Heavy metal deposition in estuary sediments downstream of intensive peri-urban and horticulture development

Final Report - Coffs Harbour City Council Environmental Levy Program

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Executive Summary

Throughout the mid-north coast of New South Wales, the coastal topographies are peppered with sweeping paddocks, seaside suburbs, and pockets of lush bush. The countryside where urban and rural land uses intermingle, known as peri-urban areas, have become a focal point for environmental research in recent decades.

As evidenced by previous research undertaken by Southern Cross University in conjunction with Coffs Harbour City Council, once-pristine streams and estuaries in Coffs Harbour and nearby regions of New South Wales have been disturbed due increasing peri-urban development pressures, including intensive horticulture, rapid land use change, public infrastructure upgrades, industrial, and residential uses.

Pollutants from these disturbances are transported through erosion or rainfall and often deposit in sediments. Natural depositional environments, such as estuaries can accumulate elevated levels of contaminants in sediments which may reflect the extent of upstream developments. To look for a relation between the extent of peri-urban activities with estuarine ecosystem health, we used dated sediment cores to evaluate differences in the extent of estuarine sediment pollution in six Coffs-area estuaries.

We collected twenty-five, saltmarsh, and seagrass sediment cores from six estuaries across a land-use gradient (Boambee, Coffs, Hearnes Lake, Corindi, Wooli, and Clarence estuaries). Development in each catchment varied greatly, from relatively undisturbed catchments (< 5 % developed land use, Corindi and Wooli) to highly impacted (> 75% developed land use, Coffs, Boambee). Sediment cores were analysed for ^{210}Pb radionuclides as well as metal, metalloid, and phosphorous sedimentary fluxes using multiple lines of evidence approach to evaluate linkages between land use and sediment quality.

Overall, there was little sediment contamination within the region. Only 16 of 353 samples exceeded soil quality guidelines (SQG) low-range values, indicating an overall low risk of ecotoxicity in blue carbon sediments of this region. Contaminant flux rates were orders of magnitude lower than other literature reports from more developed estuaries overseas. Geoaccumulation index (a measure of deviation from naturally occurring background trace element concentrations) calculations also revealed near pristine sedimentary environments.

Cadmium, arsenic, iron, and manganese had linear to exponential positive correlations between concentrations, sediment flux, geoaccumulation index and catchment development. With increasing agricultural or urban catchment land cover between < 5 % to 30 %, mean concentrations of arsenic, copper, iron, manganese, and zinc increased between 1.5 to 4.3-fold, potentially indicating a threshold response from blue carbon sediment quality to catchment development. Fluxes of phosphorous, cadmium, lead, and aluminium responded similarly, increasing 1.2 to 2.5-fold.

Exponential increases in phosphorus flux to estuary sediments may precede eutrophication observed in more developed estuaries. Cadmium and zinc deposition probably co-pollute with phosphorous due to their presence as impurities in fertilisers used for agriculture. Overall, our multiple lines of evidence revealed how catchment development drives blue carbon sediment quality across a regional scale.

1. Introduction

Seagrass, saltmarsh, and mangrove habitats (termed 'blue carbon' ecosystems) play an important role in the global marine carbon (C) cycle [1]. While much of the literature has focused on C sequestration in blue carbon sediments [2, 3], their ability to improve estuarine water quality via contaminant removal is also a valuable ecosystem service [4-6]. Sediments of blue carbon habitats bury anthropogenic contaminants, such as phosphorous, trace metals, and metalloids [7-9] along with carbon, preventing terrestrially derived pollutants from reaching ecologically and commercially important coastal waters [10]. Catchment urbanisation and agriculture can accelerate the accumulation of contaminants in coastal sediments [11]. Development disturbs soils, promotes erosion, and leaching of contaminants from fertilisers, industrial, and natural sources [12, 13], which eventually reach estuaries [9, 14]. Due to their low-lying topography, blue carbon habitats consistently receive and accrete sediments [15] which can reflect the development in the adjacent terrestrial environment [16, 17].

Several techniques have been used to resolve contaminant history in blue carbon sediments. Radionuclide dating, such as with ^{210}Pb, is a valuable tool to date sediments and link sedimentary profiles to historical anthropogenic development [18]. By comparing nutrient and trace metal/metalloid concentrations in sediments dated to before development, the deviation from pre-industrial sediment quality can be assessed [17, 19]. Other metrics, like the geoaccumulation index (I_{geo}), are often-used to assess the difference between recent sediments from their previous natural (background) state [20-22]. Multivariate statistical methods, such as principal component analysis (PCA), can then be used to determine the specific impacts of different land uses on sediment quality [23, 24]. Combined, these geochronological and statistical analyses may reveal the role blue carbon sediments have in retaining anthropogenic contaminants across temporal, spatial, and land use gradients.

Here, we hypothesize that increasing catchment development will accelerate sediment accumulation and the burial of contaminants in blue carbon habitats. We rely on ^{210}Pb dated sediment cores from mangrove, saltmarsh, and seagrass habitats across a land use gradient in six estuaries. To resolve linkages and thresholds in catchment development resulting in a response in sediment quality, we measured contaminant concentrations, flux rates, and geoaccumulation indices. Our study identifies the extent to which anthropogenic development influences contaminant burial in blue carbon ecosystems.

2. Materials and methods

2.1 Study area

This study was undertaken in six estuaries with similar geomorphology and climate, spanning ~140 km along the subtropical New South Wales (NSW) north coast (Figure 1). All estuaries contained *Avicennia marina* mangrove, *Sporobolus virginicus* and *Juncus krausii* saltmarsh, and *Zostera marina* seagrass vegetation with organic-rich sandy to fine-grained sediments [25]. In this region of Australia, strong episodic rainfall promotes the mobilisation of contaminants into estuaries [14, 26], with estuary sediments retaining contamination histories [9, 16]. The upstream catchments contain mostly podzol, ferrosol, and humic clay soils. Land use varies in each catchment from peri-urban residential and agricultural (Boambee and Coffs), intense horticulture and large-scale livestock grazing (Hearnes and Clarence), to a high degree of land conservation with undisturbed National Park and native vegetation (Corindi and Wooli) (Figure 1). Coffs, Hearnes, Corindi, and Wooli estuaries hydraulically connect with an area of biodiversity and commercial importance, the state-protected Solitary Islands Marine Park.

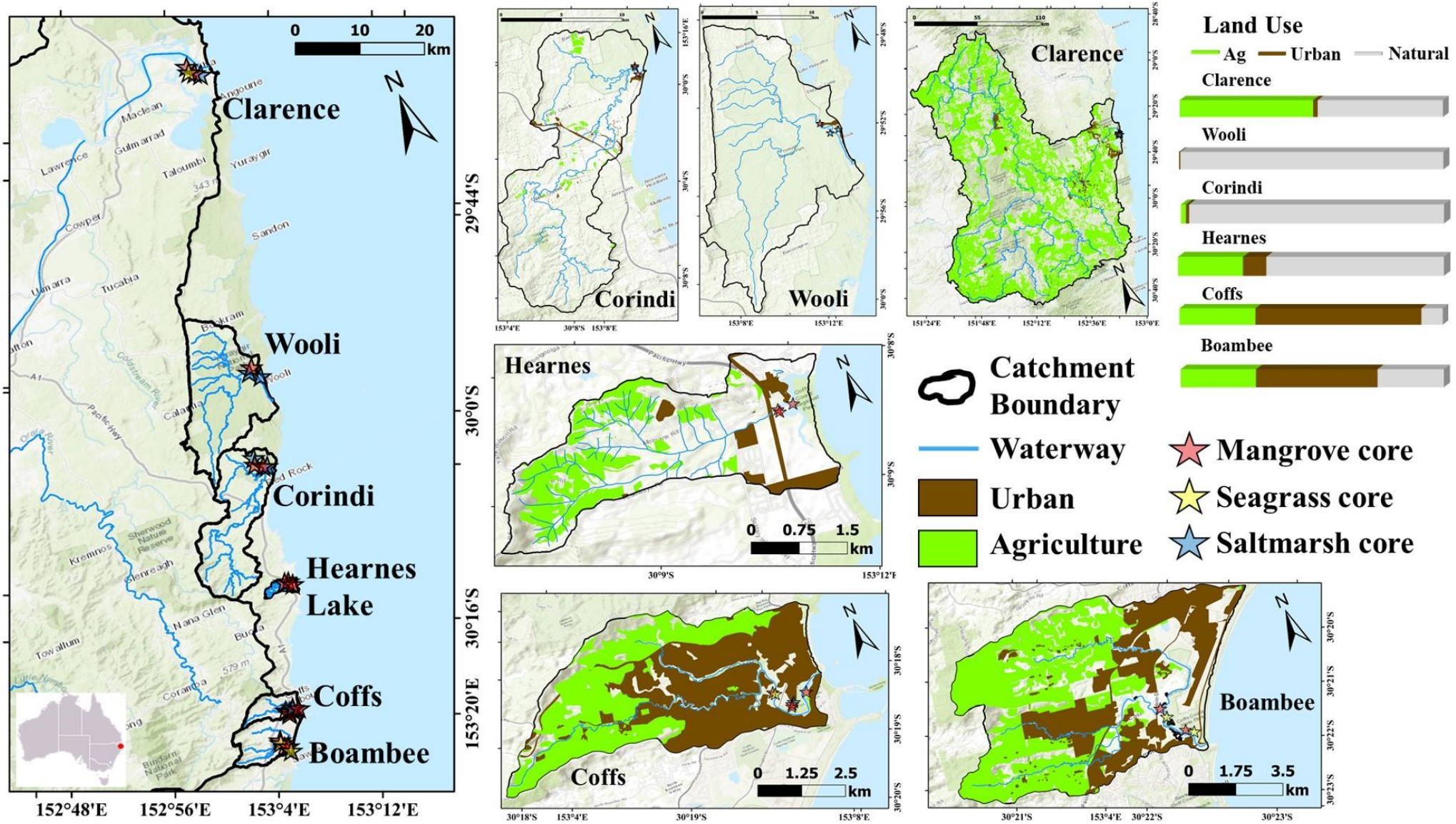

Figure 1. Location, land use, and sample sites (stars) for and mangrove, seagrass, and saltmarsh sediment cores (n = 16, 4, and 5, respectively) of 6 estuary catchments on the subtropical coast of Eastern Australia. Agricultural land use is green. Urban land use is brown. Catchments range from natural (Corindi, Wooli) to heavily developed (Boambee, Coffs).

2.2 Sample collection and metal, metalloid, and phosphorous determination

We collected 25 sediment cores (16 mangrove, 5 saltmarsh, and 4 seagrass) from six sites across a land use gradient (Figure 1) using a 50 cm long, 5 cm diameter Russian peat auger or 6.7 mm inner-diameter PVC pipes. Peat auger cores were sectioned into 2 cm intervals upon return to the lab. Cores taken in the PVC pipe were extruded from the top of the tube and sectioned into 2 cm intervals in the field. Compaction was accounted for in core depth measurements on-site [27]. Metal, metalloid (As, Cu, Pb, Cd, Zn, Cr, Hg, Fe, Al), and phosphorus (P) contents were measured in each sediment interval. A 1:3 HNO3/HCl acid digest was used to extract contaminants from sediments then analysed on an APHA inductively coupled plasma mass spectrometer (ICP-MS). To confirm accuracy and precision of the instrument, sediment reference materials were digested (AGAL 12) with each sample batch. Instrument drift was routinely monitored by re-analysing our mid-point calibrations every 20 samples using internal Sc, Ge, Rh, and Ir standards.

2.3 ^{210}Pb dating

^{210}Pb and ^{226}Ra activities from core samples were counted using Canberra High Purity Germanium (HPGe) gamma detectors. Samples were packed into plastic petri dishes (broad energy Germanium detectors) or plastic vials to a height of 27 mm (well detectors). To obtain sufficient sample mass, we combined two 2-cm sediment intervals from Wooli, Corindi, Coffs, and Boambee cores. All samples were sealed with PVC electrical tape (petri dish) or epoxy resin (vials) for at least 21 days to establish secular equilibrium between ^{222}Rn and its granddaughter ^{214}Pb. ^{210}Pb and ^{226}Ra decay was counted from the 46.5 keV and 295.2, 351.9, and 609.3 keV gamma peaks, respectively. Radionuclide counts per minute were multiplied by a correction factor that integrates background gamma ray intensity and detector efficiency determined from standard (USGS Rocky Flats) calibrations. Unsupported (or excess) ^{210}Pb ($^{210}Pb_{xs}$) was calculated by taking the difference of ^{210}Pb and ^{226}Ra activities for each dated sediment interval.

The ^{210}Pb and ^{226}Ra equilibrium horizon was not always reached. Therefore, we calculated sediment ages using the constant initial concentration (CIC) model [28] which generates an average rate of sediment accumulation down the entire core. Sediment ages were calculated as:

$$Interval\ age = year\ of\ collection - \frac{average\ interval\ depth}{sediment\ accumulation\ rate}$$

When surface mixing was evident in sediment radionuclide profiles, these surface mixing layers were excluded [29]. While all data from Boambee, Corindi, Wooli, Clarence, and 5 of the 6 Coffs cores are specific to this study, the ^{210}Pb data from Hearnes Lake and 1 Coffs mangrove core were originally reported elsewhere [9, 16].

2.4 Data analysis

Sediment metal and metalloid contents were compared to the Australia New Zealand Environment and Conservation Council (ANZECC) sediment quality guidelines (SQG) to assess the extent of contamination [30]. As ANZECC framework has no SQG for P, we used SQG from Persaud, et al. [31]. Geoaccumulation index (I_{geo}) was calculated to assess the extent of pollution in the sediment cores [20]. Geoaccumulation index was calculated for each contaminant using the equation:

$$I_{geo} = log_2(\frac{C_n}{1.5B_n})$$

where C_n is the measured contaminant content in sample *n* and B_n is the background concentration from *n*'s sample location. The factor of 1.5 is introduced to compensate for variability in background concentrations due to natural lithogenic fluctuations. There are 7 classes of pollution in the

geoaccumulation index: Class 0 ($I_{geo} \leq 0$, unpolluted) ranging to Class 6 ($I_{geo} > 6$ = severely polluted). To assess geological background values at the most local scale, contaminant contents from the bottom interval of each sediment core were used as background values for all calculations.

Delineations for each catchment were obtained from government databases [32] and confirmed flow path tools in ESRI ArcMap v 10.5.1 on the upper limits of 1 m interval contour layers [33]. Land use data was obtained from NSW DATABASE and modified by-hand by creating polygon shapefile layers from satellite imagery in ArcMap v. 10.5.1 (based on December 2018 imagery). We quantified land use in 3 categories: *Urban*- roads, communication infrastructure, commerce, manufacturing, industrial, mining, and residential areas (including rural residential, houses, apartments, lawns, parks); *Agricultural*- grazing, horticulture, farm infrastructure, production forestry, animal husbandry, and abandoned horticultural land that remained cleared and had no current urban use; and *Conserved*- undisturbed land cover with native vegetation, protected and maintained land (residential and/or national park, municipal nature reserve, state and/or national forest), and wetlands. Waterways were not considered in land use cover calculations. Due to lack of distinct separate effects between agriculture and urban land uses, we combined these land uses as 'developed' in further analyses.

Principal components analysis (PCA) was performed in XLSTAT (v 2021.1) software to reveal complex correlations between multiple contaminants, land use, and estuary/catchment size. Contaminant concentrations and sedimentation rate data were found to be normally distributed after Box-Cox transformation [34] and used as explanatory variables. Land use percentages (conserved and developed), estuary size, and catchment to estuary ratios were entered as supplementary variables to observe how different land use categories correlate with contaminant concentrations in the PCA space. Best fit lines were calculated for land use with mean contaminant concentrations, fluxes, and I_{geo} using regression analysis.

3. Results and Discussion

3.1 Land use and sedimentation rates

Land uses in each catchment ranged from highly conserved (Table 1) (Corindi and Wooli: > 85 % conserved land) to highly developed (Coffs, Boambee, and Clarence: 50 to 90 % agriculture and/or urban land use).

Table 1. Characteristics, number of sampled sediment cores (M = mangrove core, SM = saltmarsh core, SG = seagrass core), and land use of six estuaries sampled in this study. Predominant impact was determined by the percentage and proximity of land uses in the upstream catchment.

	Lat.	Long.	Cores	Catchment area	Estuary area	Catchment to estuary ratio	M	SM	SG	Conserved	Ag	Urban	Total Developed	Pre-dominant impact
Estuary	Decimal °		M, SM, SG	km^2	km^2		ha	ha	ha	%	%	%	%	
Clarence	153.33	-29.42	2, 1, 1	22,716.0	0.02	1.1E+06	521	195	1907	45.2	50.7	1.7	52.4	Ag
Wooli	153.27	-29.89	2, 1, 0	184.0	3.7	49.7	86.0	66.9	9.4	98	0.0	0.5	0.5	None
Corindi	153.23	-29.98	2, 1, 1	148.0	1.9	77.9	37.1	52.7	2.4	85.0	1.9	1.2	3.1	None
Hearnes	153.21	-30.13	3, 0, 0	6.8	0.1	68.0	6.1	3.2	0.1	24.8	24.4	8.8	33.2	Ag
Coffs	153.14	-30.30	4, 1, 1	24.5	0.5	49.0	20.1	1.4	0.2	8	28.4	62.1	90.5	Urban
Boambee	153.11	-30.35	3, 0 ,2	48.5	1.0	48.5	33.1	2.9	6	24	28.6	46.2	74.8	Urban

All cores displayed exponential decay of $^{210}Pb_{xs}$ (Figure 2). Sedimentation rates ranged from 0.03 to 1.54 cm yr^{-1} (mean of 0.46 ± 0.10 cm yr^{-1}), which is within or below the range of sedimentation rates from blue carbon systems often reported in the literature [35-38]. Year to depth models (Figure 2)

revealed that some bottom sediments date from beyond the range of ^{210}Pb dating (Corindi saltmarsh, 19 cm depth, year < 1900) to 1990s (Boambee M3L and SG6 cores).

There was high variability in sedimentation rates across cores and habitats within each estuary as expected for estuarine sedimentary environments [39]. Mean sedimentation rates in each estuary displayed no clear trend with land use percentages ($R^2 = 0.06$). Boambee cores had mean elevated sedimentation rates (0.95 ± 0.22) compared to the other cores (0.36 ± 0.02), although the cause is not clear from our observations. Sediment delivery to estuaries is expected to vary with hydrology, erosion rate, sediment yield, distance from disturbance, and other parameters [40-42].

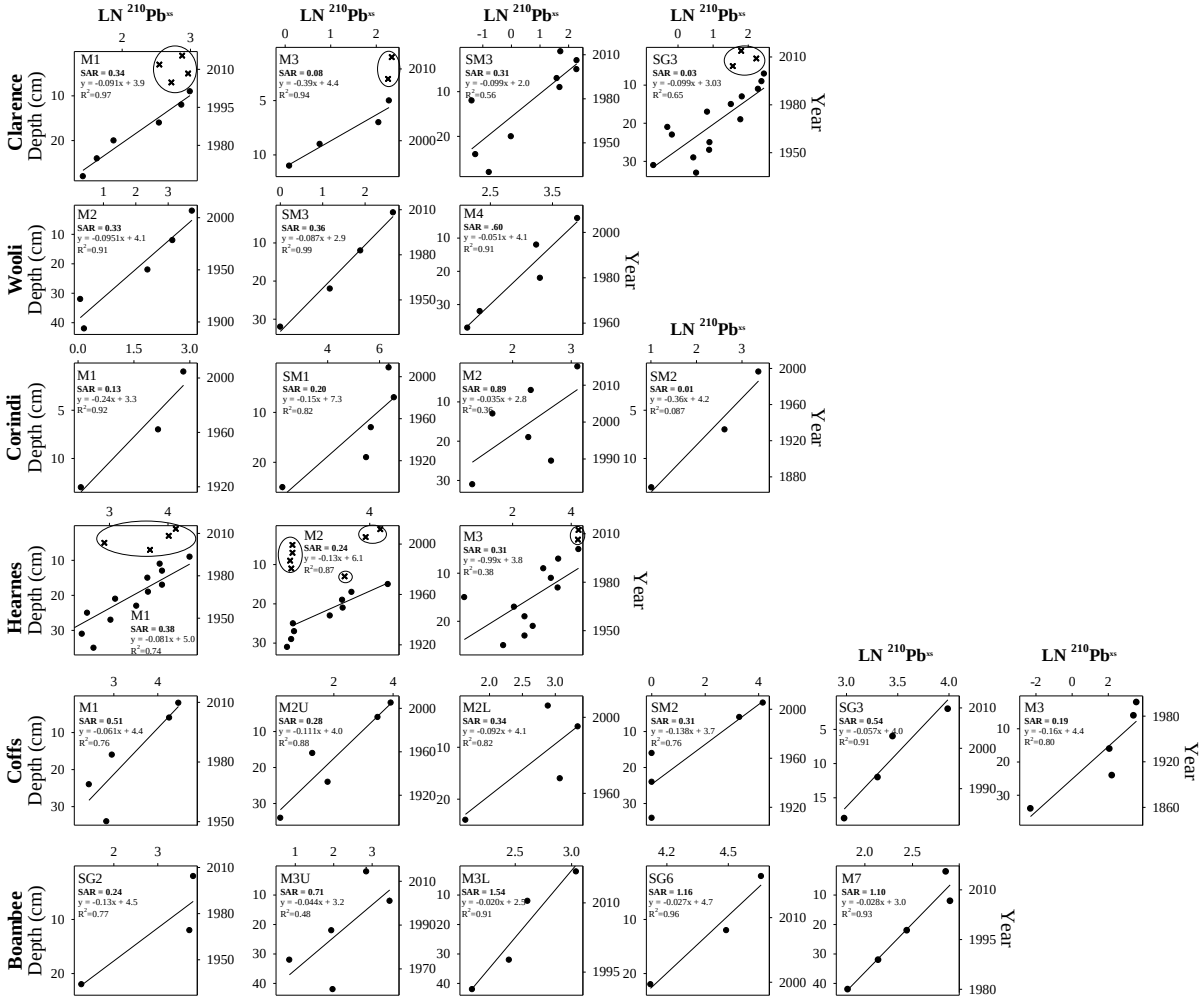

Figure 2. Natural-log of excess ^{210}Pb (LN ^{210}Pb$_{xs}$) decay and year-to-depth profiles from 25 sediment cores. Circled 'X' data points in Clarence and Hearnes cores represent surface mixing layer observations excluded from constant initial concentration dating model calculations. M = mangrove core; SM = saltmarsh core; SG= seagrass core. Please note different scales of each axis for each core.

3.2 Concentrations, fluxes, and geoaccumulation indices

Metal, metalloid, and phosphorous concentrations seldom exceeded the default guideline SQG values (16 of 353 samples). No samples exceeded high-range SQG values. Despite the relatively pristine catchment, there was anomalous contamination of sediments with As and P in one Corindi saltmarsh core. Phosphorous exceeded the SQG of 600 mg kg^{-1} (from Persaud et al. 1993) Between 12 and 32 cm depth in Corindi SM1 core, reaching a maximum in the 30-32 cm interval (1488 mg kg^{-1}). Arsenic concentrations in this interval (27.8 mg kg^{-1}) also exceeded the ANZECC SQG (20 mg kg^{-1}). This was the only exceedance of As for all samples/estuaries. Coffs Creek mangrove M3 core had Pb

concentrations exceed the ANZECC SQG of 50 mg kg^{-1} from 4-8 cm depth (Pb concentration 62.5 and 67.2 mg kg^{-1} in 4-6 and 6-8 cm depth, respectively).

Chromium was the only element to exceeded ANZECC SQG (80 mg kg^{-1}) in multiple estuaries. Chromium contents in surface (2-4 cm depth) sediments of Corindi SM2 core were 87.4 mg kg^{-1}. Yamba site 3 saltmarsh and mangrove cores (SM3 and M3) had several high Cr contents. Bottom sediments (32-34 cm) of M3 had Cr contents of 82.2 mg kg^{-1}. SM3 had Cr contents between 84.3 to 113.6 mg kg^{-1} from 8 to 10 and 22-34 cm.

The contamination we observed was anomalous and not widespread. Incidents of isolated contamination could due to discrete anthropogenic inputs (i.e. illegal dumping of wastes) or exceedances of SQG may be driven by geochemical processes, such as pyritization of trace metals [43] or redox dissolution and precipitation dynamics [44], as was demonstrated in Hearnes Lake surface sediments [9].

A correlation became apparent when some sediment trace element concentrations were compared to catchment land use. Concentrations of Cd, Zn, Pb, Cu, and Fe increased exponentially, and Mn increased linearly with developed land use (Figure 3). A similar relationship was observed for P, with the exception of the Corindi estuary, driven by the peculiarly polluted Corindi SM1 core (see previous paragraph). Catchment land use cover > 30% resulted in concentration increases between 1.5 to 4.25-fold for Zn, As, Cu, Fe, and Mn. This result suggests a catchment land use threshold of ~30% development after which blue carbon sediment contaminant concentrations increase significantly.

Chromium, Hg, and Al concentrations lacked any apparent relationship with development (Figure 3). This region lacks a major manufacturing industry and sources of Hg and Cr. The lack of relationship between development and Hg is probably due to relatively uniform atmospheric deposition across this region [45]. The anomalous Cr and Hg pollution observed within and across estuaries may reflect the great localised variability in metal, metalloid, and nutrient deposition and diagenesis within these constantly evolving blue carbon sedimentary environments [46]. Overall, sediment contaminant concentrations were lower than sediments of more developed estuaries in major metropolitan areas in Australia [47-49].

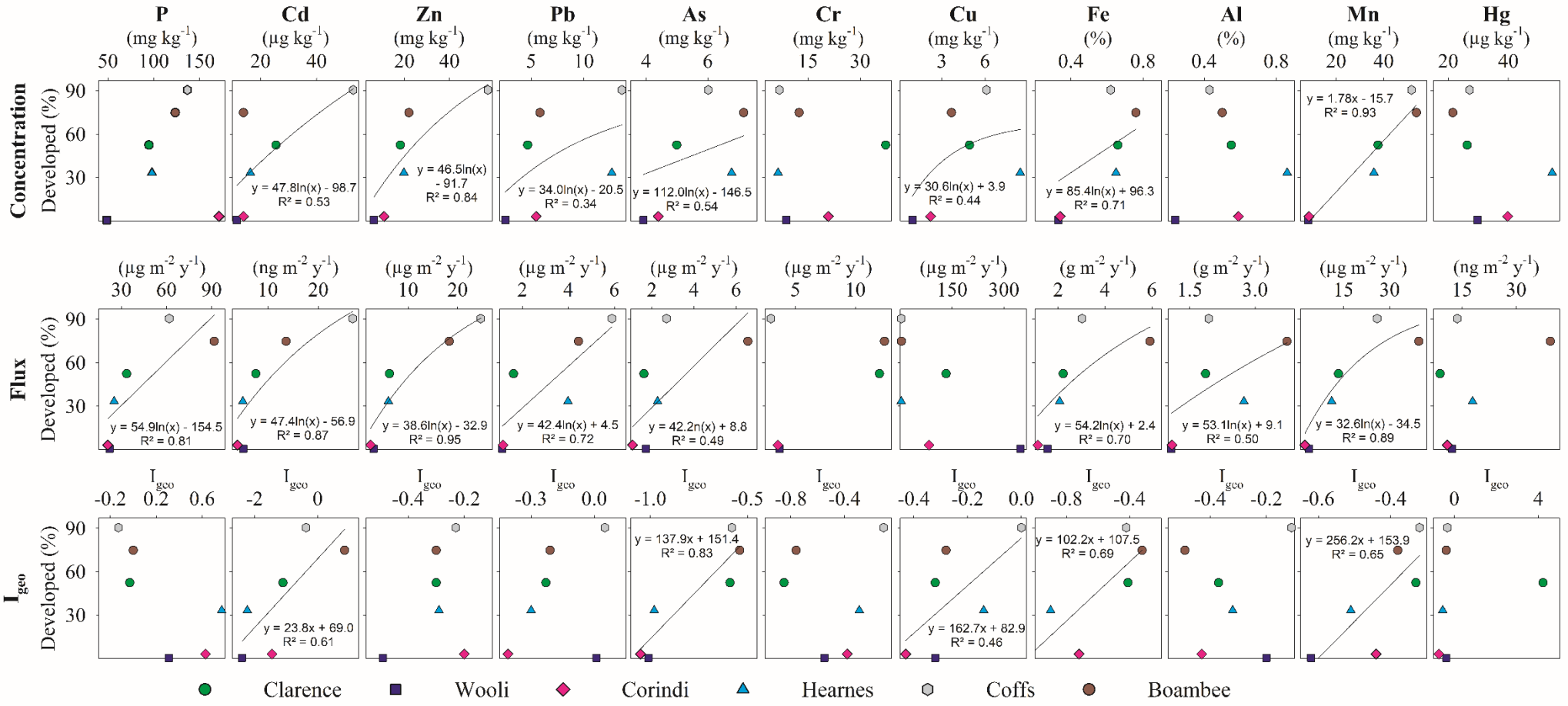

Figure 3. Mean concentrations, fluxes, and geoaccumulation indices (I_{geo}) of metals, metalloids, and phosphorus from sediment cores compared to developed land use percentage from six estuaries. All habitat types (mangrove, saltmarsh, and seagrass) were averaged together here to obtain means for all sediment cores within each estuary. Lines of best fit (linear or exponential) are presented for elements with significant relationships with land use. I_{geo} values range from < 0 (no pollution), to I_{geo} > 4 (heavy pollution). Note the different scales of each axes.

Despite no direct relations between development and sedimentation rates, the influence of development on contaminant flux was clearer. Abundant lithogenic metals (Fe, Al, Mn) displayed positive correlations between fluxes and catchment development (Figure 3), likely reflective of greater deposition of terrestrially-derived minerals [50]. Dissolved fractions of Cd, Zn, and Pb probably bind with these lithogenic metals during aquatic transport [51, 52]. Cd, Zn, and Pb may be introduced from roads, agriculture, and industrial activities [53]. While P concentrations and I_{geo} varied across the land use gradient, P fluxes had an exponential increase with development (Figure 3). The negative trend of P I_{geo} may be driven by recent relatively large deviations from background P concentrations in more pristine sediments of less disturbed catchments. As development continues to expand in this region, increasing P fluxes may be antecedent to eutrophication that has persisted in more impacted subtropical Australian estuaries [54, 55]. These fluxes of P, Cd, Zn, Pb, Cu, Hg are relatively low compared to areas with a higher population density or more intense urban activities where fluxes of these elements were orders of magnitude greater [19, 56-60].

Overall, mean I_{geo} values for most elements across all estuaries were negative or near 0 (Figure 3), indicating minimal sediment pollution. The one exception to this trend was the severe contamination of Hg observed in the Clarence sediments (mean $I_{geo} > 4$, Figure 3), driven by the extremely low contents of Hg (< 1 ng kg^{-1}) at the bottom of the Clarence M3 core. Indeed, the relatively low sedimentation rate in this core (0.19 cm yr^{-1}, Figure 2) indicate the age of bottom sediments (35 cm depth) is beyond the ~150 year scope of ^{210}Pb dating [61] and may predate the onset of intensified anthropogenic atmospheric Hg emissions [62]. When data from this core are excluded, mean I_{geo} in the Clarence sediments indicate no Hg contamination ($I_{geo} = -0.1 \pm 0.3$).

Although negligible pollution for most elements was observed throughout the six regional estuaries, development was often related with the degree of contamination. There were strong positive correlations between I_{geo} and development for Cd, As, Cu, Fe, and Mn (Figure 3). Despite no significant pollution, the evident influence of development on increasing I_{geo} with respect to certain metals and metalloids demonstrates that this measure of contamination is especially sensitive to minor deviations from the geological background and may be a valuable tool to assess contamination across smaller (regional) scales.

3.3 Principal component analysis

Two principal components (PC1 and PC2) were extracted representing 36.81 and 19.45 % of the variability, respectively (56.26 % cumulative). Factor loadings indicate elevated sedimentation rates and increasing concentrations of elements associated with increased sedimentation (i.e. Al, Fe) [39], agrochemicals (P, Cd, Zn, As, Hg) [63], or industrial activities (Pb, Zn, Hg Cd, Hg) [64] were strongly positively correlated with PC1. The small angles between these metals on the PCA biplot (Figure 4) imply an association and similar source. Therefore, we attributed multivariate factor loadings of PC1 to represent an anthropogenic signature from development within blue carbon sediments.

As shown in Figure 4, the estuaries affected by urban or agricultural development had greater concentrations of contaminants typically associated with agriculture, urbanisation, or lithogenic origin indicative of sediment deposition (i.e. P, Cu, Pb, Zn, As, Cd, Hg, Fe, and Al). The observations most correlated with PC1 were the superficial sediments (the top ~20 cm) of the Hearnes, Coffs, Boambee, and select Clarence samples. Thus, the recently deposited sediments from the more developed estuaries were characterised by elevated mean sedimentation rates and greater concentrations of metals, metalloids, and phosphorous.

While the geophysical processes governing catchment erosion and estuarine sedimentation are likely similar, catchment size (and thus fluvial transport distance necessary before deposition) and estuary morphology appear to drive sediment contaminant accumulation. The size of the catchment and estuary, in addition to less development, has likely preserved blue carbon sediment quality in the

larger catchments of Corindi and Wooli. Observations from larger catchments (Wooli, Corindi, Clarence) clustered away from the smaller, more developed catchments (Figure 4), and were strongly associated with catchment to estuary ratios (PC2) rather than the influence of development and associated lithogenic contaminant inputs (PC1).

Catchment size and estuary surface area explained elevated sedimentation rates and increased contaminant flux in one highly cultivated estuary of the Baltic sea, while anthropogenic land use drove increased contamination in larger catchments [24]. Despite similar estuary size and intense urban land uses, recent ICOLL sediments of a 7.5 km^2 catchment in nearby southeast Australia were more enriched than the adjacent 20.8 km^2 catchment [65]. While these catchments were from a more temperate region of Australia, analogous episodic catchment erosion and deposition are assumed to govern sedimentation and contaminant accumulation. Our PCA results and the existing literature imply terrestrially derived contaminant mobilisation to blue carbon sediments may occur on a slower timescale in larger catchments. Comparing our results to the literature provides further evidence suggesting that, while our catchments and estuaries may be relatively small, these blue carbon sediments still function as important geophysical barriers to commercially and ecologically important marine ecosystems.

While development may accelerate sediment deposition into estuaries by 5-10% [66] and increase estuarine contaminant loads [67], erosion and deposition processes will naturally contribute terrestrial materials to blue carbon sediments [68]. Sediment deposition is most strongly focused at the upper reaches of tidal intrusion, where fluvial discharge meets the salt wedge [69]. Hence, trace metals/metalloids from less disturbed catchments may take longer to reach the lower reaches of estuaries or coastal oceans.

The PCA data from the relatively undeveloped estuaries (Corindi and Wooli) imply that these blue carbon sediments are influenced by natural erosion/deposition. Metals strongly associated with PC2 (Mo, Ni, Cr) were present in low to background levels in sediments from Hearnes and Clarence catchment soils [70]. Previous water quality investigations in the region [14] suggest these elements are probably present in concentrations that reflect lithogenic origin only.

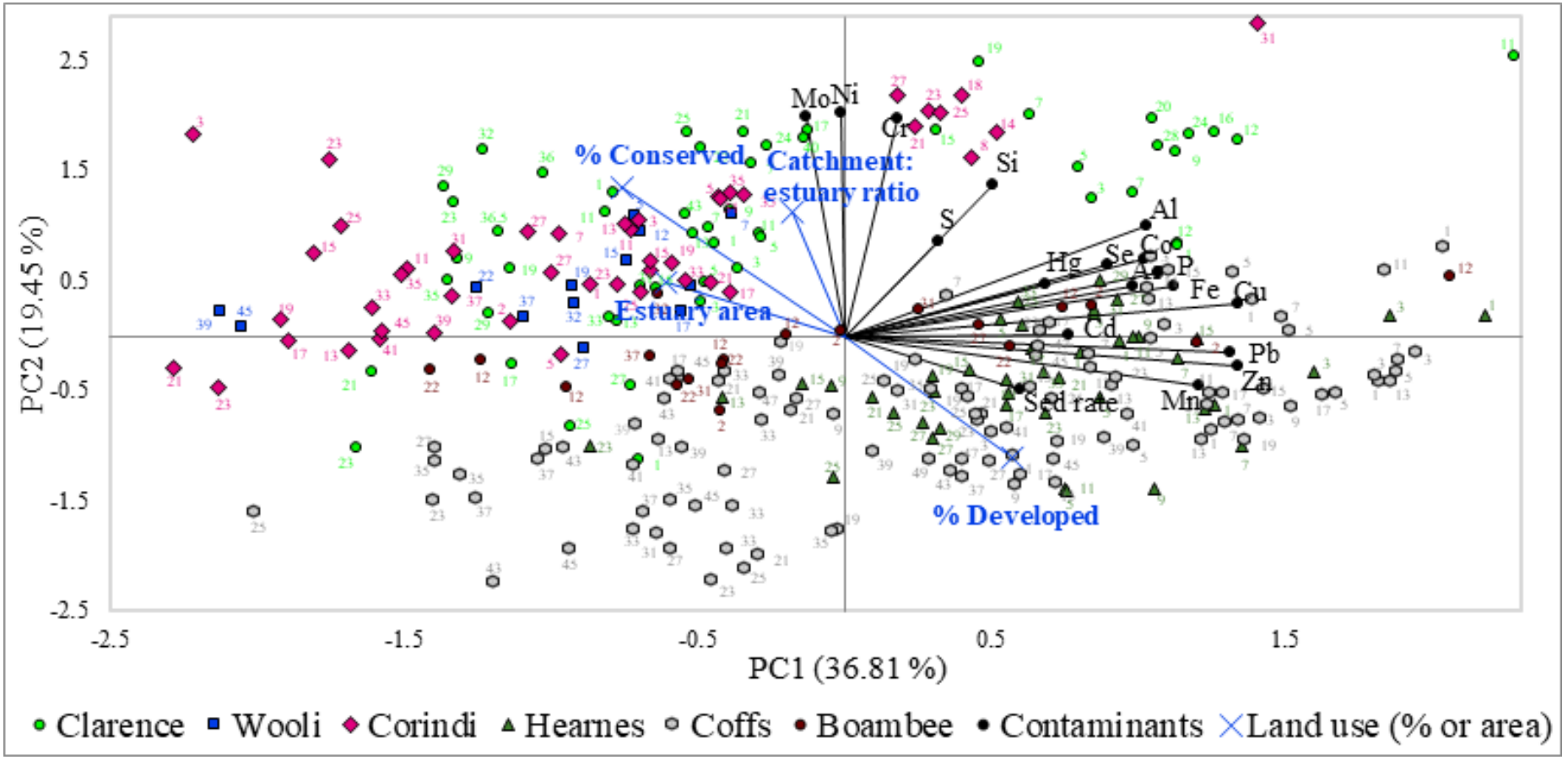

Figure 4. Principal component (PC) and explained variabilities distance biplot of observations (sediment sample intervals, coloured dots) and explanatory variables (contaminant concentrations, black dots) or land characteristics (blue crosses). Angles between variables represent their correlation with one another. Variables with angles < 90° between them are closely correlated, variables with 90° angles have no correlation, and variables with angles approaching 180° are negatively correlated. Vector length of variables represents their contributions to the principal components. Numbers next to observations represent depth of sample.

4. Conclusions and recommendations

Our results demonstrate the capacity of blue carbon habitats to sequester contaminants and ultimately preserve estuarine and nearshore ocean water quality while facing increasing anthropogenic pressures [71]. Overall, sediments were unpolluted with only 16 of 353 samples exceeding SQG default (low-range) values and I_{geo} values indicating relatively pristine sediments. Contamination was not widespread and may be driven by discrete pollution (i.e. illegal dumping of waste) or geochemical processes.

However, multiple lines of evidence (concentrations, fluxes, and I_{geo}) converge to the conclusion that catchment land use drives blue carbon sediment contaminant accumulation for Cd, As, Fe, and Mn (Figure 3), but not necessarily Al, Hg, Cu, Pb, or Cr. Cadmium and As are environmentally toxic [72], and changes in sediment redox conditions control the mobilisation of all of these elements to estuarine surface and groundwaters [73, 74]. Our results showed that > 30 % development in our catchments led to more than 1.5-fold increases in Zn, As, Cu, Fe, and Mn concentrations.

Other elements had less pronounced, but environmentally significant, relationships with land use. Increasing P flux with regional development (whether agricultural or urban land use) may be a precursor to persistent estuarine eutrophication as sediments may turn from a P sink to a P source as observed elsewhere [75, 76]. Reduction of fertiliser use, sediment trapping and removal, and flocculation with inorganic particles are possible mechanisms to reduce P input into estuaries [77-79]. Cu contamination (as revealed by increasing concentrations and I_{geo}) is persistent in more developed estuaries likely driven by fungicide use or industrial activities [16]. Accelerated sediment delivery and subsequent infilling of these regional estuaries may reclaim tidal areas leading to the restriction of mangrove and saltmarsh growth, burial of seagrass, and constriction of fish habitats [80].

Catchment geomorphology was also an influence on blue carbon sediment contamination. Our results suggest contaminant accumulation in sediments of large catchments and estuaries is a slower geophysical process than in smaller catchments with higher anthropogenic land use cover. In these regional coastal areas of Australia land use conflicts are still incipient compared to larger urban areas. Thoughtful development may preserve estuarine ecosystem health until extensive and intensive development takes place [81, 82]. Our results suggest that dense urbanisation or agriculture should be avoided in small coastal catchments and established in upper catchments if blue carbon ecosystem health preservation is to be prioritised.

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