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Sediments as archives of industrialisation: evidence of atmospheric pollution from coastal wetlands in southern Sydney, Australia.

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Abstract

The history of heavy metal pollution in southern Sydney was reconstructed from wetland sediments using chemical analysis. Seven wetlands along the Pacific coast were examined for present day concentrations of acid-extractable Cd, Cu, Fe, Pb and Zn. Additionally, four of these sites were cored in order to assess past levels of these metal contaminants, changes in organic content and magnetic susceptibility variations. The low nutrient status and closed catchments of the study sites suggested that the pollutants were predominantly derived from atmospheric sources. Surficial sediments were enriched with Cd, Cu, Fe, Pb and Zn levels 5.0, 16.4, 22.7, 8.2 and 22.5 times baseline levels respectively. In some cases, the concentrations of trace metals were in excess of environmentally acceptable levels. The results show a strong spatial association between sources and levels of pollutants, and the increase in metals levels in sedimentary records corresponds well to documentary historical evidence.

This study demonstrates the utility of coastal wetlands in the reconstruction of atmospheric pollution histories, and their particular vulnerability to contamination from airborne pollutants in urban areas.

Keywords

Air pollution, baseline levels, heavy metalsurban wetlands.

1. Introduction

The reconstruction of pollution histories has considerable value in gauging the timing and magnitude of past phases of industrialisation and has been widely used in Northern America and Europe, covering time spans ranging from several millennia (eg: Hong et al., 1996; West et al., 1997) to a few hundred years (eg: Perkins et al., 2000*; von Gunten et al., 1997; Gilbertson et al., 1997). However, the sedimentary evidence needs to be examined with caution, because recorded changes can result from variations in atmospheric inputs, wind regimes, groundwater influx, catchment erosion events, swamp productivity changes, trace metal mobility, catchment fires and the presence of certain kinds of bacteria (Damman, 1990*; Clymo, 1983*; Aaby, 1986*; Alloway, 1990b*; Kuster and Rehfues, 1997*; Dearing and Foster, 1986*; Oldfield, 1977). Interpretation of changes relies, therefore, on a sound knowledge of local site characteristics: catchment hydrology, sedimentation, vegetation and land-use history.

Heavy metals have been produced in enormous quantities by modern industrial processes (Nriagu, 1996*, 1979*) and their often exponential increase in recent sediments is seen as indicative of human impact on atmosphere and hydrosphere. The vast majority of literature on the history of heavy metals in the environment is concerned with reconstructing the impact of urban and industrial effluent on polluted lake, estuarine and marine environments (e.g: Bruland et al., 1974*; Nriagu, 1984*; Chenhall et al., 1992*, 1994*; Zwolsman et al., 1993*; Peters, 1994*; Croudace and Cundy, 1995*; Ohmsen et al., 1995*; Emmerson et al., 1997*; Irvine and Birch, 1998*). The reconstruction of *atmospheric* pollution histories began in Scandinavia during the early 1960s (Steinnes, 1997*) and has been widely applied in northern latitudes where ombrotrophic peat bogs, generally considered to give the clearest reflection of atmospheric conditions through time, are widespread and abundant.

Mid-latitude and semi-arid regions are strongly under-represented in historical studies of atmospheric pollution due to the lack of rainwater-fed bogs. . In Australia, the distribution of ombrotrophic peats is extremely limited, and these often offer poor temporal resolution for pollution studies due to slow sedimentation rates. Australia and New Zealand, however, are ideal locations in which to gauge the environmental effects of industrialisation, having been settled by industrial colonists at the onset of the industrial revolution. They have been geographically isolated from northern hemisphere pollution sources, and the industrial history of both nations is well documented.

Perkins et al. (2000) demonstrated the value of coastal interdunal wetlands as archives of atmospheric pollution on the shores of Lake Michigan (USA), and it seemed likely that a record could be obtained from similar sedimentary basins in Australia.

In southern Sydney, where the predominant geology is nutrient-poor Quaternary Sands overlying siliceous Hawkesbury Sandstone, a number of coastal wetlands exist in which atmospheric metal inputs are dominant (Johnson, 1994; Martin, 1994) and which we contend represent a good archive of air pollution levels in southern Sydney during the past two centuries.

2. Study Sites

Four major sites were selected for reconstruction of the pollution history, whilst a number of other swamps were sampled to determine modern pollution distribution patterns (see Fig. 1). All sites have closed catchments free of inflowing streams, and all are subject to pollution sources located outside their topographic catchment boundaries. *Trenerry Bog* is part of a small system of urban wetlands at Trenerry Reserve in the suburb of Coogee, 9 kms SSE of Sydney city. The wetlands are unique in that they are perched on a coastal clifftop and fed by an aquifer percolating through the Triassic Hawkesbury Sandstone. The bog itself is clothed by diverse wet-heath and wetland vegetation, the history of which was studied palynologically by Daly (1993; Dodson et al., 1995*).

Kurnell Fen, located 18 kms south of Sydney, is a remnant of a formerly extensive fenland which has been largely consumed by the construction of an oil refinery, brickworks and sand mines. The fen's sediments record a history of vegetation and land-use change extending back some 6,000 years (Martin, 1994). The swamp surface is vegetated with *Baumea* sedge and surrounded by Swamp Oak (*Casuarina distyla*) and *Melaleuca ericifolia* thickets. The site is situated in a north-oriented Pleistocene aeolian dunefield, low lying areas of which were flooded during Holocene marine transgression from 7000 BP (Roy and Crawford, 1981*).

Jibbon Lagoon and *Wise's Wetland* (field appellation) are both located in the Royal National Park (declared 1879). The former is a coastal lagoon 25 kms from Sydney surrounded by coastal heath and coastal forest vegetation communities. The swamp itself has standing water to a depth of 0.5 m and is thickly vegetated with *Eleocharis sphacelata* rushes. It was formed on Hawkesbury Sandstone bedrock as rising Holocene sea levels breached the Bate Bay sand barrier (Roy and Crawford, 1981*) and redeposited the sediment as a barrier dune across the deflation hollow in which the swamp now lies. *Wise's Wetland* is a perched swamp five kilometres inland from the Pacific Ocean and 33.5 kms SSW of Sydney. It is enclosed by escarpments of Hawkesbury Sandstone and densely covered with cutting grass

(*Gahnia sieberana*), swamp paperbarks (*Melaleuca quinquenervia*) and Waratah (*Teleopea speciosissima*). It was selected as a ‘control’ site for the study.

In addition, surface samples were collected from *Little Bay Swamp*, *OTC Swamp*, *Kurnell Fen South*, *Blue Hole Swamp* and *Jibbon South* – see Figure 1.

Figure 1. Location of study sites.

Southern Sydney experiences a warm temperate coastal climate. Average annual precipitation is 1236 mm, peaking in April (135 mm). Average temperature maxima vary from 26°C in January to 16.7°C in July, and minima of 17.4°C and 6.4°C for the same months. High afternoon summer humidity is promoted by warm moisture-laden air currents. During summer, the dominant wind direction is southerly, often shifting to northeasterly in the afternoons. In winter, winds are generally west-north-westerlies in the morning, tending southerly in the afternoon (Bureau of Meteorology, 1979*, 2002*)

3. Methods

Sediment was extracted from the centre of the four key sites using a Russian D-section corer, wrapped in plastic film and refrigerated to inhibit microbial activity. In addition twenty-five surface samples were collected from each of the wetlands to determine present-day patterns of trace metal distribution.

Prior to analysis, sediment cores were passed through a Bartington Magnetic Susceptibility Meter. One centimetre sample slices were taken at 2.5 cm intervals and tested for pH and redox potential prior to drying (24 hours at 105°C) to determine moisture content (*sensu* Bengtsson and Enell, 1986). The uncontaminated centre of each slice was extracted and reserved for chemical analysis, whilst the remainder was ignited (2 hours at 550°C) to determine organic content.

Duplicate 0.30 gram subsamples of dried sediment from the cores and surface samples were digested at 150°C in a solution of concentrated HNO₃:HCl in a ratio 4:1. After digestion, any acid-insoluble residue was weighed and metals concentrations determined by flame-emission spectrophotometry.

As the inorganic component of the sediment was found to be insoluble quartz sand, only metals in organic compounds were released into solution (see Fig. 2). The raw concentration values were corrected for organic content (LOI) and converted to enrichment factors, which compare each sample to the background (in this case pre-industrial) level. The following formula (adapted from West et al., 1997) was used to calculate enrichment factors (EF) from concentration data:

$$EF = \frac{(concentration_{sample}) / (LOI_{sample})}{(concentration_{background}) / (LOI_{background})}$$

In each case the background level was derived from the pre-industrial sediments of 35 cm depth (Table I).

Table I. Baseline concentrations (µg.g⁻¹) of trace metals in southern Sydney derived from pre-industrial wetland sediments.

Figure 2. Insoluble residue by organic content of samples.

Dating of the sediments from Trenerry Bog and Kurnell Fen was assessed biostratigraphically with reference to the pollen studies of Daly (1993) and Martin (1994). The first appearance of exotic *Pinus* pollen in the core was assumed to indicate 1840, the date when pine pollen first appears in the southern Sydney region (Peters, 1994). The sediment-atmosphere interface was assigned to the year 2000 and the intervening dates calculated by a linear model (Bennett, 1998*). Jibbon Lagoon sediments were dated with reference to the ^{210}Pb chronology of Mooney et al. (2001*) and the organic content curves of Trenerry Bog and Kurnell Fen, whilst Wise's Wetland sediments could not be satisfactorily dated.

The sediment data was analysed using Principal Components Analysis (PCA), Canonical Variates Analysis (CVA), t-tests and Analysis of Variance (ANOVA) using SYSTAT version 8.0. PCA was used to determine which sites, samples and variables were most closely correlated (Prentice, 1986). CVA is a discriminant analysis applied to provide an indication of the degree of within-site versus between-site variation (Gittins, 1980; Engelman, 1996*; Emmerson et al., 1997*), as well as to draw out changes in heavy metals composition through time. As there were insufficient data to compare each trace metal and sediment variable individually, a paired comparison t-test was applied to the upper and lower sample from each sediment core using Cd, Cu, Fe, Pb, Zn and magnetic data. The ANOVA employed a Tukey pairwise mean comparison, which produces a matrix of probabilities that compare the significance of differences between, in our case, metals concentrations in sampling sites (*sensu* Wilkinson and Coward, 1996*).

4. Results

4.1. Surface samples

In surface sediments, the highest levels of Copper, Lead and Zinc are found at OTC Swamp, whilst Iron and Cadmium are most concentrated at Kurnell Fen (see Table II). Cadmium appears to be highly mobile in the sediments from all sites, and its concentrations are in many cases close to or in excess of levels warranting environmental investigation (ANZECC, 1992*).

Table II. Average concentrations of heavy metals in surface sediments in Sydney. The maximum concentration for each site is given in parentheses. Levels above recommended environmental limits (ANZECC, 1992) are marked with an asterisk (*).

The results of the Tukey pairwise-mean-comparison ANOVA are summarised in Table III, clearly showing that metals concentrations at OTC Swamp are in most cases significantly higher than a number of the other sites. Zinc levels at Little Bay, and Iron levels at Kurnell are also relatively high.

Table III. Significant metal concentration differences between all sites. Where indicated by the metal's chemical symbol, sites in the columns have significantly higher metal concentrations than sites in the rows; e.g: Trenerry has significantly higher Lead concentrations than Jibbon S.

Maps of the heavy metals enrichment (compared to background level) and within-site variation for the four core sites are shown in Figure 3. A clear spatial pattern is evident, *viz*: enrichment of Cadmium, Copper, Lead and Zinc are related to each site's proximity to Sydney. Iron follows a different trend entirely, suggesting that its source or behaviour is different to the other metals.

Figure 3. Heavy metals enrichment maps.

CVA of surface sample metal concentrations showed that Trenerry Bog and Blue Hole Swamp experienced the greatest within-site variation, and Jibbon Lagoon the least. Mahalanobis distances produced by the CVA incorrectly classified two samples from Trenerry Bog as belonging to OTC Swamp and Jibbon Lagoon respectively. Mahalanobis distances compare each sample value to the site mean and reassign them to site groups accordingly. The greater the Mahalanobis distance between a sample and a site mean, the less likely it is that the sample belongs to that site (Engelman, 1996*). The misclassifications appear to relate to similarities in sediment type and standing vegetation between the study sites.

4.2. Sediment cores

Results of the organic content, heavy metals and magnetic susceptibility analyses are presented with dating in Figure 4. Some caveats, however, are necessary for their interpretation.

Figure 4. Changes in organic content, heavy metals enrichment and magnetic susceptibility in sediment cores.

First: Wetland productivity is assumed to have remained stable throughout the historic period as demonstrated by Chant (1993) for Trenerry Bog, Martin (1994) for Kurnell Fen, and Johnson (1994) for numerous swamps of the Kurnell Peninsula.

Second: The trace metals are thought to be held primarily in the organic matrix of the sediment, as indicated by Figure 2. For Trenerry Bog this was demonstrated by Chant's (1993) study, where the sediment was ignited before chemical analysis, leaving no trace of the heavy metals record. Third: The heavy metals and inorganic material found in the sediment must be predominantly atmospherically derived. Johnson (1994, p. 128) found that the dominant source of mineral cations in Kurnell Peninsula swamps was atmospheric and Martin wrote of Kurnell Fen: "the cation concentration is high for an old podsolised dune-land overlying the very nutrient-poor Hawkesbury Sandstone; it is unlikely that these ions come from the groundwater." (1994, p. 329). Groundwater samples collected from Kurnell Fen and Trenerry Bog at the time of coring were analysed for levels of Cd, Cu, Fe, Pb and Zn (Table IV). With the exception of iron concentrations at Kurnell, the levels of all analysed elements were below accurate detection limits for the AAS.

At Trenerry Bog, in an effort to gauge trace metal mobility, an additional water sample was obtained by compression of a peat monolith. The results are also given in Table IV, and show slightly elevated levels of all metals except Pb. Table IV. Trace metal concentrations ($\mu\text{g}\cdot\text{g}^{-1}$) in groundwater samples from Trenerry Bog and Kurnell Fen, and the peat monolith from Trenerry (see text).

At both Trenerry Bog and Kurnell Fen, a marked decline in organic content around the end of the nineteenth century is followed by increases in heavy metal enrichment and mineral-magnetic particles. Of particular note is the almost perfect agreement of the magnetic susceptibility curves from these two sites, suggesting a strong regional signal.

The records from Jibbon Lagoon and Wise's Wetland behave quite differently. At Jibbon Lagoon, the same decline in organic content is accompanied by modest increases in Copper, Lead and Zinc. Iron levels barely change, and Cadmium actually declines. The sediments of Wise's Wetland exhibit almost no change at all, with the exception of the magnetic susceptibility curve, which may be registering the same regional phenomenon recorded at Trenerry Bog and Kurnell Fen.

Figure 5. PCA biplot of core samples in relation to sediment variables. The two factors explain 75% of total variance.

These results are summarised effectively in the PCA biplot (Fig. 5) where the upper sediments of Trenerry Bog and Kurnell Fen appear in the top-right quadrant due to their high Pb, Cu and Zn enrichment. The pre-industrial samples (T7-T5 and K5-K4) are placed near samples from the distal Jibbon site, corresponding to a background level. Wise's Wetland samples are differentiated by low trace metal enrichment and sedimentological differences, low moisture and organic content.

Table V. Canonical loadings for the Canonical Variates Analysis score plots (Fig. 6)

The results of the Canonical Variates Analysis (CVA) are presented in Figure 6 with their respective factor loadings in Table V. In the upper graph, samples from Kurnell Fen appear in the top-left due to their high Iron enrichment, whereas Trenerry Bog samples appear at top-right where Zinc, Cadmium and Lead loadings are highest.

The middle graph again differentiates between the heavy metals composition of each site, isolating sample J4 with its unusually high Cadmium enrichment. In this as well as the lower graph, samples T3 and K2 deviate from otherwise linear trends, showing a tendency toward higher Iron and Copper enrichment. These particular samples both belong to the first half of the twentieth century, suggesting a temporary change in pollution source at that time.

Mahalanobis distance measures misclassified the pre-industrial sediments of Trenerry Bog and Kurnell Fen as belonging to the Wise's Wetland or Jibbon Lagoon sites. The results show that the pre-industrial sediments from Trenerry and Kurnell have stronger affinities to the sediments of the National Park sites than to their metal-enriched upper strata. A comparison of the PCA and CVA results shows similar trends, affirming the robustness of these analyses. The t-tests (Table VI) revealed that the net changes in levels of trace metals and magnetic particles were statistically significant ($p < 0.05$) at Trenerry Bog, Kurnell Fen and Jibbon Lagoon, whilst at Wise's Wetland there was no significant change.

Table VI. t-tests for changes in metals and magnetics through time.

Figure 6. Core sample scores plotted against canonical variates. The three factors (Table V) account for 100% of group dispersion.

5. Discussion

5.1. Spatial aspects of trace metal pollution

The close proximity of all the sites to the maritime influence of the Pacific Ocean undoubtedly results in a dilution of trace metals in sediments. Several authors have noted that heavy metal ions compete with sea-spray-derived Sodium and Chloride ions in sediment sequestration processes (Damman, 1990*; Mackereth, 1965*; Steinnes, 1997*). Johnson (1994*) showed that sediments from the Kurnell Peninsula ocean front had significantly higher levels of Mg, Na, K and Ca than a site 2 kilometres inland. Additionally, the prevailing winds at all of the sites are southerly in winter and northeasterly in summer. The major pollution sources in southern Sydney are located to the north and west of the study sites, so the full magnitude of industrial impact is not expected to be recorded in the wetlands.

With the notable exception of Fe (discussed further below), site levels of all trace metals exhibit a strong spatial affinity to the location of air pollution sources. In southern Sydney, the predominant point-source of airborne pollutants is the North Botany Industrial Zone (NBIZ), which surrounds Sydney Airport. In the 1970s, the NBIZ could lay claim to having the highest concentration of heavy industry in Australia, and to be the most inefficient and heavily-polluting industrial complex in Sydney (Butlin, 1976*). Sydney Airport, Australia's busiest, is also an important emission source, producing over 500 kg of sulphur dioxide per day (FAC, 1990*). The sites nearest the NBIZ, Little Bay, OTC swamp and Trenerry Bog, have higher concentrations of Cu, Pb and Zn than more distant sites.

Levels of Cu and Pb are particularly significant in the OTC swamp sediments. This site is further from the ocean front than the others and therefore subject to less marine competition in metals sequestration. It is a small rain-fed swamp situated on a hilltop within a government prohibited area proclaimed in 1825 (Jeans, 1973*). The site is notable for its remnant Eastern Suburbs Banksia Scrub and wet heath communities (Benson and Howell, 1995*), and for this reason, part of the site has been incorporated into the Botany Bay National Park. Given its relatively pristine environs, we find it difficult to attribute the observed pollutant levels to non-atmospheric sources.

The role of wind dispersal of pollutants is highlighted by the lower-than-expected impact recorded at Kurnell Fen, which is located adjacent a large oil refinery and other noxious industries. We contend that because these industries are downwind of the fen, much of their emissions were carried northward over Botany Bay and may in fact register more strongly at sites such as Little Bay and OTC Swamps. Sediment and vegetation type may, as suggested by the CVA misclassifications, play a decisive role in the uptake and retention of trace metals by surface sediments.

In terms of trace metal enrichment, the same spatial pattern of decreasing enrichment with increasing distance from the NBIZ is observed (Fig. 3). Surficial sediments are enriched with Cd, Cu, Pb and Zn levels up to 5.0, 16.4, 8.2 and 22.5 times baseline levels respectively at Trenerry Bog. These levels of enrichment are much lower than those found in Botany Bay estuarine sediments polluted by the

NBIZ, where Cu is enriched by a magnitude of 45, Pb by 28 and Zn by 56 (Birch et al., 1996*).

Diffuse pollution sources must also be considered, of which motor vehicle emissions are presently the most important. Urbanisation and road networks are most concentrated near those sites that record the highest levels of metal contamination. Without examining the isotopic composition of the metals (e.g: Monna et al., 1997*) it is not possible to differentiate between the industrial and vehicular contributions to sedimentary levels. We consider that both noxious industry and vehicle emissions have played a significant role in the regional air pollution signal.

Iron concentrations do not follow the same spatial pattern as the other trace metals. Iron is most concentrated in the Kurnell Fen sediments. Whilst produced by industrial processes, Fe also occurs naturally in the Quaternary sands of the Kurnell Peninsula (Wallace, 1973*). The Hawkesbury Sandstones that underlie all of the study sites are bound together with iron oxide (Griffin, 1963*). High Fe levels may be indicative of the antiquity of the fen (*sensu* Mackereth, 1965*; Oldfield, 1977*) which began accumulating over 7,200 years ago (Martin, 1994). The Kurnell oil refinery, located near Kurnell Fen, may be producing Fe-rich emissions. Iron-fixing bacteria are favoured by acidic and reducing conditions (Alloway, 1990b*; Doyle and Otte, 1997*) and their presence is noted to cause high levels of iron enrichment in similar wetlands of the Sydney region (Buchanan, 1980*). The degree of spatial variation and the correlation between Fe enrichment and redox potential at Kurnell hint to the presence of such bacteria in the fen sediments, fixing Fe from pollution sources and iron-rich wind-blown sands.

5.2. Metal mobility

In all of the examined sediments, the heavy metals extracted by acid digestion were held in the organic fraction. For this reason the enrichment factors express enrichment per unit organic matter. Whilst metal mobility within organic complexes is limited, the possibility of mobility must be considered before any reconstruction of past conditions is attempted.

Lead (Pb) is widely regarded as being relatively immobile in organic sediments (Perkins et al., 2000*; Martinez-Cortizas et al., 1997*; Farmer et al., 1997*; Lee and Tallis, 1973*), although this may depend on the hydrology of the wetland (see, for example, Stewart and Ferguson, 1994*). Lead is not an essential element for plant growth, and is not remobilised by hygrophytes as Cu and Zn can be (Alloway, 1990b*; Gorrez and Frenzel, 1997*; Damman, 1990*). Therefore, Lead profiles from organic sediments may be used to gauge the mobility of other elements in the sediment column.

A comparison of the groundwater and peat monolith water samples from Trenerry Bog (Table IV), although unreplicated, may indicate that Pb is the least mobile of the analysed elements. At this site, Pb enrichment begins to increase from 20 cm depth, mirrored by Cu, Fe and magnetics (Fig. 4). Cd and Zn, however, exhibit an increase from 25 cm depth. The pattern is replicated in the sediments of Kurnell Fen. At Jibbon Lagoon and Wise's Wetland, only Cu follows the Pb curve. Cadmium clearly deviates from the Pb, Cu and magnetic profiles, and it is suggested that this toxic trace metal is highly mobile within the sediments of the wetlands under study. The mobility of Zn and Fe may be dependant on plant uptake and hydrological characteristics (Perkins et al., 2000*). Cu, Pb and magnetics are regarded as

relatively immobile and should provide the most useful results for reconstruction of the region's pollution history.

5.3. An air pollution history of southern Sydney

The changing organic content of sediments over time can be used to indicate changes in atmospheric dust deposition and catchment erosion, so long as changes in wetland productivity are known (Dearing and Foster, 1986*; Aaby, 1986*). Where wetland productivity has remained stable and fluvial sediment transport is excluded, such as the sites in this study, changes in organic content can be readily interpreted in terms of wind-blown erosional inputs.

Results from Trenerry Bog, Kurnell Fen, and, to an extent, Jibbon Lagoon show a regional-scale increase in atmospheric dust levels beginning just prior to the year 1900. This increase broadly coincides with the introduction of sheep and cattle grazing and broadscale land clearing on the Kurnell Peninsula (Cridland, 1950*) and the rapid urbanisation of Sydney's southeastern suburbs (Randwick Municipal Council, 1986*). Drought and bushfire ravaged the Kurnell Peninsula in the 1920s (Dickson, 1973*) and the sand content of sediment cores peaks at this time as massive transgressive dune movement was initiated (see Pickard, 1972*). Martin's (1994) study showed that pollen of fire-dependant colonial species such as *Acacia*, *Banksia* and grassy-heath plants increased in Kurnell Fen sediments after these events. The increase in organic content from the 1950s on is interpreted as indicating increased landscape stability as urban development slackened.

Magnetic susceptibility measurements can provide an indication of net changes in atmospheric particulate concentrations produced by industrial processes through time (Tolonen and Oldfield, 1986*; Hunt et al., 1984*; Thompson et al., 1980*; Richardson, 1986*). The perfect correspondence of magnetic susceptibility, Pb and Cu curves for Trenerry Bog and Kurnell Fen suggests a regional air pollution signal, beginning at some time between 1880 and 1900. It was at this time that historical documents record the rapid establishment of heavy industry within the NBIZ (Jeans, 1979*; GHD, 1993).

Natural sources of heavy metals cannot adequately explain the increase in metals enrichment from the end of the nineteenth century. Important natural sources include windblown dusts, fires and volcanic eruptions (Nriagu, 1979*). As the region's surface geology consists of aeolian sands overlain by nutrient-poor podzols, and heavy metals bind poorly to sand particles (Mann and Ritchie, 1995*), windblown dust is an unlikely explanation. Changes in erosion recorded through organic content variations do not agree temporally with changes in trace metal enrichment in the cores. Fires have decreased in the region since European settlement (Daly, 1993), particularly during the last half-century when metals enrichment is greatest. Recent volcanism in Australia is confined to the Pleistocene period, so this too can be discounted. The clear temporal coincidence of the increases at Trenerry Bog, Kurnell Fen and Jibbon Lagoon point to a regional scale pollution source such as could only be expected from atmospheric input.

An important temporary change in atmospheric pollutant composition occurring in the 1920s – 1950s was detected by the CVA (Fig. 6). Historical reports note the severe pollution problems caused by the operation of the Bunnerong Power Station between 1928 and 1946 (Randwick Municipal Council, 1986). The sediment samples of this period from Trenerry, Kurnell and Jibbon all deviate temporarily

towards higher Copper and Iron enrichment, a pattern which has been observed in sediments near a comparable coal-fired power station near Wollongong, 78 kms south of Sydney (Chenhall et al., 1992). Despite the extreme pollution from this discrete source, the magnetic susceptibility curves indicate an overall slowing of pollution rates in the 1940s perhaps as a symptom of the Second World War.

The magnetic susceptibility curve indicates, in agreement with pollution monitoring data (SPCC, 1984), that pollution attained its highest atmospheric concentrations in the 1970s. Unfortunately the coarse sampling resolution of the trace metal records does not allow us to quantitatively reinforce the magnetic data during this period.

Finally, it must be admitted that the enrichment factors presented in this study are conservative estimates only. The downcore transport of mobile elements has the potential to elevate background levels thereby decreasing the calculated enrichment of polluted upper sediments. The baseline levels in Table I should therefore be used with a degree of caution, and the values should not be regarded as representative of conditions in sites other than those described in this paper.

6. Conclusion

This study provides an indication of the degree of pollution across a variety of wetlands in the southern Sydney region, as well as establishing baseline (pre-industrial) concentrations of selected heavy metals.

This paper has demonstrated that coastal wetlands can prove suitable for air pollution studies, provided that heavy metals have remained relatively immobile in the organic fraction of the sediment, the groundwater is uncontaminated and contains naturally low concentrations of heavy metals. Careful consideration must always be given to local site characteristics: topography, hydrology, vegetation cover, sediment characteristics, climatic factors, fire regimes, etc. as these can exert a profound influence on the uptake, retention and reliability of the trace metal record. As a large coastal city, the considerations in interpreting the record of air pollution in Sydney may be more broadly applicable to similar situations around the globe, particularly those semi-arid and mid-latitude regions where air pollution histories are lacking.

Future research could calibrate a fine-resolution heavy metals record to monitored instrumental data in order to provide a model for air pollution levels in the last 200 years and beyond. Such a study would improve our understanding of the complex relationship between air and sediment, tell us about airborne trace metal levels prior to industrialisation (useful for setting long-term pollution-reduction goals), and provide a basis for epidemiological studies of the long-term health effects of pollution on society.

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Fig. 1. Location of study sites in southern Sydney. National parks and reserves are shaded, urban areas unshaded. Coring locations are denoted by stars.

Fig. 2. Acid-insoluble residue by organic content of samples

Fig. 3. Heavy metals enrichment maps. Circle size is indicative of trace metal enrichment levels, and circle width corresponds to the degree of within-site variation.

Fig. 4. Changes in organic content, heavy metals enrichment and magnetic susceptibility in sediment cores.

Fig. 5. PCA biplot of core samples in relation to sediment variables. The two factors explain 75% of total variance.

	Cd $\mu\text{g.g}^{-1}$	Cu $\mu\text{g.g}^{-1}$	Fe $\mu\text{g.g}^{-1}$	Pb $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$
Trenerry Bog	1.4	3.5	2609	28.9	11.3
Kurnell Fen	2.1	5.5	1247	26.1	20.9
Jibbon Lagoon	2.8	3.8	1347	31.4	6.3
Wise's Wetland	4.6	4.1	1543	28.0	6.9

Table I: Baseline levels from pre-industrial sediments

	Cd $\mu\text{g.g}^{-1}$	Cu $\mu\text{g.g}^{-1}$	Fe $\mu\text{g.g}^{-1}$	Pb $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$
Trenerry Bog	2.22 (3.08*)	17.5 (37.3)	2983 (5426)	75.1 (95.9)	60.6 (86.8)
Little Bay	2.45 (2.67)	17.8 (22.8)	8578 (11424)	74.1 (92.8)	126.5 (159.8)
OTC Swamp	1.96 (2.75)	38.3 (46.2)	3477 (3873)	107.4 (130.9)	106.5 (162.2)
Kurnell Fen N	2.65 (2.90)	17.6 (20.2)	20467 (30232)	59.4 (67.6)	59.5 (81.7)
Kurnell Fen S	2.16 (3.61*)	15.9 (19.4)	13184 (21289)	54.9 (59.3)	66.0 (85.7)
Blue Hole	2.19 (3.46*)	12.2 (18.0)	5739 (15674)	66.6 (98.3)	17.0 (21.5)
Jibbon North	1.53 (1.83)	12.4 (14.5)	1708 (2152)	41.1 (45.5)	21.0 (27.0)
Jibbon South	1.66 (1.93)	5.9 (9.5)	938 (1181)	30.8 (39.0)	9.6 (13.6)
Wise's Wetland	1.70 (2.0)	9.6 (13.8)	9422 (14512)	43.3 (53.1)	17.0 (23.1)

Table II: Average concentrations in surface sediments, maxima given in parentheses. Values with an asterisk (*) exceed recommended environmental limits.

	Trenerry	Little Bay	OTC	Kurnell N.	Kurnell S.
Trenerry	---	Zn	Cu	Fe	
Little Bay		---	Cu	Fe	
OTC			---	Fe	
Kurnell N.		Zn	Cu, Pb	---	
Kurnell S.		Zn	Cu, Pb		---
Blue Hole		Zn	Cu, Pb, Zn	Fe	
Jibbon N.		Zn	Cu, Pb, Zn	Fe	Fe
Jibbon S.	Pb	Pb, Zn	Cu, Pb, Zn	Fe	Fe, Zn
Wise's		Zn	Cu, Pb, Zn	Fe	

Table III: Significant metals differences between sites. Where indicated by the metal's chemical symbol, sites in the columns have significantly higher metal concentrations than sites in the rows.

	Cd	Cu	Fe	Pb	Zn
Kurnell	0.0011	0.0039	2.0424	-0.0042	0.015
Trenerry	0.0008	0.0069	0.0878	0.0041	0.022
Peat monolith	0.0023	0.0149	0.6636	-0.0165	0.0691

Table IV: Groundwater and peat monolith concentrations ($\mu\text{g g}^{-1}$)

	Factor 1	Factor 2	Factor 3
Cadmium	0.792	1.058	1.454
Copper	0.369	-3.214	-5.757
Iron	-0.757	-1.111	-1.476
Lead	-1.917	4.247	4.629
Zinc	1.610	-0.405	0.341

Table V: CVA factor loadings

	<i>t</i>	<i>df</i>	<i>p</i>	Change ($p < 0.05$)
Trenerry Bog	6.009	5	0.002	Significant
Kurnell Fen	3.500	5	0.017	Significant
Jibbon Lagoon	2.713	5	0.042	Significant
Wise's Wetland	0.749	5	0.488	Not significant

Table VI: t-tests for changes in metals and magnetic through time