly within 2.5km of the south eastern and southern coastline suggesting minimal large-scale suspended sediment transport in this protected part of the embayment, however concentrations remained well above background in the north at the mouth of Pittwater, indicating moderate tidal transfer.

Conclusions – Lake Macquarie

The current study demonstrated a novel technique to provide information on temporal change in environmental condition for a large coastal lake on a regional basis. Surficial sediment metal distributions in Lake Macquarie, derived from surveys undertaken in 1975 and 2003, were combined with ^{210}Pb activity core profiles to provide historical change and to predict relaxation rates for the entire water body. Cadmium, Cu, Pb and Zn concentrations were considerably higher in surficial sediment in 1975 than in 2003, and both vintages of data showed a strong declining trend southwards for all metals from maxima in the vicinity of Cockle Creek. For the majority of the lake, the absolute decrease in Cd was between 0.7 and 4.3 µg g^{-1}, a decrease equivalent to 25 and >75%, with a minimal increase in Cockle Bay and Dora Creek regions. Predictions of Cu Pb and Zn concentrations for the year 2020 revealed an overall improvement in sediment quality in the northern part of the lake, however the study surprisingly also identified a possible increase in surficial sediment Cu concentrations in the southern part of lake by the year 2020, assuming present conditions remained constant. ^{210}Pb activity profiles revealed mass accumulation rates were relatively uniform (14 mm y^{-1}) throughout the last ~55 years for the northern part of the lake.

Data on past and possible future changes in surficial metal concentrations for the entire lake surface has provided valuable information for estuary stakeholders to develop management strategies for improving ecosystem health in Lake Macquarie.

Conclusions – Pittwater

Sediments mantling Pittwater estuary contain elevated concentrations of Cu, Pb and Zn in the south east and south of the water way due to intense marine recreational activity, including boat yards, marinas, swing moorings and slip ways. Copper-based, anti-fouling paints are used by boats to prevent colonization of aquatic organism and sacrificial, Zn-anodes protect engine parts, whereas metal surfaces are zinc-plated to prevent rust in this salt-rich marine environment. A minor contribution of these metals is sourced from a small industrial catchment discharging in the south east as indicated by distinctive metal signatures, which differentiate maritime- and catchment-derived materials.

Normalised metal concentrations in surficial sediment taken in 1992 and again in 2007 using similar field and analytical techniques, clearly indicate that Cu, and to a lesser extent Zn, concentrations have increased over the 15-year period in this estuary, while Pb concentrations have declined. Down-core metal profiles in cores, strategically located to verify the spatial distributions, support estuary-wide distributions determined by the surficial surveys. A Pb^{210}-dated core showed the onset of contamination in the estuary coincided with urbanisation of the catchment and a significant increase in boating activity in the early 1970s. Using the results of the 1992 and 2007 surveys and assuming no change in supply and dispersion of metals in the estuary, Cu and Zn are predicted to increase in concentration and areal extent, whereas Pb concentrations and areal cover will decrease. Of the three metals, only Cu is of concern, especially in the south eastern and southern parts of the estuary where concentrations are at levels that may be adversely affecting the health of benthic animals.

The indicators and approach used in the current investigation are novel and the only technique to provide the pristine condition, the historical and possible future magnitude of anthropogenic change, as well as the past and future risk to benthic populations due to sedimentary contaminants.

Acknowledgments

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Figure 1 Study area and sample locations, Lake Macquarie.

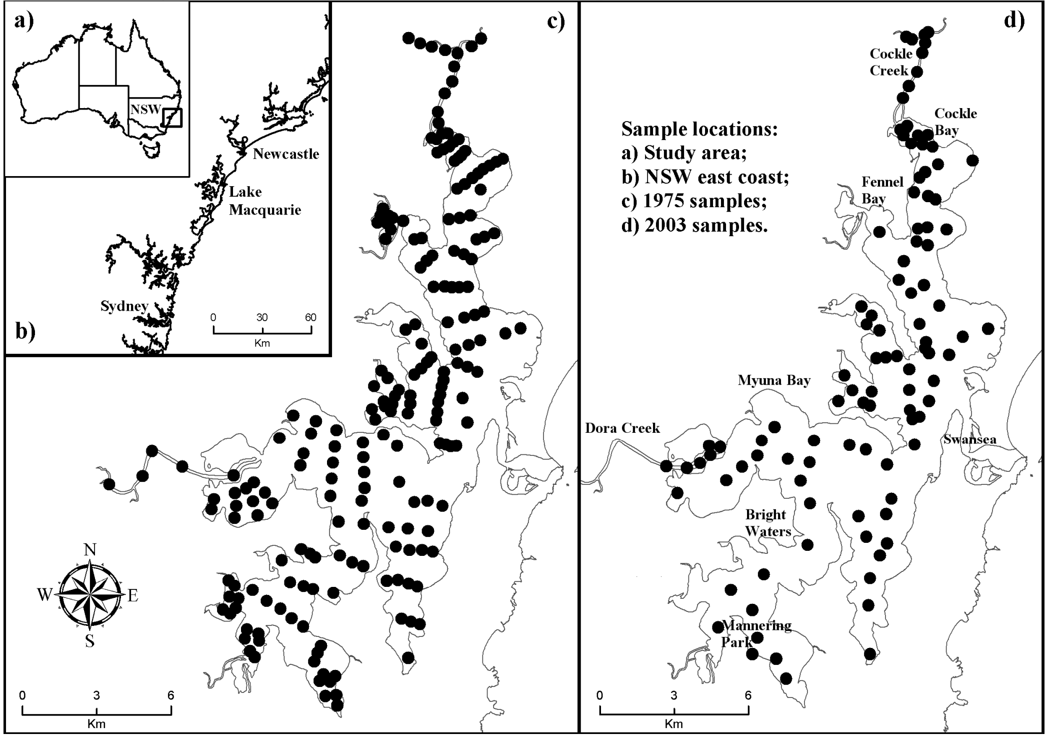


Figure 2 Sediment texture map for the 2003 study (<10% Sand; 10-50% Muddy sand; 50-90% Sandy mud; >90% Mud) and core locations.

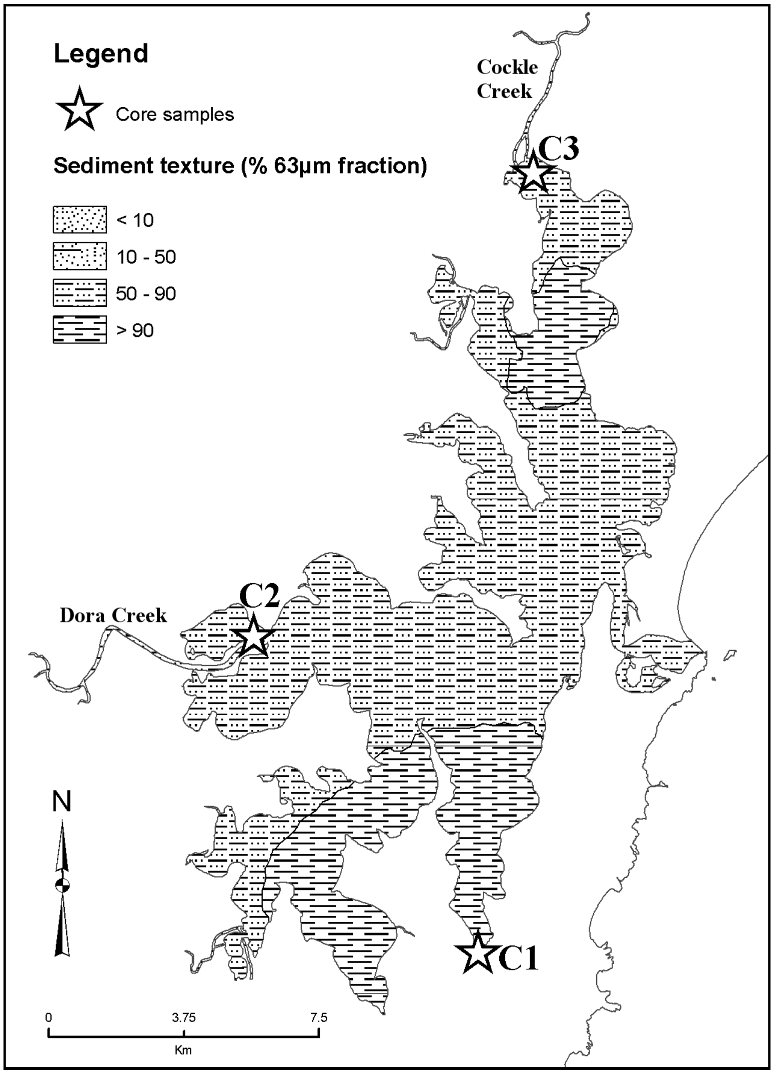


Figure 3 Sample locations in Pittwater

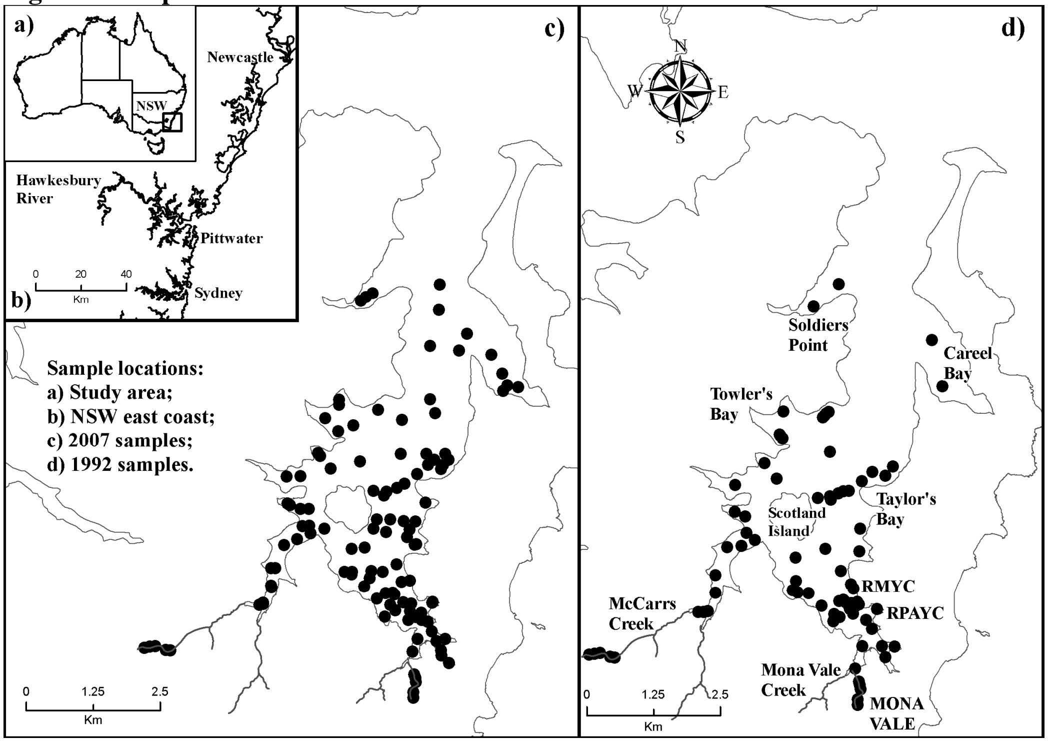


Figure 4 a) Cadmium concentrations (μg g^{-1}) 2003; b) Cd in 1975 (μg g^{-1}); c) Copper concentrations (μg g^{-1}) 2003; d) Cu in 1975 (μg g^{-1}).

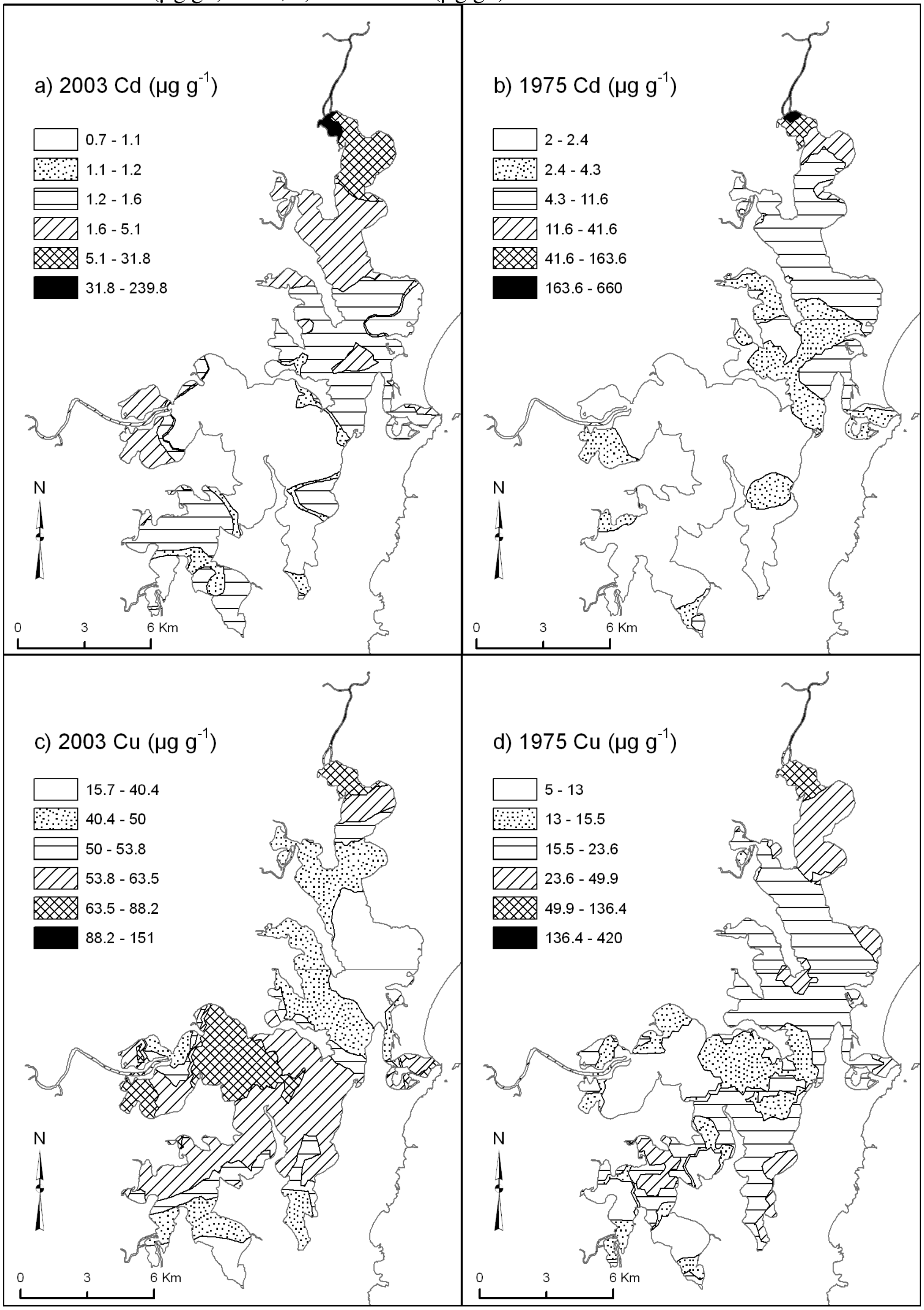


Figure 5 a) Lead concentrations (μg g^{-1}) 2003; b) Pb in 1975 (μg g^{-1}); c) Zinc concentrations (μg g^{-1}) 2003; d) Zn in 1975 (μg g^{-1}).

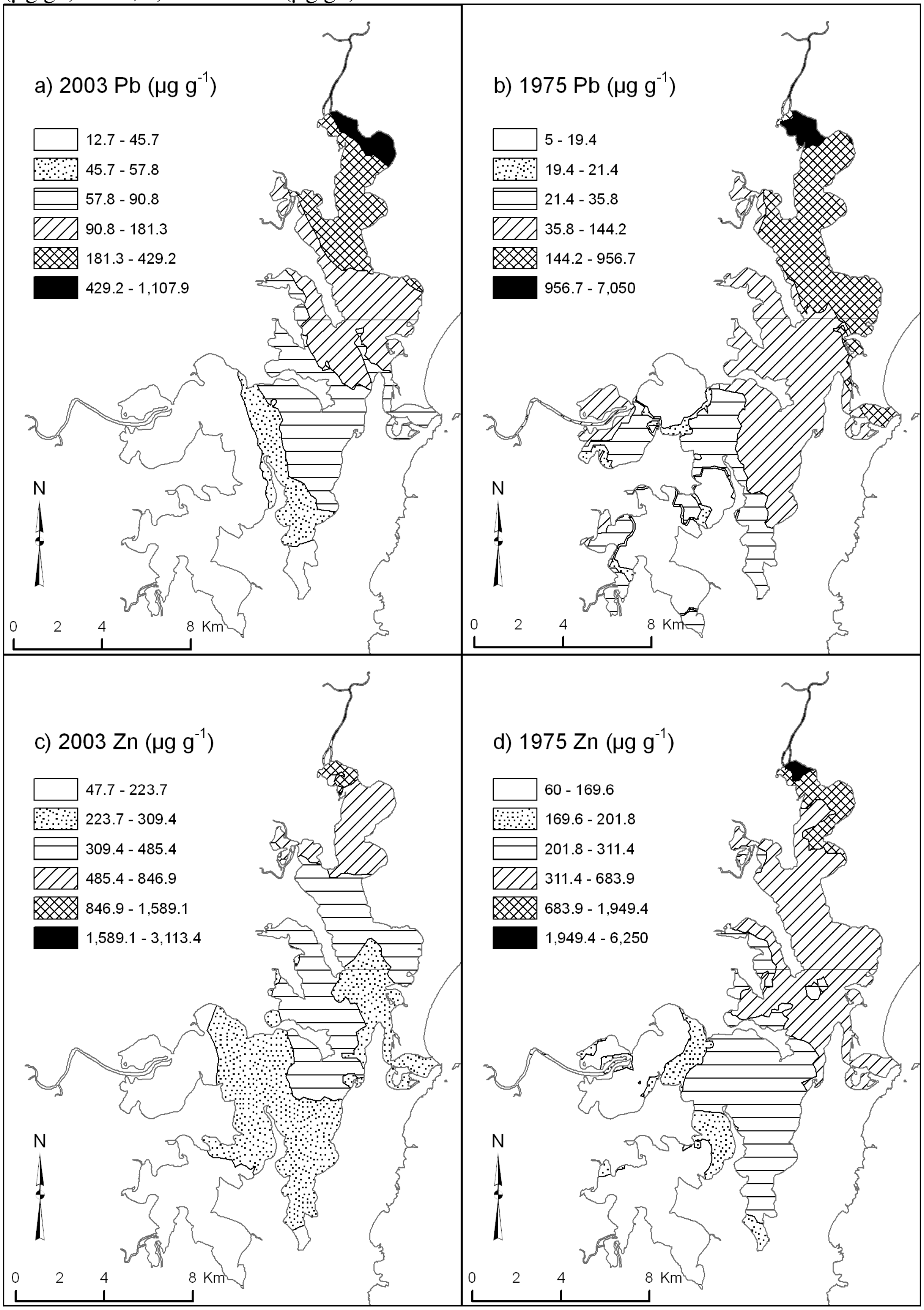


Figure 6 Absolute change (μg g^{-1}) in metal concentrations from 1975 to 2003 in Lake Macquarie for a) Cd, b) Cu, c) Pb and d) Zn.

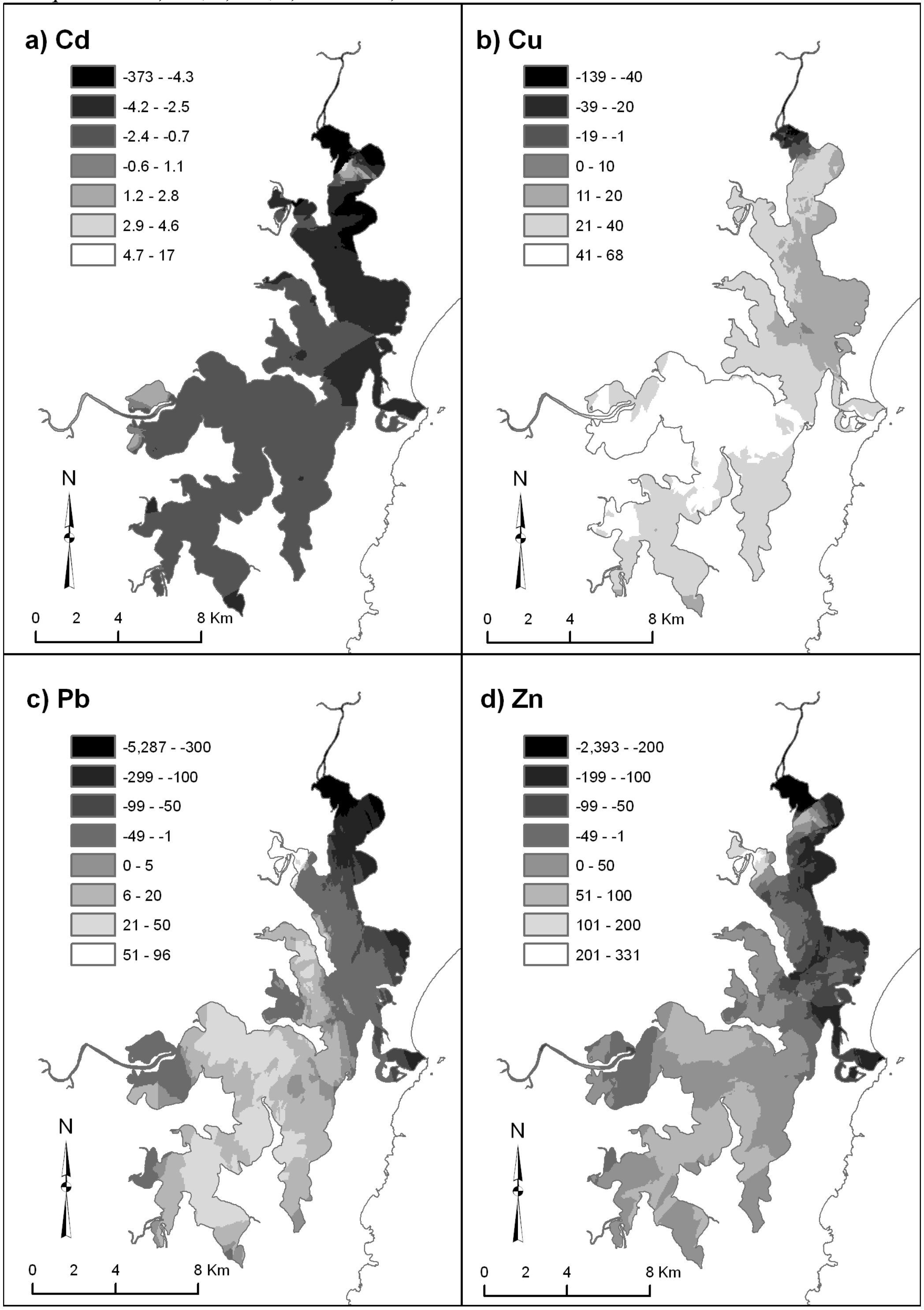


Figure 7 Percentage change in metal concentrations from 1975 to 2003 in Lake Macquarie for a) Cd, b) Cu, c) Pb and d) Zn.

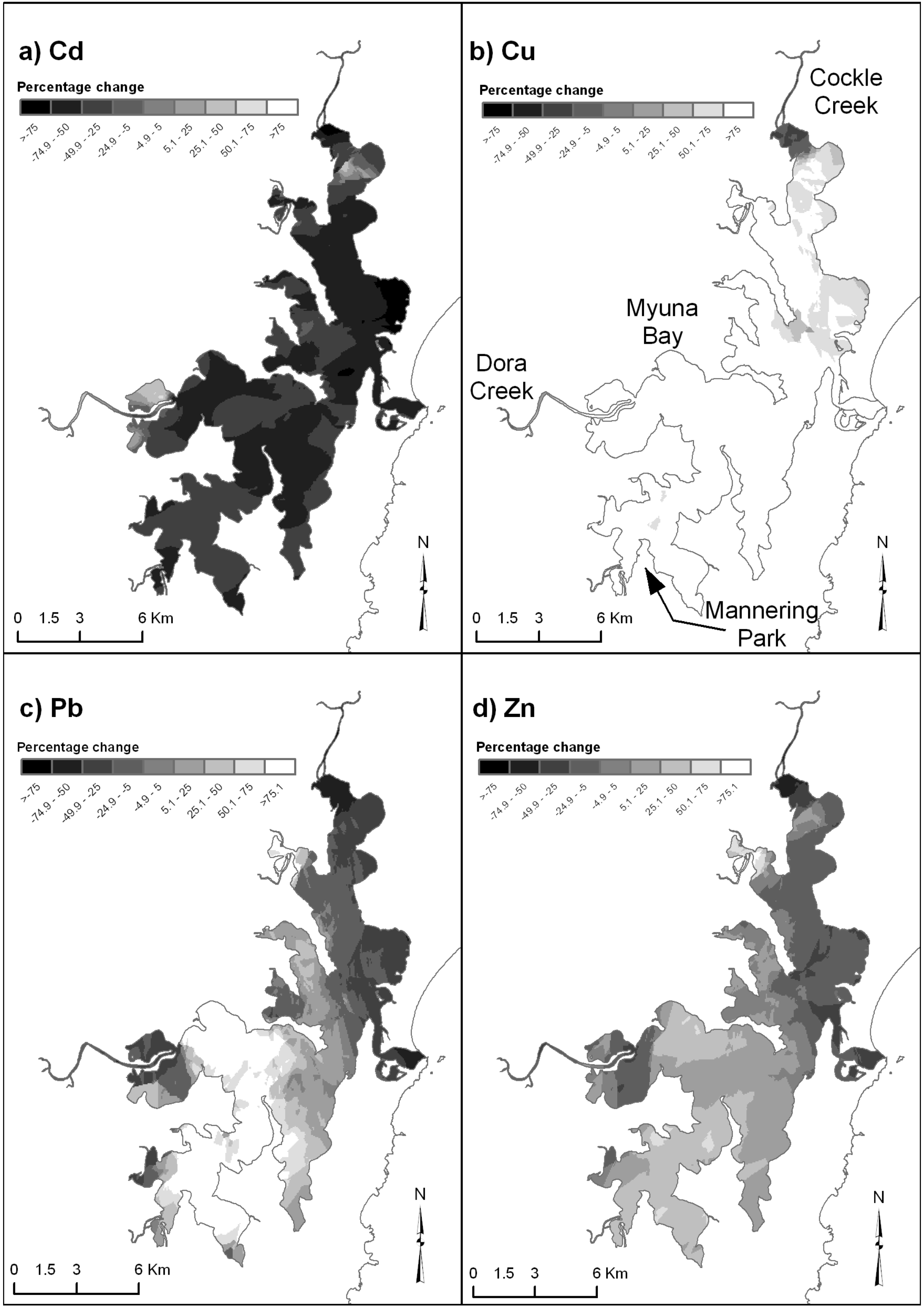


Figure 8 Lead and Zinc concentrations in Core 3 (Cockle Creek) with corresponding ages.

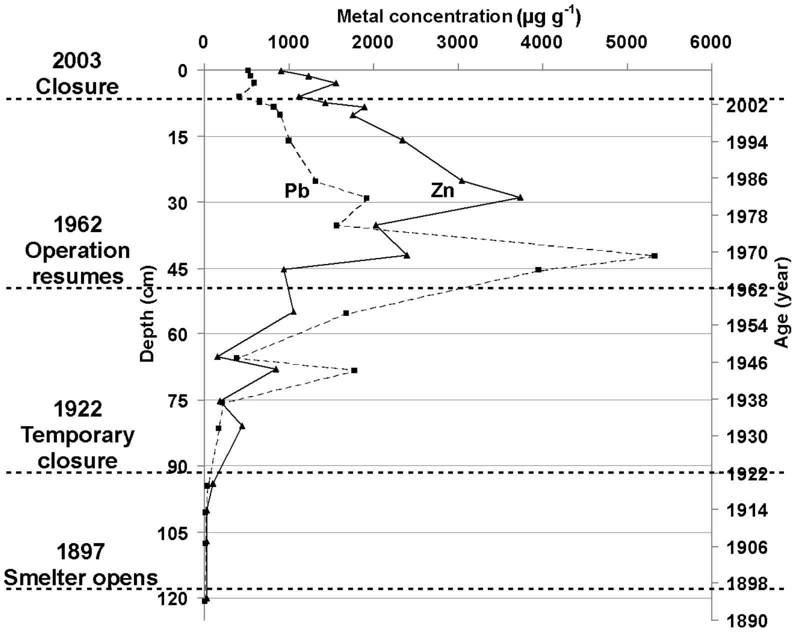


Figure 9 Copper and Cadmium concentrations in Core 3 (Cockle Creek) with corresponding ages.

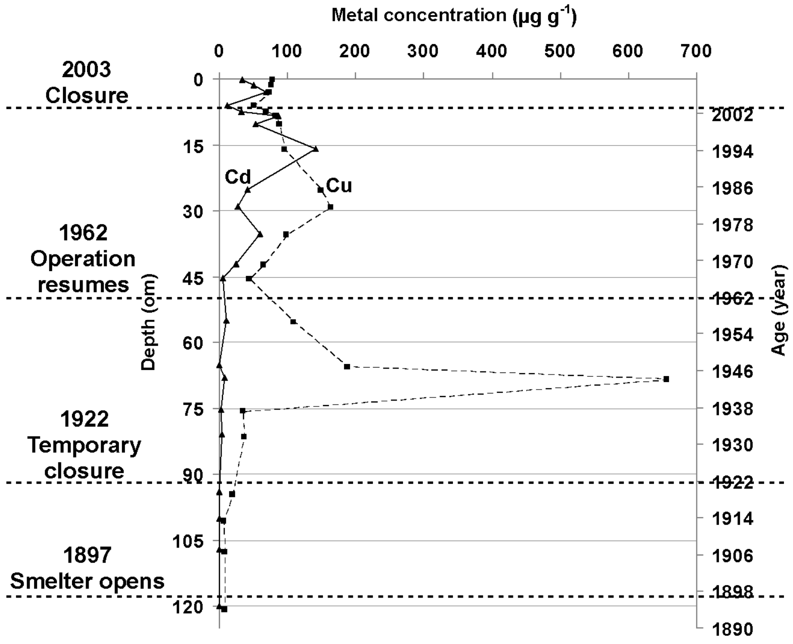


Figure 10 Change in 1) Cu over background (Bg) and 2) according to ISQG-L and ISQG-High during a) 1975, b) 2003 and c) 2020 prediction, showing corresponding change in area (km^2).

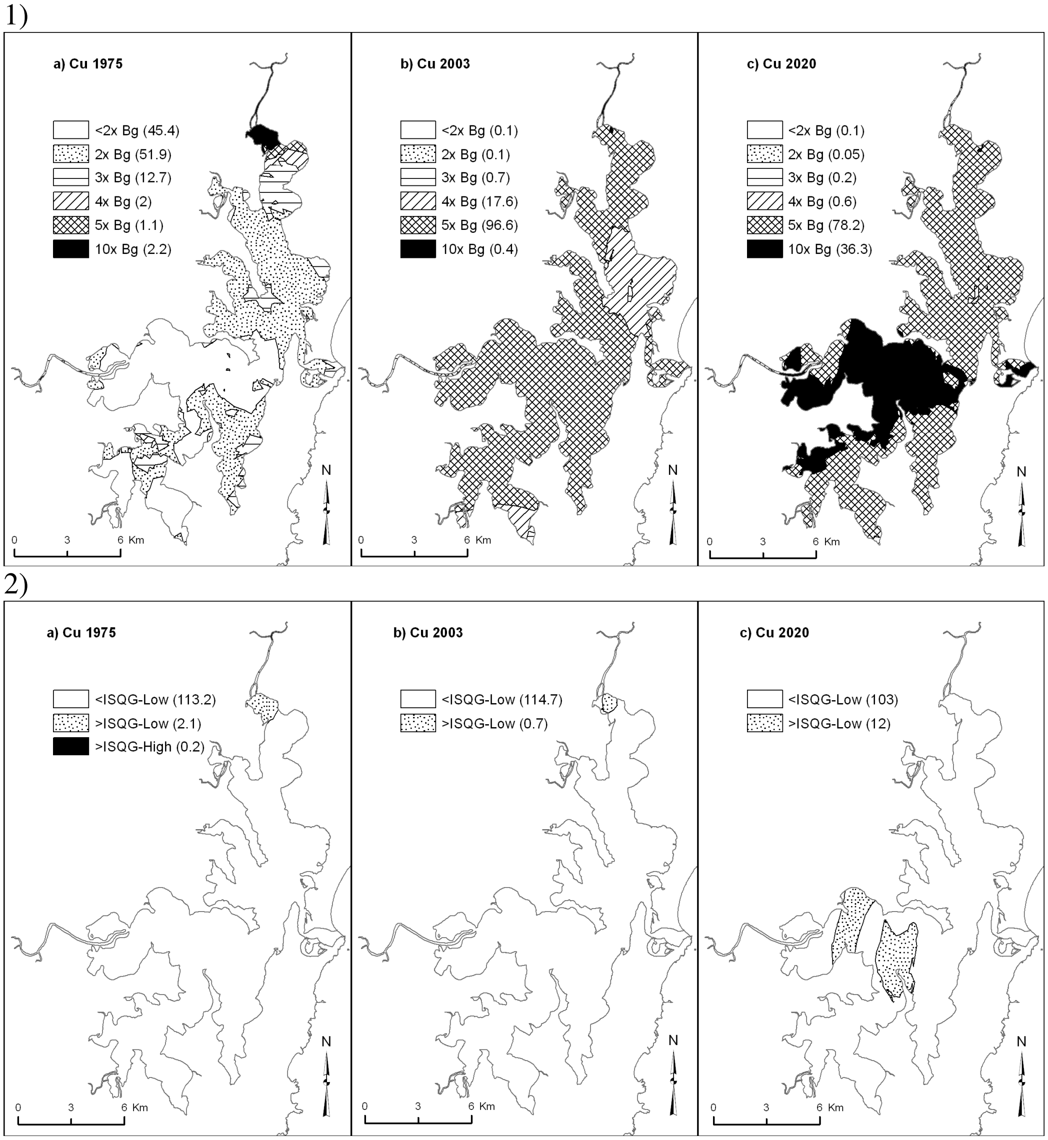


Figure 11 Change in 1) Pb over background (Bg) and 2) according to ISQG-L and ISQG-High during a) 1975, b) 2003 and c) 2020 prediction, showing corresponding change in area (km^2).

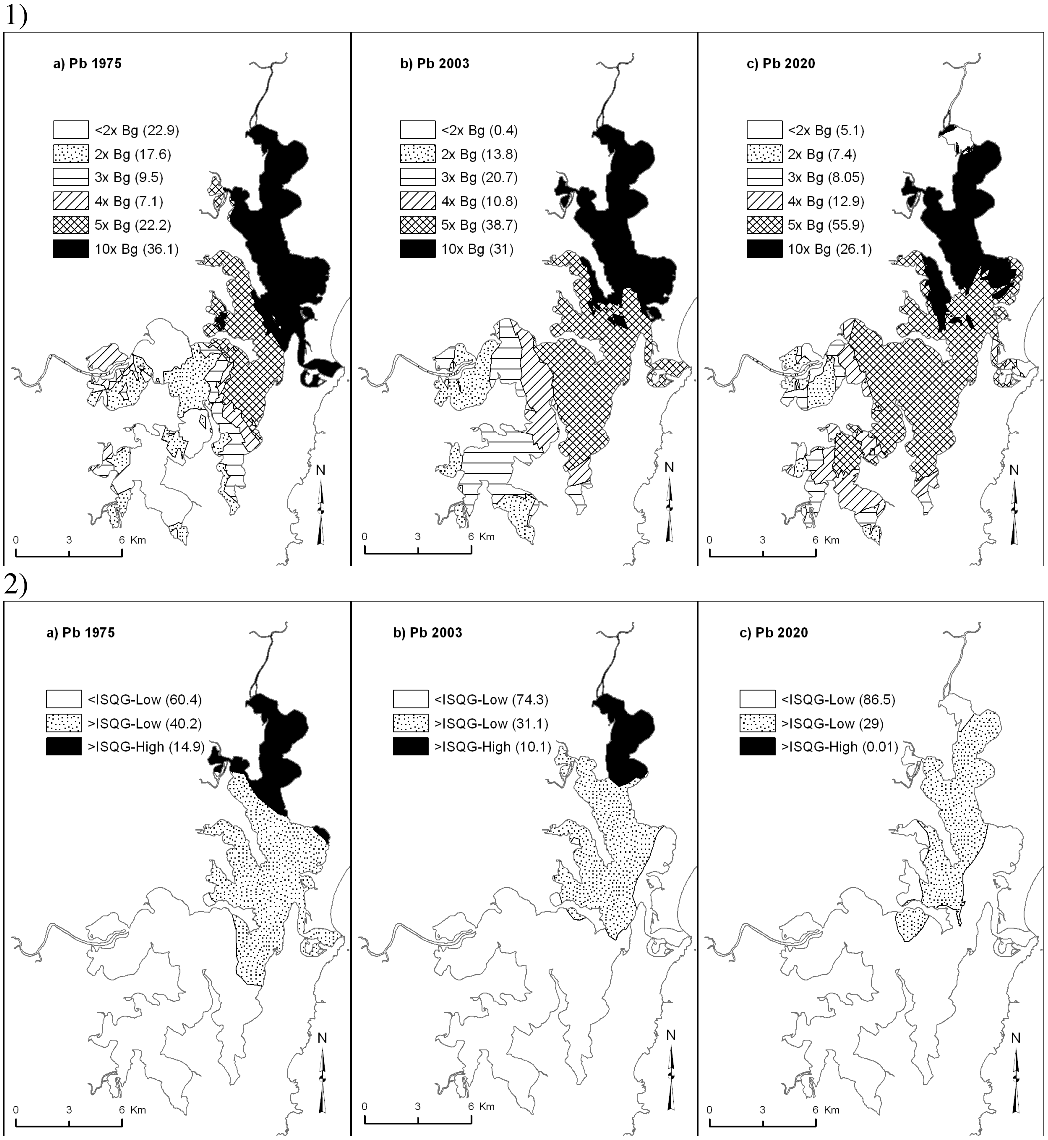
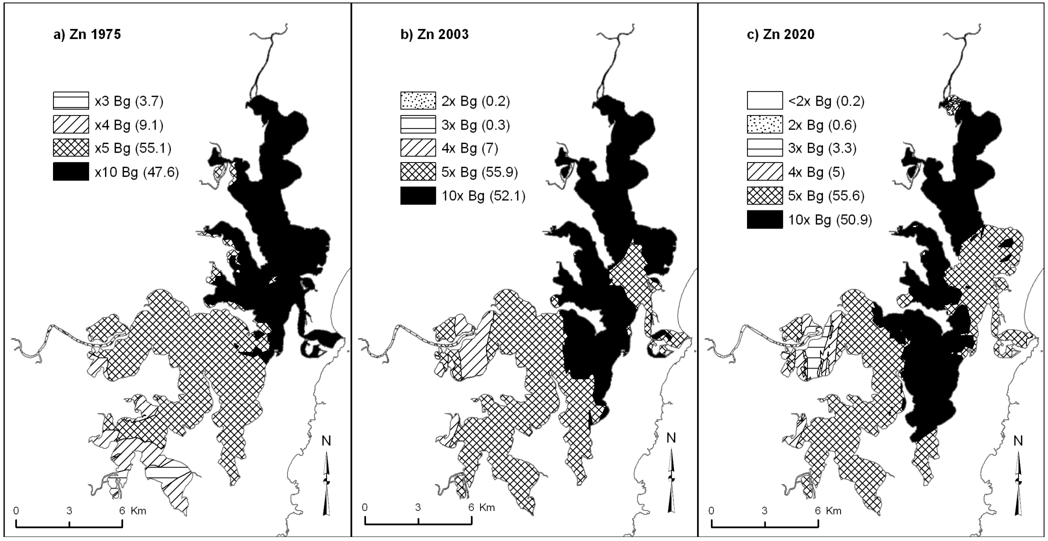


Figure 12 Change in 1) Zn over background (Bg) and 2) according to ISQG-L and ISQG-High during a) 1975, b) 2003 and c) 2020 prediction, showing corresponding change in area (km^2).

1)



2)