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Baseline

Mangrove sediments reveal records of development during the previous century (Coffs Creek estuary, Australia)

Stephen R. Conrad, Isaac R. Santos, Dylan R. Brown, Luciana M. Sanders, Michelle L. van Santen, Christian J. Sanders*

National Marine Science Centre, School of Environment, Science and Engineering, Southern Cross University, P.O. Box 157, Coffs Harbour, NSW 2540, Australia

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ABSTRACT

A mangrove sediment core was studied to evaluate possible pollution of an urban estuary in Coffs Harbour, Australia. The heavy metal and nutrient profiles revealed a ~2.5-fold enrichment in more recent sediments. Lead-210 dating showed increasing phosphorous (P) and copper (Cu) accumulation following agricultural activity and population growth in the catchment after 1950. In contrast, nitrogen (N) did not show enrichment suggesting no external sources. Mercury (Hg) depositional fluxes and recent enrichment may be associated to an increase in fossil fuel emissions in the region. Down-core lead (Pb) profiles reflect an increase in leaded gasoline in the 1950s, then a decrease as a result of phasing out leaded gasoline in 1986. The heavy metal and nutrient depositional fluxes are well preserved in mangrove sediments and were related to historical events in the catchment.

Mangroves are important to estuarine systems by protecting shorelines from erosion, trapping sediments and acting as heavy metal and nutrient sinks (Duarte et al., 2013; Machado et al., 2016; Sanders et al., 2014a). Retention of contaminants is related to mangrove roots reducing tidal and fluvial water flow, promoting sediment deposition (Kirwan and Megonigal, 2013). Metal and nutrients in mangrove sediments may be linked to land use in adjacent catchments (Brady et al., 2014; Defew et al., 2005; Harbison, 1986; Nath et al., 2014a; Nath et al., 2014b). Mangrove sediments may therefore be considered an appropriate setting for studying historical activities in a catchment (Defew et al., 2005; Marchand et al., 2011; McCaffrey and Thomson, 1980; Serrano et al., 2011), particularly when baseline levels can be defined (Miola et al., 2016; Nienhuis, 1986; Serrano et al., 2011).

Spatial distributions of heavy metal contaminants originating from point sources have previously been constructed using sediments from mangroves (Harbison, 1984). For instance, Machado et al. (2016) estimated Hg fluxes into sediments in an estuary in Brazil. The Hg flux increased during rapid industrialization in the 1950s and decreased after emission control in the 1980s. Sanders et al. (2014b) revealed that mangrove sediments are also efficient in accumulating nutrients as a result of enrichment of the catchment. Here, we use a mangrove sediment core from Coffs Creek estuary (Coffs Harbour, Australia) to assess the heavy metal and nutrient depositional history in the catchment.

Coffs Creek estuary runs through the center Coffs Harbour, on the north coast of New South Wales, Australia. Coffs Harbour has a humid subtropical climate with seasonal variations in rainfall (wet summers and dry winters). Average yearly rainfall is 1699 mm with an average of 142 precipitation days and a yearly average of 63% relative humidity (BOM, 2017). Coffs Creek estuary is wave-dominated and intermittently infilled. The catchment area is small relative to the surrounding catchments and comprises the urban and residential center of Coffs Harbour (Fig. 1). Residential and agricultural land comprise 66% of the 25 km^2 catchment area (Ryder et al., 2012). The mangrove forests of Coffs Creek are dominated by *Avicennia marina* and have an area of 20.07 ha (Brown et al., 2016). The main anthropogenic pressures on Coffs Creek estuary include elevated sediment and nutrient loads in runoff and stormwater, increased concentrations of pesticides, herbicides and potential sewage inputs from on-site systems and overflows from the city sewage system (Ryder et al., 2012).

The history of Coffs Harbour includes agriculture and urban expansion. From ~1950 banana cultivation dominated in the basin (Yeates, 1990) and aerial spraying of bananas began in 1958 (Hedditch, 2014). More recently, blueberry agriculture has taken the place of some banana cultivation, accompanied by steady population increase and intense urban development. Agricultural substances of particular concern in Coffs Harbour are arsenic (As) from pesticides and phosphorus (P) from fertilizers. In addition, copper (Cu) fungicides are also used in blueberry, banana, and avocado farms in in this region (Van Zwieten et al., 2007). An increase in traffic through Coffs Harbour commenced in the 1950s as a result of the construction of a major highway, Pacific

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* Corresponding author.
E-mail address: christian.sanders@scu.edu.au (C.J. Sanders).

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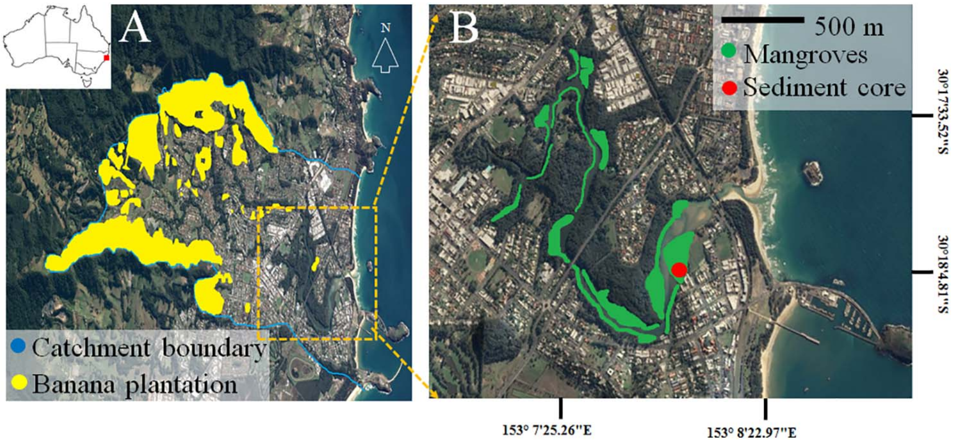

Fig. 1. A. Map of Coffs creek catchment (outlined in blue) with land historically used for banana plantations (yellow). Plantation area data provided by Coffs Harbour City Council (CHCC, 2016a, b). The catchment area is 25 km^2 and comprises the major urban center of Coffs Harbour. Residential and agricultural use makes up 66% of the catchment area (Ryder et al., 2012). B. Coffs Creek lower estuary with mangroves (green). Areal extent of Coffs Creek mangroves is 20.07 ha (Brown et al., 2016). Sediment core location indicated by red dot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Highway (Yeates, 1990). Furthermore, a small airport is located approximately 5 km from Coffs Creek.

To investigate possible pollution in the estuary, a 50 cm long sediment core was collected from the upper tidal mangroves near the estuary mouth (30°18′3.63″S, 153° 8′2.23″E, Fig. 1) with a 5 cm diameter Russian peat auger on March 16, 2016. The sediment core was sectioned into 2 cm intervals. Sediments were dried to estimate the dry bulk density (DBD) (Brown et al., 2016). The content of As, Cu, lead (Pb), nickel (Ni), zinc (Zn), mercury (Hg), aluminum (Al) and P were measured at each 2 cm interval. Metals were extracted from sediments using 1:3 HNO_3/HCl acid digestion and an APHA Inductively Coupled Plasma Mass Spectrometer (ICPMS). Sediment reference materials were digested (AGAL 12) with every batch (sourced from National Measurement Institute) to confirm the recovery of the digest. To confirm accuracy and precision of the instrument we analyzed certified reference materials after the calibration and monitored drift by re-analyzing our mid-point standards every 20 samples and routinely use internal standards Sc, Ge, Rh and Ir. Nitrogen (N) concentration were determined in a Thermo Finnigan Model Delta Plus XP with analytical precision of N = 0.1%.

Enrichment factors (EF) were calculated to distinguish natural and anthropogenic sources of heavy metal and nutrients in Coffs Creek mangrove sediment. Enrichment factors compare preindustrial baseline levels to more recent sediment elemental content. Metals and nutrients were normalized to naturally abundant metals that are often unrelated to anthropogenic sources, such as Al (Abrahim and Parker, 2008; Weiss et al., 1999). Enrichment factors between 0.5 and 1.5 indicate natural fluctuations related to normal geological weathering, while a value of EF > 1.5 or patterns of increasing EF from 1 indicate anthropogenic sources (Zhang and Liu, 2002). To calculate enrichment factor, we normalized metal content to Al (Abrahim and Parker, 2008; Miola et al., 2016), as follows:

$$EF = \frac{\frac{[metal_x]}{[Al_x]}}{\frac{[metal_{baseline}]}{[Al_{baseline}]}}$$

where EF is enrichment factor and $[metal_x]$ is content of desired element at depth x and $[Al_x]$ is content of Al at depth x and $[metal_{baseline}]$ and $[Al_{baseline}]$ are baseline contents. The baseline content was defined as the concentration found in the bottom subsample of each core (Abrahim and Parker, 2008).

Radionuclide dating (^{210}Pb) was used to determine the sediment age and accumulation rates (SAR) (Appleby and Oldfield, 1992). Sediment intervals were combined and homogenized in 4 cm intervals for dating due to limited mass. Combined intervals were dated up to 40 cm depth. Five to eight grams of sediment were packed in vials and sealed with epoxy resin for at least 21 days to allow for ^{222}Rn to establish secular equilibrium between ^{226}Ra and its granddaughter ^{214}Pb. ^{210}Pb activity was determined by measuring the 46.5 keV gamma peak in a Canberra high-purity germanium (HPGe) well gamma detector. ^{226}Ra activity was determined by averaging peaks from the daughters ^{214}Pb and ^{214}Bi (295.2 keV, 351.9 keV and 609.3 keV) (Moore, 1984). The ^{210}Pb and ^{226}Ra activities were calculated by multiplying the counts per minute by a correction factor that includes the gamma ray intensity and detector efficiency determined from standard calibrations. Excess ^{210}Pb activity was calculated by subtracting the supported ^{210}Pb (i.e., ^{226}Ra activity) from the total ^{210}Pb activity. Excess (unsupported) ^{210}Pb was used to determine ages of sediment intervals using the Constant Initial Concentration (CIC) method described by Appleby and Oldfield (1992). Age of sediments is calculated by the following equation:

$$\text{Sediment age} = \text{Year of collection} - \left(\frac{\text{average depth of sediment interval}}{\text{SAR}}\right)$$

Heavy metal and nutrient accumulation rates are defined as amount of material entering the sediment per unit area per unit time ($\mu g\ m^{-2}\ yr^{-1}$):

MAR = $[metal_x] * SAR * DBD$ where $[metal_x]$ is trace metal content in sediment sample, SAR is sediment accumulation rate, and DBD is dry bulk density of the sample. Metal accumulation rates (MAR) were calculated for each metal and each 2 cm interval in the mangrove core.

The excess ^{210}Pb ($^{210}Pb_{ex}$) vertical profile revealed a log-linear decay (Fig. 2) with counting errors below 10%. The slope shows a significant correlation between $^{210}Pb_{ex}$ and depth ($R^2 = 0.65$; n = 5; $p < 0.05$) which allows an estimate of the sedimentation rates using the CIC method. The CIC dating method assumes that the sediment accretion rate has not varied during the encompassed time span (Appleby and Oldfield, 1992). According to the ^{210}Pb CIC dating method, the SAR is 0.51 cm yr^{-1}. The sediments from the bottom interval of the core date back to 1928.

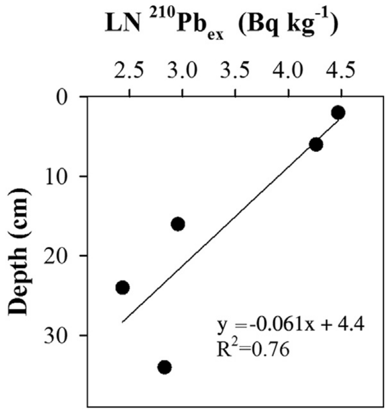

Fig. 2. Excess ^{210}Pb activity (Bq kg^{-1}) plotted against sediment depth (cm).

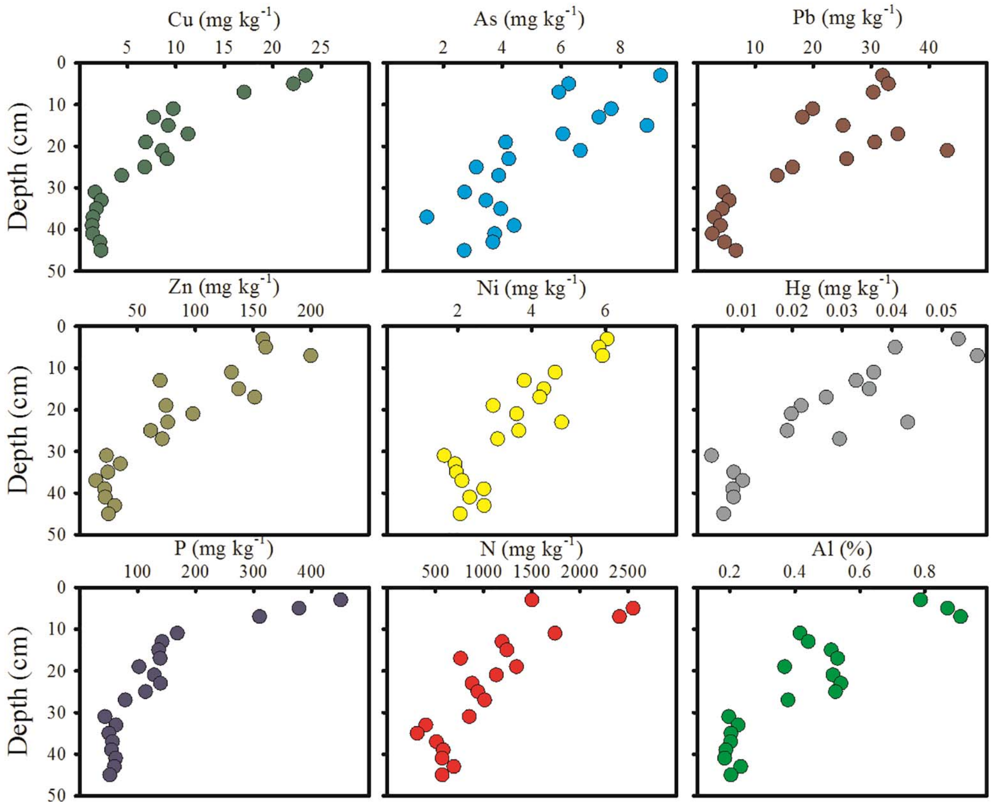

Fig. 3. Content of heavy metals in the mangrove sediment core. All values in mg kg^{-1} except for Al (%).

The profiles for Cu, As, Pb, Zn, Ni, Hg, P, N, and Al are displayed in Fig. 3. The average contents (mg kg^{-1}) of metals in mangrove sediments were 7.5, 5.0, 17.9, 79.3, 3.5, 137, and 0.023 mg kg^{-1} for Cu, As, Pb, Zn, Ni, P, and Hg, respectively. These averages are below the SQG upper guideline values of 270, 70, 220, 410, 52 and 1.0 for Cu, As, Pb, Zn, Ni, and Hg, respectively and below the effects range low (ERL) of the Australian soil quality guidelines (SQGs) (Simpson et al., 2013). Aluminum contents averaged 4212 mg kg^{-1} (0.42%).

Heavy metal contents in Coffs Creek are near the baseline concentrations of non-impacted Australian estuaries. For instance, sediments of the pristine Huon estuary in Tasmania have concentrations of 17, 16, 25, 40, and 20 mg kg^{-1} for Cu, As, Pb, Zn, and Ni, respectively (Jones et al., 2003). Mean sediment baseline content of Cu, Pb, and Zn across 38 central New South Wales estuaries was 15, 19, and 55 mg kg^{-1}, respectively (Birch, 2017). These averages are similar to ours, with Zn in sediments being comparatively higher in Coffs Creek (7.5, 17.9, 79.3 mg kg^{-1} for Cu, Pb, and Zn in Coffs Creek, respectively). The average heavy metal and nutrient content in Coffs Creek estuary sediments are comparable to undisturbed surface mangrove sediments of Trinity Inlet, with a maxima of 6.0, 5.9, 12.3, 31.2, 3.6, and 4437 mg kg^{-1} for Cu, As, Pb, Zn, Ni, and Al, respectively (Keene et al., 2010). Indeed, the metal contents in Coffs Creek are lower than other, more urbanized estuaries in Australia. For instance, Birch et al. (2013) found averages of 217, 332, and 721 mg kg^{-1} for Cu, Pb, and Zn, respectively, in estuaries of Sydney. However, these means were normalized to the fine grain sediment fraction (< 62.5 µm), and may be higher than total sediment content (Birch, 2017). In the estuary sediments of the Hunter River catchment (a large coal exporting center), Lottermoser (1998) found average metal contents of 31.5, 429, 306.7, 5.7, 0.1225 mg kg^{-1} for Cu, Pb, Zn, As, and Hg, respectively.

When measuring heavy metals in estuarine sediments it is important to separate anthropogenic sources from natural background levels (Brady et al., 2014; Machado et al., 2016). Enrichment factors were used to determine if the source of heavy metals and nutrients to the Coffs Creek mangrove sediments are from normal geological processes (Tam and Yao, 1998). Copper enrichments towards the surface sediment intervals were accompanied by an increase in Cu accumulation rates (Fig. 4). However, the 3-fold Cu enrichments were lower than the 5-fold enrichment in residential areas of Sydney's more urbanized estuaries (Birch et al., 2011). Excess Cu in Coffs Creek estuary may be associated with runoff from agricultural fungicides used on blueberry, banana, and avocado farms (Van Zwieten et al., 2007). Aerial spraying of banana plantations with agricultural chemicals started in 1958 in Coffs Harbour (Hedditch, 2014) which is in agreement with the accumulation above baseline rates in the sediment profile. While the exact source is unknown, Cu accumulation has increased over time, in conjunction with the banana cultivation and population (Fig. 4).

Phosphorus enrichment (maximum EF = 2.2 at surface) and accumulation increased from 1987 to 2016, reaching a maximum of 110 µg m^{-2} yr^{-1} at the surface. The enrichment of P in conjunction with the increasing accumulation implies an anthropogenic source. However, the N fluxes did not show enrichment and indicate natural fluctuations (Fig. 4). The lack of correlation between N and P enrichment suggests that either there was no anthropogenic source or that the N is consumed within the water and/or sediment column. However the P accumulation begins to rise above baseline rates in conjunction with Cu and the beginning of aerial banana treatments in 1958 (Fig. 4). A shift from banana plantation to residential land use occurred starting in the mid-1970s (Ryder et al., 2012). The more recent rapid increase in enrichments and accumulation rate of P and Cu occurred after banana plantations were cleared and land was repurposed for housing. Mobilized agricultural soils by land use change (agricultural to urban) have likely caused a more recent increase in P and Cu deposition in the estuary.

However, re-suspended soils may not be the only source of contaminants. There have been several incidences of sewage spills in Coffs Harbour, two of which led to closures of Coffs Creek in 2004 and 2005 (Chapman, 2004; Ryder et al., 2012). While P accumulation may be increasing, rates of P accumulation in Coffs Creek are much lower than the accumulation rates in more impacted regions. For instance,

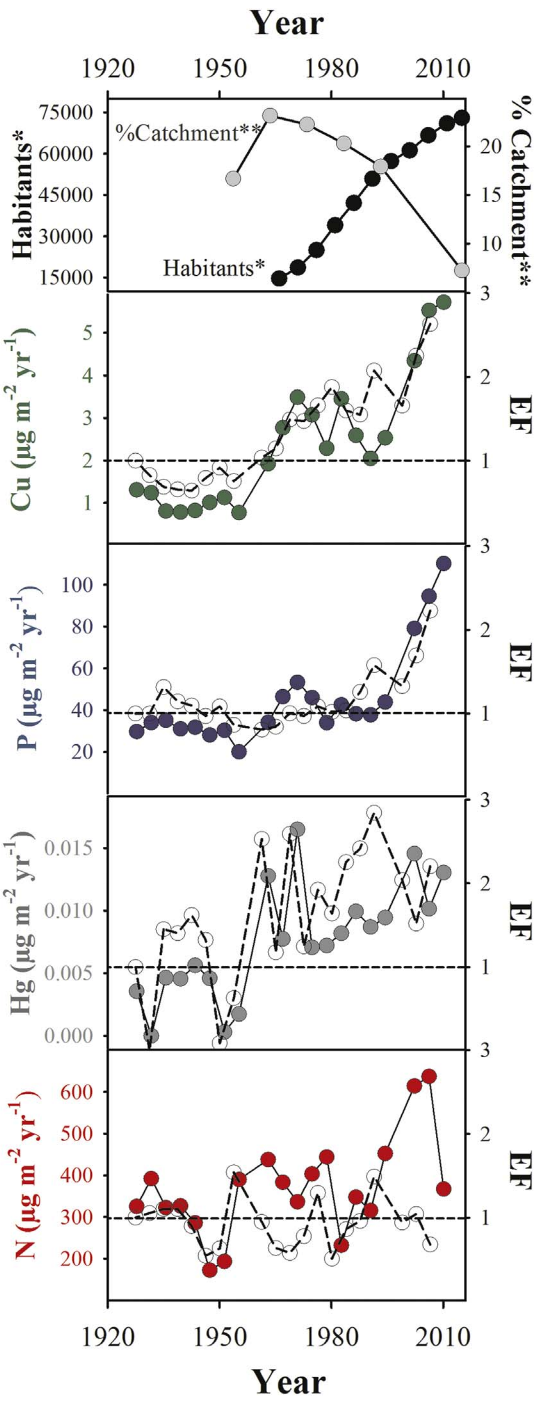

Fig. 4. Coffs Harbour population and percent of catchment land used as banana plantation over time compared with enrichment factors (open circles and dotted line) and accumulation rates (colored circles) of Cu, P, Hg and N in the mangrove sediment core. Accumulation rates and enrichments reflect pre-agricultural, agricultural, and then residential use of the basin. *Coffs Harbour Population from 1966 to 2015 (ABS, 2016). **Percent of catchment land used as banana plantation in 1954, 1964, 1974, 1984, and 2016. Data from Coffs Harbour City Council (CHCC 2016a, b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

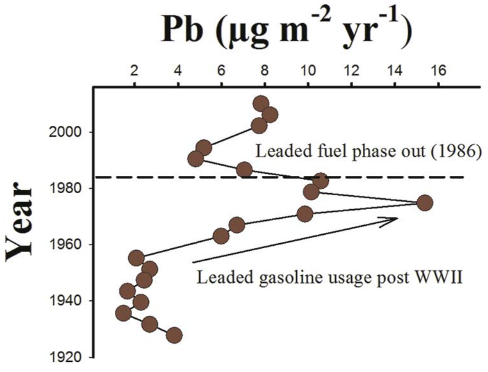

Fig. 5. Accumulation rate of Pb (µg m^{-2} yr^{-1}) in the mangrove sediment core over time.

previous studies on marsh vegetation in the southeastern United States observed P accumulation rates between 0.2 and 1.3 g m^{-2} yr^{-1} (Craft et al., 2007; Loomis and Craft, 2010). Disturbed mangroves near the industrialized city of Sao Paulo, Brazil accumulate P at a rate of 17 g m^{-2} yr^{-1} (Sanders et al., 2014a) and in Guanabara Bay, Rio de Janeiro 0.2 mg m^{-2} yr^{-1} (Borges et al., 2009). The mean P accumulation for Coffs Creek sediment is orders of magnitude lower than the mangrove wetland in these highly impacted areas.

Enrichment of Hg has been observed since 1971 (Fig. 4). Mercury accumulation steadily increased towards the surface intervals, with the highest accumulation rate observed at the surface (0.013 µg m^{-2} yr^{-1}). The Hg enrichment may be attributed to increased fossil fuel emissions from vehicular or aviation traffic to and from Coffs Harbour, as well as from coal fired power plants and metal smelting which are major sources of Hg emissions in Australia (Pirrone et al., 2010). Since Hg is volatile and can travel long distances in the atmosphere before deposition (Figueiredo et al., 2013; Selin, 2009), distant sources may be contributing to Hg deposition in Coffs Creek. While emissions of NSW have declined since 2006, Hg accumulation continues to fluctuate. In addition to fossil fuel emissions, increased nutrient loading and subsequent algal blooms may be partly responsible for the increase in Hg deposition (Machado et al., 2016; Ryder et al., 2012). Algal blooms are strongly related to increases in population density which may coincide with increased Hg enrichment towards surface sediments in this estuary (Church et al., 2006).

A clear trend emerged when Pb accumulation was plotted against time (Fig. 5). Lead enrichment increased from approximately 1956 to 1975 along with an increase in leaded gasoline usage in the region. Expansion of the Pacific Highway and personal automobile use in Coffs Harbour increased greatly during this time (Yeates, 1990). Lead enrichment decreased from 1979 until 1991, where baseline levels were once again reached. Leaded petrol was phased out in Australia in 1986, which is reflected in the decrease in the Pb accumulation and enrichment along the sediment column. Other sediment profiles have documented a rise and fall in deposition of Pb in conjunction with leaded petrol usage in the Switzerland and the United States (Marcantonio et al., 2002; Weiss et al., 1999). Thus, our observations build on the existing literature demonstrating a decrease of Pb accumulation following source management.

In summary, the Cu, As, Pb, Zn, Ni, Hg, N and P contents from sediments from Coffs Creek mangroves do not indicate toxicity. However, clear trends of increasing accumulation and slight enrichments above baseline concentrations were detected for Zn, Cu, Pb, Hg, and P. Mangrove sediments recorded changes in P and Cu in conjunction with agricultural cultivation in the basin, and more recently when housing replaced banana plantations along the catchment. Furthermore, the history of fossil fuel use in the area was recorded by Pb signatures and Hg enrichment. This work shows heavy metal and nutrient depositional fluxes and recent historical signatures along the catchment which defines shifting baselines in this region of Australia.

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