Investigating water quality in Coffs coastal estuaries and the relationship to adjacent land use

Part 1: Sediments

Final Report - Coffs Harbour City Council Environmental Levy Program

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Executive Summary

Coffs Harbour City Council engaged Southern Cross University to perform water quality investigations in coastal estuaries with funding from the Environmental Levy Program. Topics of concern include the rapid expansion of the blueberry horticultural industry and potential implications to waterways and the Solitary Islands Marine Park (SIMP).

This report focuses on sediment analysis from Hearnes Lake downstream of a catchment with intensive horticulture land use. Sediments investigations can provide insight into the average chemical composition of the catchment in the last several decades.

Here, we use 3 dated sediment cores and 17 surface sediment samples to assess possible historical contamination related to agricultural activities.

We rely on four major lines of evidence to assess potential influences of changes in land use to sediment quality: (1) comparisons to sediment quality guidelines, (2) enrichment factor calculations (i.e., deviation from natural concentrations), (3) spatial distributions, and (4) fluxes to sediments in the last ~80 years resolved from ^{210}Pb profiles.

^{210}Pb profiles revealed the sediment cores dated back between 1937 to 1943, with sedimentation rates ranging from 0.5 to 5.8 g cm^{-2} year^{-1}. Higher sedimentation values occurred after 2004 likely due to increased catchment erosion.

Only 2 out of 69 samples had arsenic (As) levels exceeding Australian and New Zealand Environment Conservation Council (ANZECC) sediment quality guidelines (SQG). The two As-enriched samples were also enriched in iron (Fe), implying geological rather than anthropogenic As sources. No samples of lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), or zinc (Zn) in sediments exceeded guidelines.

Trace metals (As, Cd, Cu, Pb, Zn and Cr) and nitrogen (N) had increased fluxes into the sediments in the last 15 years. These increased fluxes seem to be primarily related to increased erosion of soils rather than chemical contamination. In spite of some moderate localised contamination, no widespread enrichment was observed for As, Cd, Cu, Pb, Zn, or Cr since the development of the blueberry industry starting in year 2002.

However, a clear link was established between the sediment P profile and recent agricultural expansion. Phosphorus enrichment increased by nine-fold and sediment fluxes by over forty-fold (up to 12.6 mg m^{-2} yr^{-1}) during the expansion of blueberry cultivation within the catchment since 2002.

The implications of sediment P increases were not assessed for Hearnes Lake. Typically, similar waterways would slowly release sedimentary P to the water column, potentially contributing to eutrophication and decreased water quality.

We recommend the management of sediment erosion and phosphorus fertilizer use to prevent environmental changes in downstream waterways, including the Solitary Islands Marine Park.

1. Introduction

Nutrient enrichment and heavy metal pollution can cause environmental problems, including eutrophication of waters, loss of biodiversity, and have toxic health effects for humans (Hakanson 1980, Thrupp 1991, Hopkinson and Vallino 1995, Fulton et al. 1999, Birch 2017). As a result of irrigation, rainfall, and soil erosion, substances applied to agricultural fields may runoff and contribute excess nutrients and heavy metals to surface waters of riverine and estuarine systems. Riparian vegetation within estuarine systems, such as mangroves and marshes, have the ability to sequester pollutants (Peterjohn and Correll 1984, Tam and Wong 1993, Sanders et al. 2014, Machado et al. 2016, Conrad et al. 2017). These coastal wetlands dampen water flow with roots and stems, inducing sediment deposition (Meade 1972, Kirwan and Megonigal 2013). Sediments of wetland areas reflect upstream activities (Peterjohn and Correll 1984, Tam and Wong 1993, Sanders et al. 2014, Machado et al. 2016, Conrad et al. 2017). Indeed, Sanders et al. (2014) demonstrated greater nutrient accumulation from mangrove sediments of a highly developed estuary in Brazil compared to a more pristine nearby forest. Tam and Wong (2000) found mangrove sediments were a sink of trace metals from upstream agricultural activities and wastewater discharge. Due to their ability to sequester nutrients and heavy metals from surface waters, coastal wetland sediments may perform a valuable ecosystem service.

The application of techniques to establish chronologies in wetland sediments are well documented and are especially valuable when reconstructing pollution histories (Valette-Silver 1993). Techniques for sediment dating include the use of radionuclides from the uranium-238 (^{238}U) decay series (Krishnaswami and Lal 1978). The application of lead-210 (^{210}Pb) dating is useful for evaluating the effects of recent (last ~100 years) anthropogenic changes (Breithaupt et al. 2018). For example, Machado et al. (2016) demonstrated the effectiveness of pollution source management via decreased mercury (Hg) flux to estuarine sediments in Brazil after waste management legislation changes. Conrad et al. (2017) found depositional trends of lead (Pb), copper (Cu), and phosphorus (P) from dated wetland sediments in a developed Australian estuary in congruence with local agricultural and urban land uses.

Examples of common agricultural chemicals which can persist in the environment and contribute to ecosystem degradation include nitrogen (N), P, Cu, Pb, Hg, arsenic (As), cadmium (Cd), chromium (Cr), and zinc (Zn) (Fujii 1988, Hooda et al. 2000, Lambert et al. 2007). These elements can accumulate in the soil or be leached into surface waters via surface

runoff during high rainfall events (Crecelius et al. 1975, Hart et al. 2004) or groundwater pathways (Santos et al. 2011, Sanders et al. 2012). In addition, the overuse of nutrients has resulted in fertilization of coastal areas, which may affect the contaminant accumulation capacity of these ecosystems (Alongi 2014, Sanders et al. 2014, Ferreira and Lacerda 2016). Data on the extent of contamination as well as nutrient and organic material accumulation are valuable in determining possible solutions to environmental management issues (Hakanson 1980, Simpson et al. 2013).

This work investigates whether the estuarine sediments of Hearnes Lake will record the land use history of this agriculturally developed catchment. Our observations achieve this by:

1) Quantifying nutrient and trace metal amounts in sediment samples and comparing them to Australian and New Zealand Environment Conservation Council Soil Quality Guidelines (ANZECC SQG)
2) Calculating sediment accretion rates and age of sediments down core using the constant rate of supply (CRS) ^{210}Pb dating method
3) Assessing the historical rate of accumulation and possible enrichment of trace metal and nutrient contaminants based on sediment core chronologies and spatial distribution along surface sediments

2. Materials and Methods

2.1 Study site

To evaluate the extent of the effects of agriculture in a coastal catchment, we selected an intermittently closed-open lake or lagoon (ICOLL) with a history of intensive agricultural use (Hearnes Lake, NSW, Australia). ICOLLs, including Hearnes Lake, open to the sea during times of intense rainfall and are common on the East Coast of Australia (Haines et al. 2006, Sadat-Noori et al. 2016). This area is of special concern because it is a habitat protection zone within the Solitary Islands Marine Park (SIMP). The SIMP is a hotspot of marine biodiversity including algae (150+ species), corals (90+ species), and fish (280+ species) (Harriott et al. 1994, Malcolm et al. 2010). The area of the Hearnes Lake catchment is 6.8 km^2, of which 1.09 km^2 is currently used for horticulture (16 %), with an additional 0.58 km^2 of abandoned horticultural land (CHCC 2016). Land use history of the catchment includes cattle grazing, residential development, mining, timber milling, banana cultivation, and most recently (post year 2000) blueberry cultivation. There is also residential development near the lake. The main water input into Hearnes Lake is Double Crossing Creek, which drains most of the catchment. The catchment land is steep rising from sea level to 269 metres above sea level within ~4 km.

Previous agricultural activities in the basin are known to have used As pesticides and herbicides. Current practices include the continuing application of N and P fertilisers, organic pesticides, and fungicides containing Zn and Cu (Simpson 2017). Recommendations for N and P fertilisers in the blueberry industry are 121 kg ha^{-2} yr^{-1} N and 83 kg ha^{-2} yr^{-1} P (Doughty et al. 1988), though actual fertilization rates applied by local farmers is unknown. Clearing of the land for residential development began in 1969 (Council 2006). A stone quarry mining argillite and other clay aggregates has operated in the basin for over 80 years (Council 2006). Two timber mills which treated woods with chromated copper arsenate (CCA) operated in the basin beginning ~1950.

2.2 Sediment collection and processing

Sediment cores and surface sediment samples were taken from within the estuarine system (Figure 1). Samples were collected on 31 October 2017. Surface samples were taken from bare and vegetated sediments on lake margins and on the lake bottom. Three sediment cores

were taken with a 6.2 cm inner diameter PVC coring device, 36cm in length, from *Avicennia marina* and *Sporobolus spp.* vegetation from islands and margins of the lake. Sediment cores were sectioned into 2 cm intervals in the field and placed in plastic bags for transport. Surface sediments were placed in the oven at 40° C until they were dry (approximately 7 days).

An intact (non-homogenized) portion of sediments was treated with 30 % hydrogen peroxide (H_2O_2) to remove organic matter. Sediments were left overnight to dry and peroxide treatment was repeated until the samples stopped reacting, indicating no more organic material. A solution of sodium hexametaphosphate was used as a deflocculating agent before grain size analysis in a concentration of approximately 3.5 g sodium hexametaphosphate per 100 ml of water. Our solution was diluted from 5 g 100 ml^{-1} (Di Stefano et al. 2010) due to less sediment mass being treated. Sediments were added to the mixture and stirred. Sediments were sieved for gravel (> 1 mm), sand (> 67 µm), and fine grain (< 67 µm) fractions. Each level of the sieve was washed and the sediment slurry was put into pre-weighed 600 ml beakers to dry out at 105° C (Di Stefano et al. 2010). After water evaporated, dried sediments were weighed to obtain mass of each fraction.

For sediment dating, we measured radionuclides from the ^{238}U decay series in a high-purity germanium (HPGe) planar gamma detector. Sediment core intervals were placed into pre-weighed petri dishes with identical geometries and sealed to establish equilibrium between radium-226 (^{226}Ra) and its granddaughter ^{214}Pb. The 46.5 keV gamma peak was used to determine ^{210}Pb activity. ^{226}Ra activity was determined by averaging peaks from its daughters ^{214}Pb and Bismuth-214 (^{214}Bi) (295.2 keV, 351.9 keV and 609.3 keV) (Moore 1984). ^{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. Self-absorption corrections were determined following Cutshall et al. (1983). Excess (unsupported) ^{210}Pb was used to estimate ages of sediment intervals using the constant rate of supply (CRS) model (Appleby and Oldfield 1978).

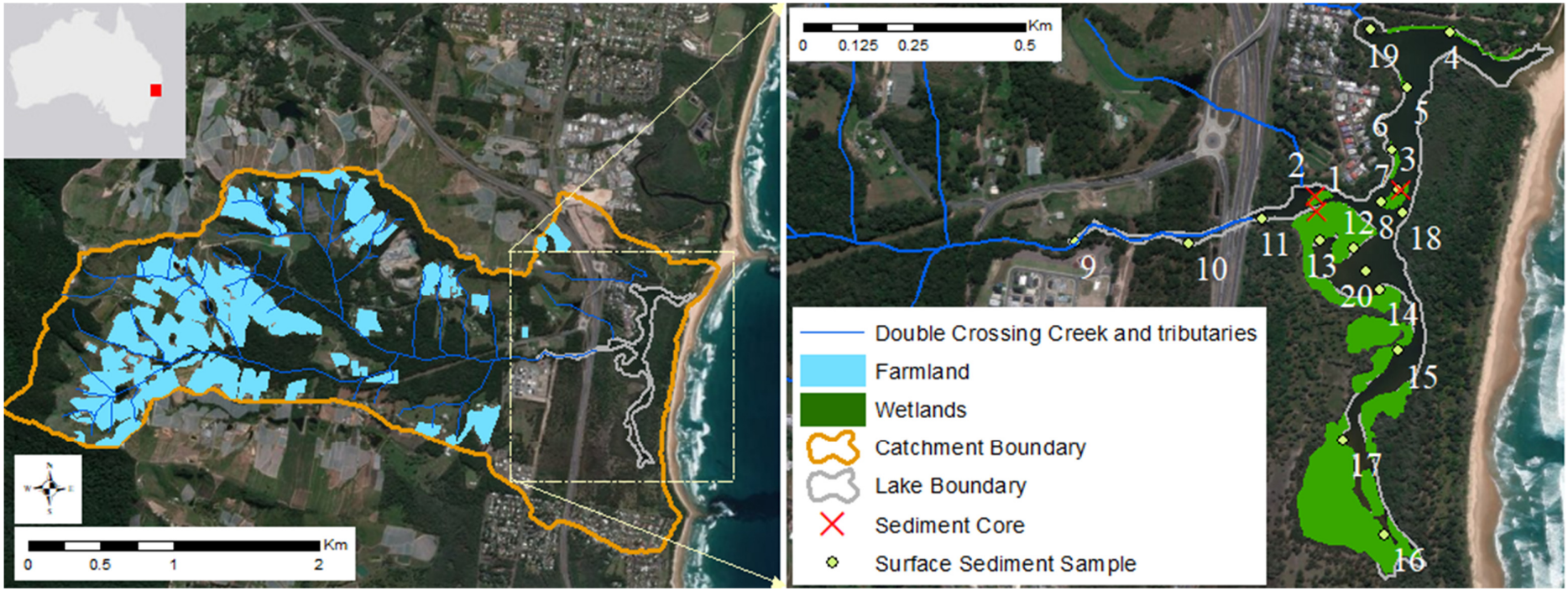

Figure 1. Left panel: The location of intermittently closed-open lake/lagoon (ICOLL) of Hearnes Lake (outlined in grey) on the east coast of Australia. The main input into the estuary, Double Crossing Creek, and its tributaries, are highlighted in blue. Catchment boundary highlighted in orange. Catchment area is approximately 6.8 km^2 (Council 2006). Blue polygons are land currently used for agriculture within the catchment (approximately 1.1 km^2). Right panel: Close up of Hearnes Lake and sample locations. Sample locations 1 through 3 (crosses) were locations of sediment core samples. Other numbers (circles) are surface sediment sample locations. Wetlands (*Avicennia marina* mangrove and *Sporobolus spp*. marsh) are highlighted in green.

2.3 Metals and nutrient content, enrichment, and fluxes

The content of As, Cu, Pb, Cd, Zn, Cr, iron (Fe), aluminium (Al), sulphr (S), and P were measured at each 2 cm interval and in each of the surface samples. Metals were extracted from sediments using 1:3 nitric/hydrochloric (HNO_3/HCl) acid digestion and an APHA Inductively Coupled Plasma Mass Spectrometer (ICPMS) at SCU's Environmental Analysis Laboratory (EAL). Sediment reference materials were digested (AGAL 12). To confirm accuracy and precision of the instrument we analysed certified reference materials after the calibration and monitored drift by re-analysing our mid-point standards every 20 samples and routinely use internal standards scandium (Sc), germanium (Ge), rhodium (Rh), and iridium (Ir). Nitrogen and organic C concentration were determined in a Thermo Finnigan Model Delta Plus XP with analytical precision of N = 0.1 %.

For interpreting vertical profiles, metal concentrations were normalized to Al since Al can be indicative of particle size in estuary sediments and fine grain sediments are more efficient at binding heavy metals (Santschi et al. 2001, Birch 2016). This was accomplished by dividing the metal content by the Al content at the same depth, divided by the background content. Background content was determined from the bottom sediment interval of the core which is determined here to have been deposited before major development in the basin (Conrad et al. 2017). Flux rates into sediments were determined by multiplying sediment mass accretion rate (MAR) with metal content as outlined elsewhere (Borges et al. 2009). Pearson's correlation coefficients were used to obtain insight into geochemical drivers of metals.

3. Results

3.1 Sediment characteristics and ^{210}Pb dating

Sediment dry bulk density (DBD) in all cores decreased towards the surface (Figure 2). Sand content along the cores usually increased towards the bottom, with mean sand being 38, 47, and 44 % in Cores 1, 2, and 3, respectively. ^{210}Pb activities of Core 1 were relatively depleted at 5 and 7 cm concurrent with an increase in sand content. ^{210}Pb activities of Core 2 were constant between 5 and 11 cm depth and 25 to 31 cm depth (approximately 2.6 Bq kg^{-1} for all intervals between these depths, Figure 2). Core 3 surface layers displayed a similar trend of consistent $^{210}Pb_{ex}$ activities in the surface sediment intervals (0-5 cm depth), implying some mixing. The CRS model was chosen as the sediment profiles indicated historical variation in the rates of sedimentation.

Mass accumulation rate over time was estimated using the CRS model (Figure 3). Mass accumulation rate varied from 0.52 g cm^{-2} year^{-1} in 1937 in Core 2 to 5.8 g cm^{-2} year^{-1} in 2013 in Core 1. Inventories of ^{210}Pb were 0.32, 0.31, and 0.28 decays per minute (dpm) cm^{-2} for Cores 1, 2, and 3, respectively. Based upon our calculated mass accumulation rates using the CRS model (Appleby and Oldfield 1978) the bottom sediments of the cores (between 32-36 cm depth) date back to 1940, 1937, and 1943 for Cores 1, 2, and 3, respectively.

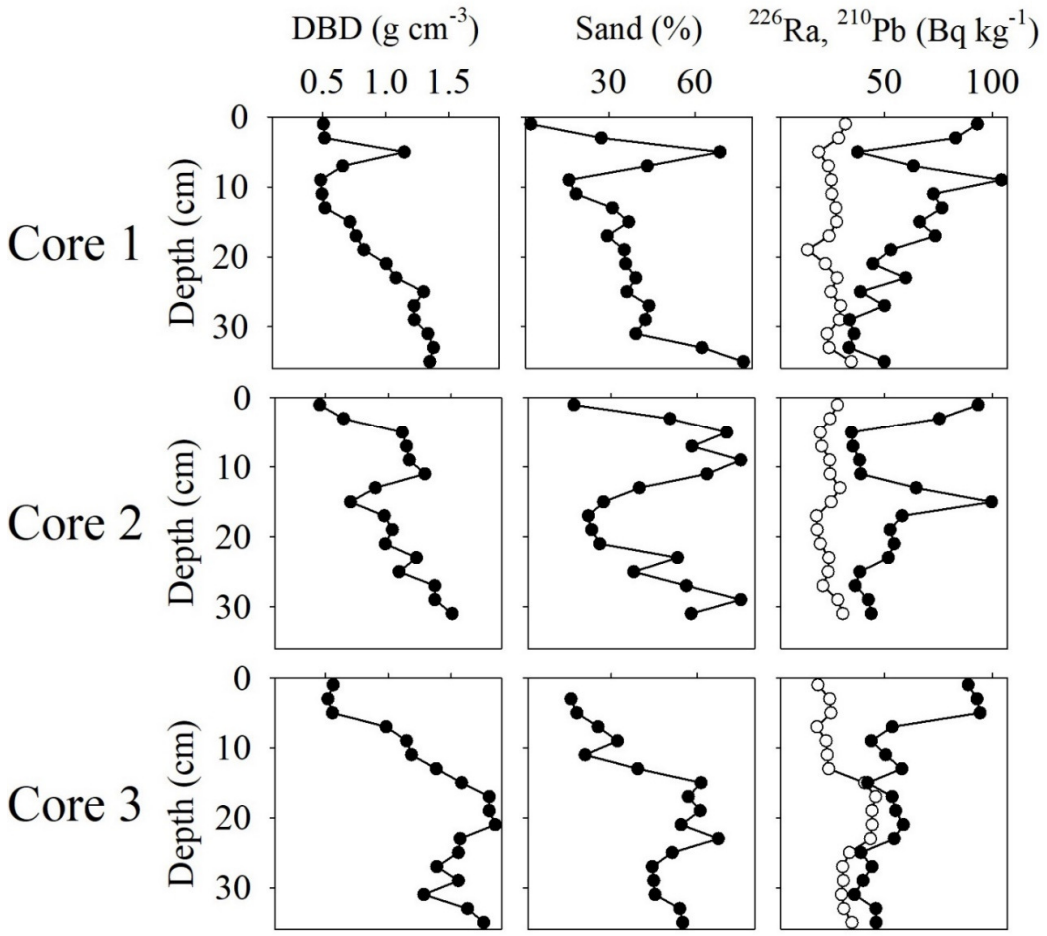

Figure 2. Dry bulk density (DBD), sand content, and ^{226}Ra (white circles) and ^{210}Pb (dark circles) activities plotted against depth from Hearnes Lake sediment cores.

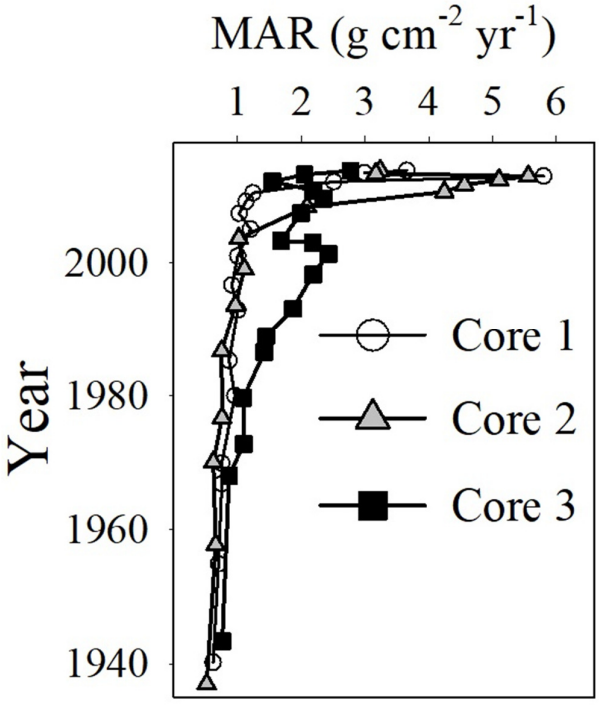

Figure 3. Mass accumulation rate (MAR, g cm^{-2} yr^{-1}) plotted against sediment ages calculated using the constant rate of supply (CRS) ^{210}Pb dating model (Appleby and Oldfield 1978) from Hearnes Lake sediment cores.

3.2 Metals and nutrient contents

The maximum contents found for Cd, Cu, Zn, P, and Fe were all observed in surface sediments (0-2 cm depth) of Core 1 (Figure 4). Contents of As in Core 2 and Core 3 were greatest at 25 cm depth. In Core 3, Cd contents followed a similar pattern to As contents, becoming elevated below 25 cm and reaching a maximum at 25 cm depth (Figure 4). The content of P in Core 1 and Core 3 was relatively steady before becoming elevated around 15 cm depth. In Core 3, contents of Al, Fe, Zn, Pb, and Cu appeared relatively depleted between depths of 17 to 23 cm, before becoming elevated above these depths. Core 2 displayed no obvious trends in metals contents, which may indicate mixing taking place in the sediment column at the location of sampling. Two trends were apparent in metals contents of Core 1 (top row, Figure 4). Contents Al, Pb, and Cu were elevated from 21 to 9 cm depth, then rapidly decrease leaving contents relatively depleted at 5 cm depth, followed by a sharp increase from 5 cm depth to the surface. Contents of Fe, As, Cd, Zn, and P followed similar trends to one another, rapidly increasing from 9 cm depth to surface sediments.

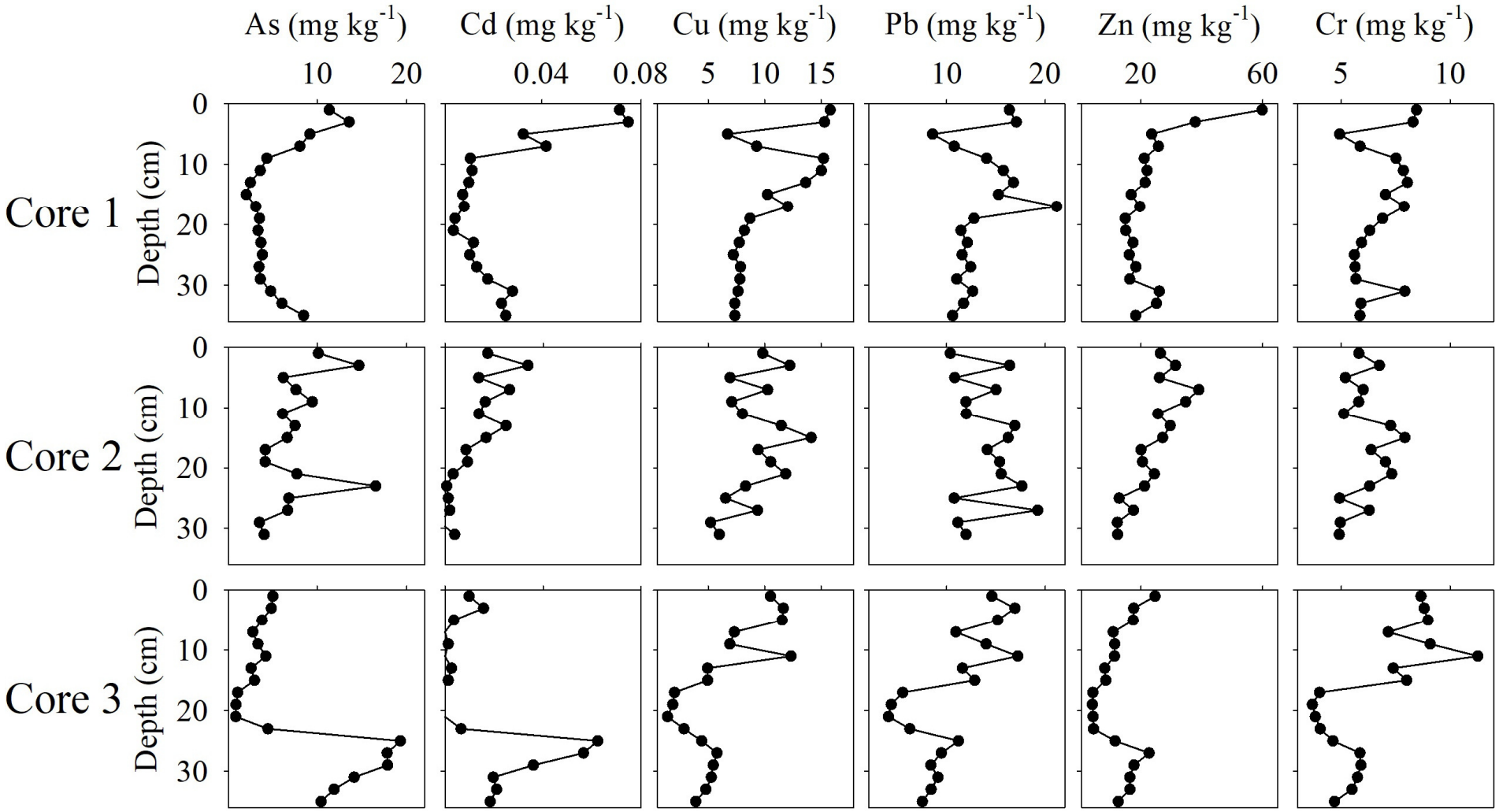

Figure 4. Contents of trace metals plotted against depth from Hearnes Lake sediment cores.

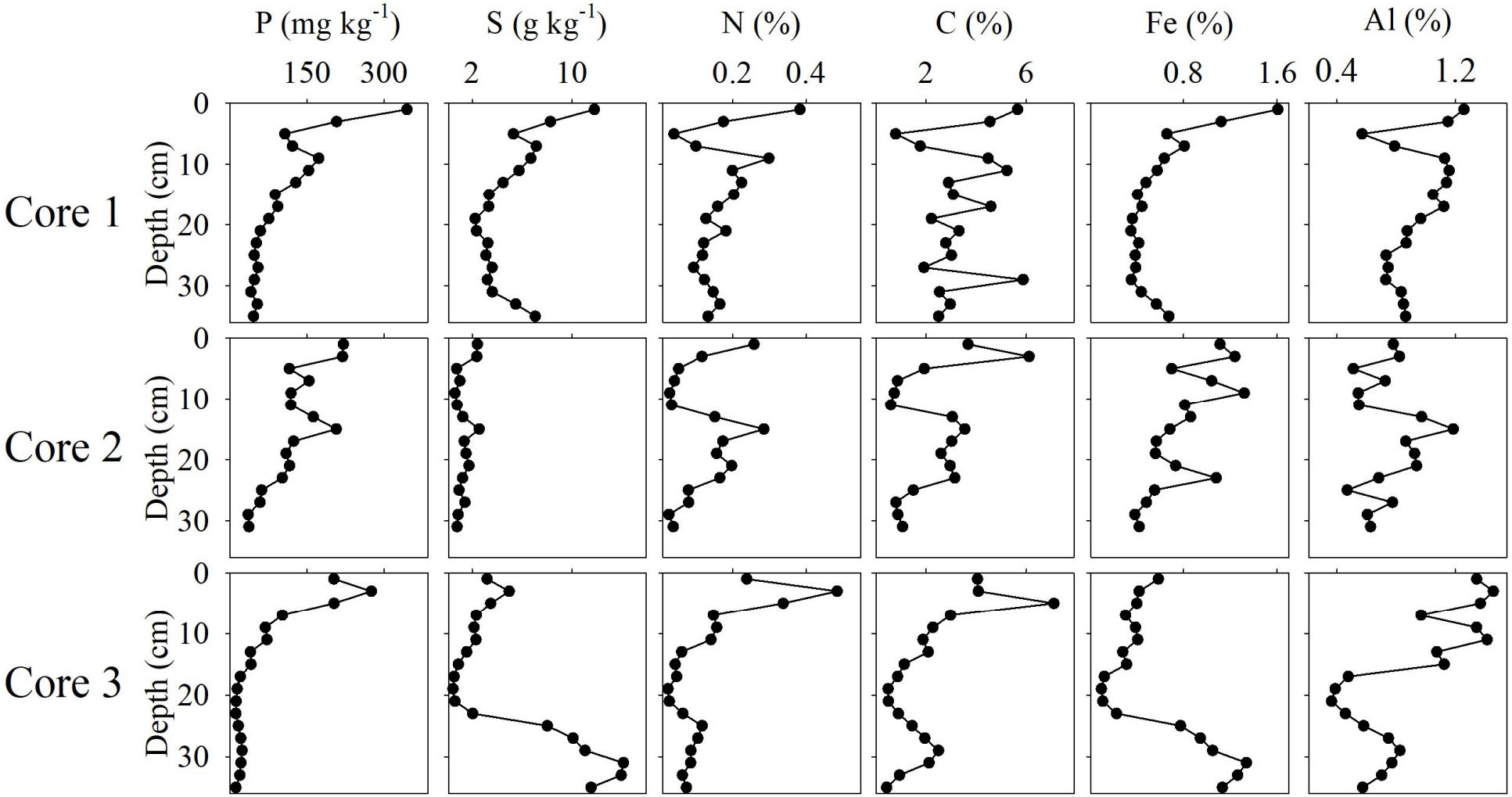

Figure 4 (cont.). Contents of major elements plotted against depth from Hearnes Lake sediment cores.

Surface Cd contents ranged from below detectable limit at Site 16 and to highest at Site 7 (0.52 mg kg^{-1}, Figure 5). Sites 10 and 11 (locations within Double Crossing Creek) and Sites 18 and 19 also showed relatively high levels of Cd (0.04 mg kg^{-1}). Content of Cu was highest at a location within the creek (Site 11). Content of Zn was highest at Site 7 (26.31 mg kg^{-1}). Content of P and Al were highest at Site 5 (352 mg kg^{-1} and 1.43 %, respectively).

Contents of As at Sites 12 and 13 exceeded the ANZECC sediment quality guideline (SQG) value of 20 mg kg^{-1} (37.24 and 22.61 mg kg^{-1}, respectively, Table 1). These coincided with high concentrations of Fe. Indeed, As and Fe were highly significantly correlated ($p < 0.001$) in these sediments (Table 2). Content of As in Core 3 at 25 cm depth was near the SQG guideline value (19.29 mg kg^{-1}), also occurring with high Fe (Figure 4) which may be interpreted as a natural rather than anthropogenic source. According to the SQG line of evidence framework, further analysis should be conducted to determine bioavailability of As in lake sediments (Simpson et al. 2013). The biogeochemical processes that may be governing the occurrence of As along the sediment column are discussed further below. No other samples exceeded ANZECC SQG values.

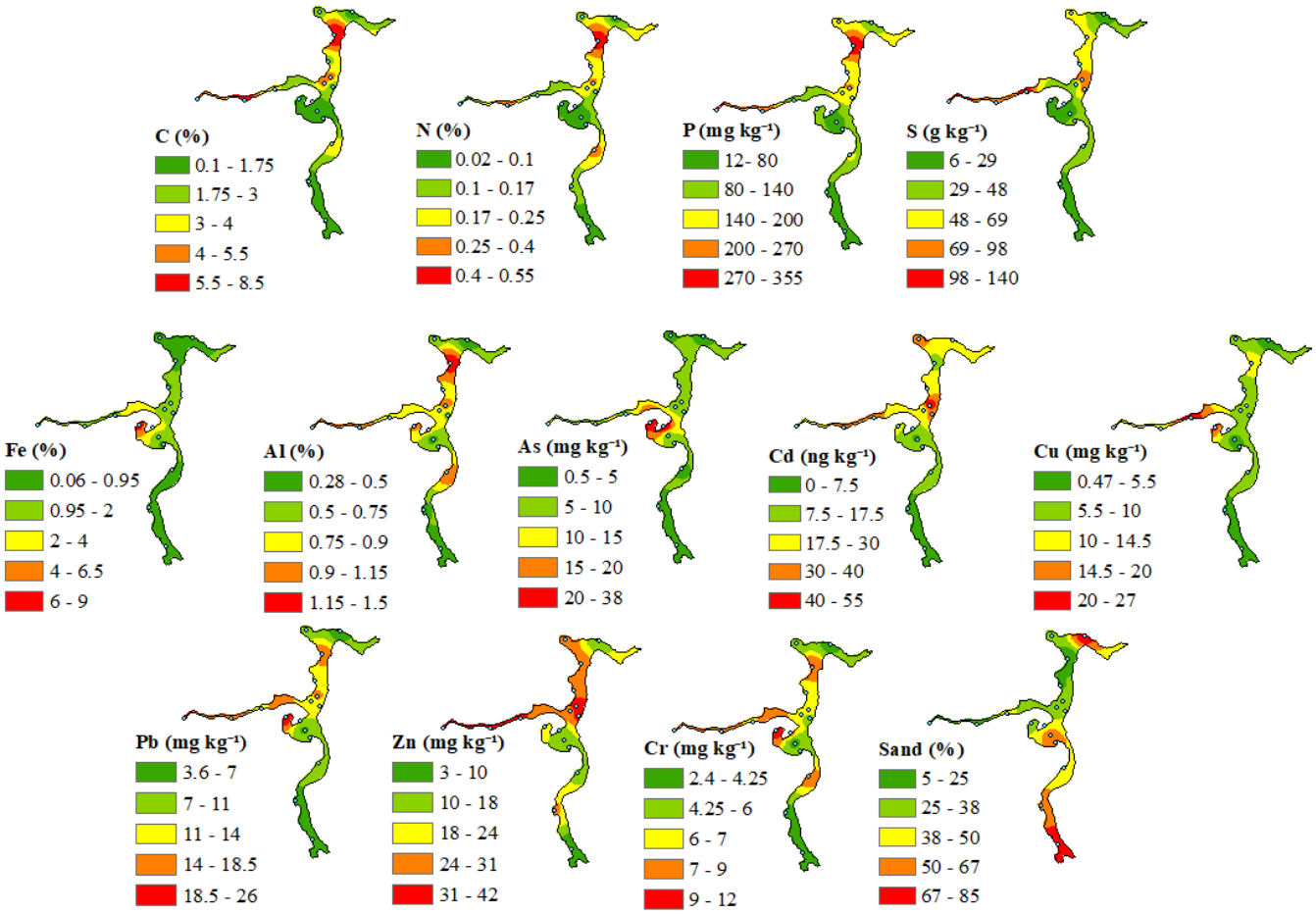

Figure 5. Contents of major elements and trace metals from surface sediment samples around Hearnes Lake. Dots are locations of surface sediment grabs. Red indicates highest contents found, while green areas indicate less concentrated areas. Only Sites 12 and 13 exceeded the ANZECC sediment quality guidelines (SQG) recommended value of 20 mg kg^{-1} for As (37.24 and 22.61 mg kg^{-1}, respectively, areas in red).

Table 1. Minimum, maximum, and mean (± standard error) contents of elements analysed in Hearnes Lake core and surface sediment samples compared to ANZECC sediment quality guideline (SQG) values. No samples exceeded ANZECC SQG High values. Only two of sixty nine samples exceeded SQG guideline values for As (surface samples at sites 12 and 13). Metals contents below the guideline values indicate no adverse ecosystem effects, while contents between SQG guideline and high values indicate possible adverse effects depending on toxicity and bioavailability of contaminant (Simpson et al. 2013). (BDL = below detectable limit)

Element	Units	ANZECC SQG	Sediment core observations (n=52)		Surface sediment observations (n=17)		
		Guideline - High	Min - Max	Mean ± SE	Min - Max	Mean ± S.E.	> SQG
As	mg kg^{-1}	20 - 70	2.1 - 19.3	6.7 ± 0.6	0.5 - 37.2	8.8 ± 2.1	2 out of 69
Cd	µg kg^{-1}	1500 - 10000	BDL - 70	20 ± 2.5	BDL - 520	200 ± 4	None
Cu	mg kg^{-1}	65 - 270	1.4 - 15.3	8.4 ± 0.5	0.5 - 22.5	9.5 ± 1.7	None
Pb	mg kg^{-1}	50 - 220	4.4 - 21.2	12.6 ± 0.5	3.7 - 25.7	11.6 ± 1.4	None
Zn	mg kg^{-1}	200 - 410	4.1 - 58.9	19.6 ± 1.4	3.4 - 40.8	24.3 ± 2.7	None
Cr	mg kg^{-1}	80 - 370	3.7 - 11.3	6.5 ± 0.2	2.4 - 11.9	6.3 ± 0.6	None
Fe	%	n/a - n/a	0.2 - 1.6	0.6 ± 0.05	0.1 - 8.7	1.5 ± 0.5	n/a
Al	%	n/a - n/a	0.4 - 1.4	0.9 ± 0.04	0.3 - 1.43	0.8 ± 0.1	n/a
S	mg kg^{-1}	n/a - n/a	460 - 14,142	3,947 ± 502	672 - 13,835	5208 ± 971	n/a
P	mg kg^{-1}	n/a - n/a	12 - 344	97 ± 10	12 - 352	145 ± 22	n/a
N	%	n/a - n/a	0 - 0.5	0.1 ± 0.01	0 - 0.5	0.2 ± 0.03	n/a
C	%	n/a - n/a	0.4 - 7.1	2.7 ± 0.2	0.2 - 7.9	2.4 ± 0.5	n/a

Table 2. Pearson's correlation coefficients of all elements from sediment samples. Bold numbers represent highly significant correlations (**p > 0.001**). n = 69

	As	*Cd*	*Cu*	*Pb*	*Zn*	*Cr*	*Fe*	*Al*	*S*	*P*	*N*	*C*
As	1.00											
Cd	**0.44**	1.00										
Cu	0.23	0.30	1.00									
Pb	0.21	0.13	**0.79**	1.00								
Zn	0.24	**0.65**	**0.60**	**0.47**	1.00							
Cr	0.22	0.08	**0.73**	**0.83**	0.33	1.00						
Fe	**0.69**	0.20	**0.46**	**0.42**	0.24	**0.42**	1.00					
Al	0.05	0.08	**0.62**	**0.71**	0.29	**0.90**	0.10	1.00				
S	0.32	**0.64**	0.23	0.04	**0.43**	0.11	0.11	0.18	1.00			
P	0.05	0.34	**0.60**	**0.53**	**0.74**	**0.50**	0.13	**0.57**	0.22	1.00		
C	-0.14	0.17	**0.48**	**0.44**	0.36	**0.49**	-0.16	**0.67**	0.14	**0.64**	1.00	
N	-0.06	0.20	**0.49**	**0.43**	**0.39**	**0.53**	-0.06	**0.71**	0.21	**0.75**	**0.78**	1.00

3.3 Enrichment factor and fluxes

Enrichment factor (EF) of Cd ranged from 0.2 to 2.2 in Core 1 (Figure 6). Core 2 displayed a greater enrichment since 2011, and reached a maximum EF > 6. Core 3 was moderately enriched compared to the other two cores, with an EF between 2 and 4 occurring between 1968 and 1987. A slight enrichment of As (EF maxima = 2.5) was only observed in Core 3 from 1968-1987 (Figure 6). Trends of enrichment in Core 1 and Core 3 ranged between 0.5 and 1.5, likely reflecting natural variation of accumulation of As in sediments from these locations (Zhang and Liu 2002). The maximum EF for As was at Site 13, which exceeded ANZECC SQG (using bottom core interval mean as baseline content, EF = 3.7). Moderate enrichment of Zn was found in Cores 1 and 2, while Core 3 displayed natural variations. No significant enrichments were noted for metals Cu, Pb, Cr, or Fe and were therefore not included in Figure 6.

Phosphorus enrichment was the most pronounced of any elements analysed. Moderate to severe P enrichment was observed in all three sediment cores. In Core 1, enrichment of P occurred after 2005 and reached severe to moderate enrichment in surface sediments (EF = 5). There were several pulses of P enrichment in Core 2. Phosphorus becomes slightly enriched from 1958 to 1977 (EF = 2.5), declines to EF ~2 from 1977 to 1994 and then increases again to ~3 from 1994 to 2004. From 2004 to 2008 the EF remains steady around 3.0. Post 2008, enrichment increases to the surface, with surface sediments being moderate to severely enriched (EF > 5). Core 3, taken from the mangrove island at the widening of Double Crossing Creek into the main estuary, displayed the most severe enrichment. EF began to elevate beginning in 2003 and reached a maximum of ~9 in near surface sediments.

Flux rates of most elements showed an increasing trend towards the surface (Figure 7), congruent with the increased mass accumulation rates in more recent sediments (Figure 3). Flux of P increased over 40-fold in Core 1. Phosphorus flux was greatest at the surface sediments of Core 1 (12.6 mg m^{-2} yr^{-1}). In Core 3 P flux was greatest in 2013 (5.6 mg m^{-2} yr^{-1}). Patterns of Cd flux resembled those of P in Cores 1 and 2. In Core 1, Cd flux increased sharply from 2010 to the present. In Core 2, Cd flux increased from 1987. Core 3 had the greatest Cd flux of 0.9 µg m^{-2} yr^{-1} deeper in the core. In Core 3 there was a trend of slightly elevated flux rates of Al between 2001 and 2010. The trend is the same for Cu, Cr, and Pb.

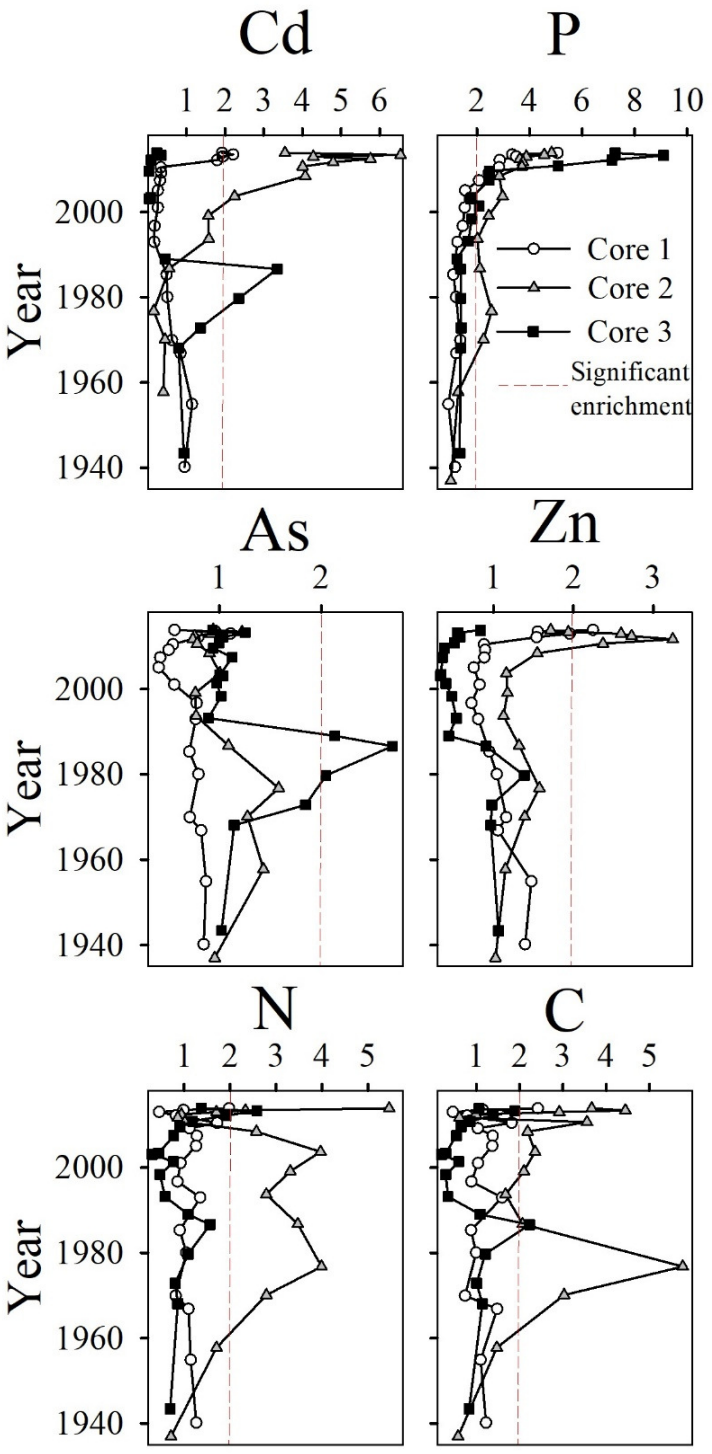

Figure 6. Enrichment factors (EF) of Cd, P, As, Zn, N, and C from Hearnes Lake sediment cores. EF values above 1 indicate anthropogenic sources of contaminants. EF above 2 was considered a significant enrichment (right side of red line) as the same amount of the contaminant was present from anthropogenic activities as was from natural amounts. EF above 5 indicates severe enrichment (Abrahim and Parker 2008). Metals were normalized to aluminium (Al) (Conrad et al. 2017).

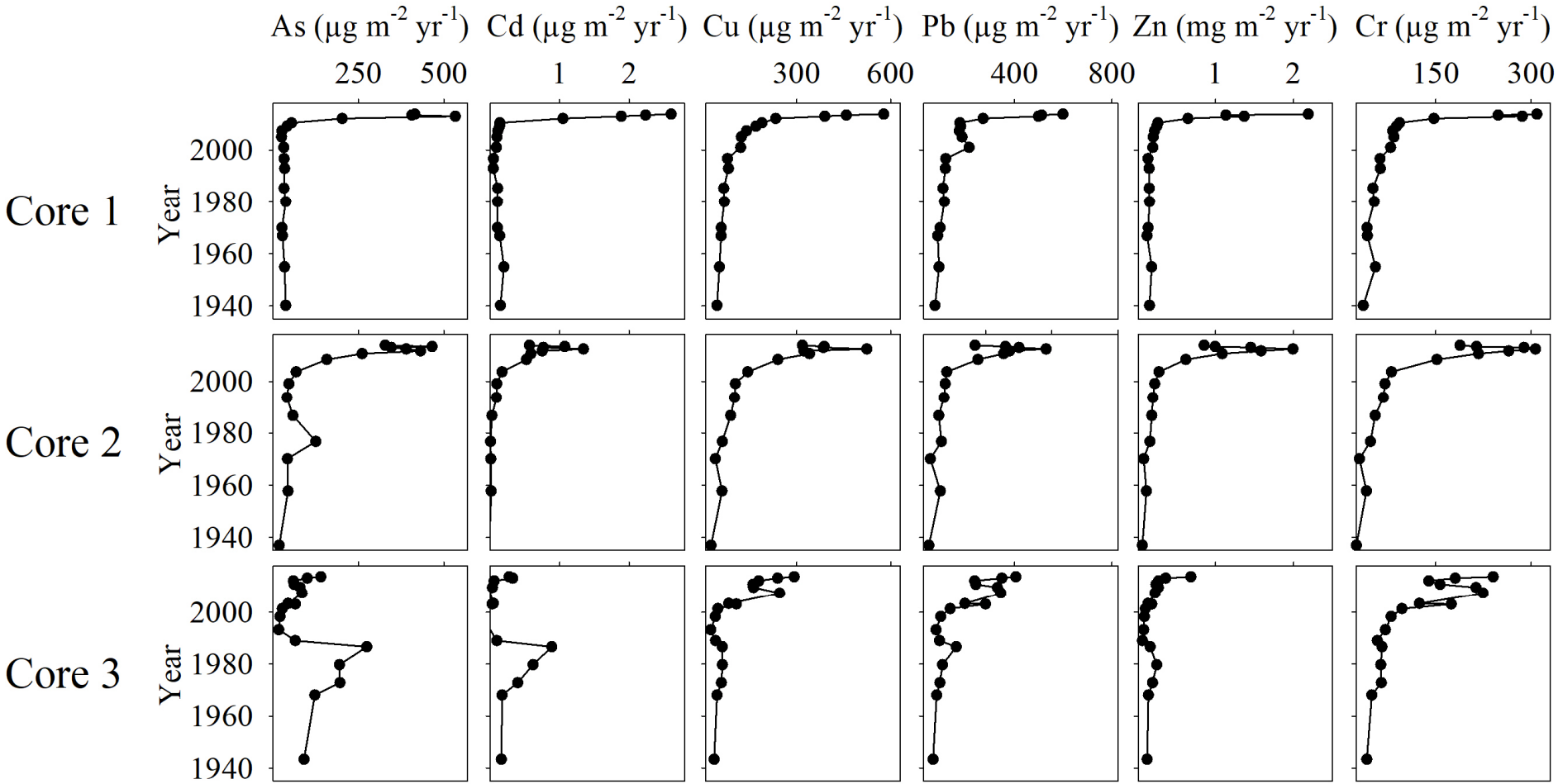

Figure 7. Sediment flux of all elements compared with sediment ages from Hearnes Lake sediment cores. Flux calculated as amount of contaminant present in sediment times sediment mass accumulation rate calculated using ^{210}Pb radionuclide counting. Flux values represent amount of contaminant entering sediment per area per time (µg m^{-2} yr^{-1} or mg m^{-2} yr^{-1} as denoted).

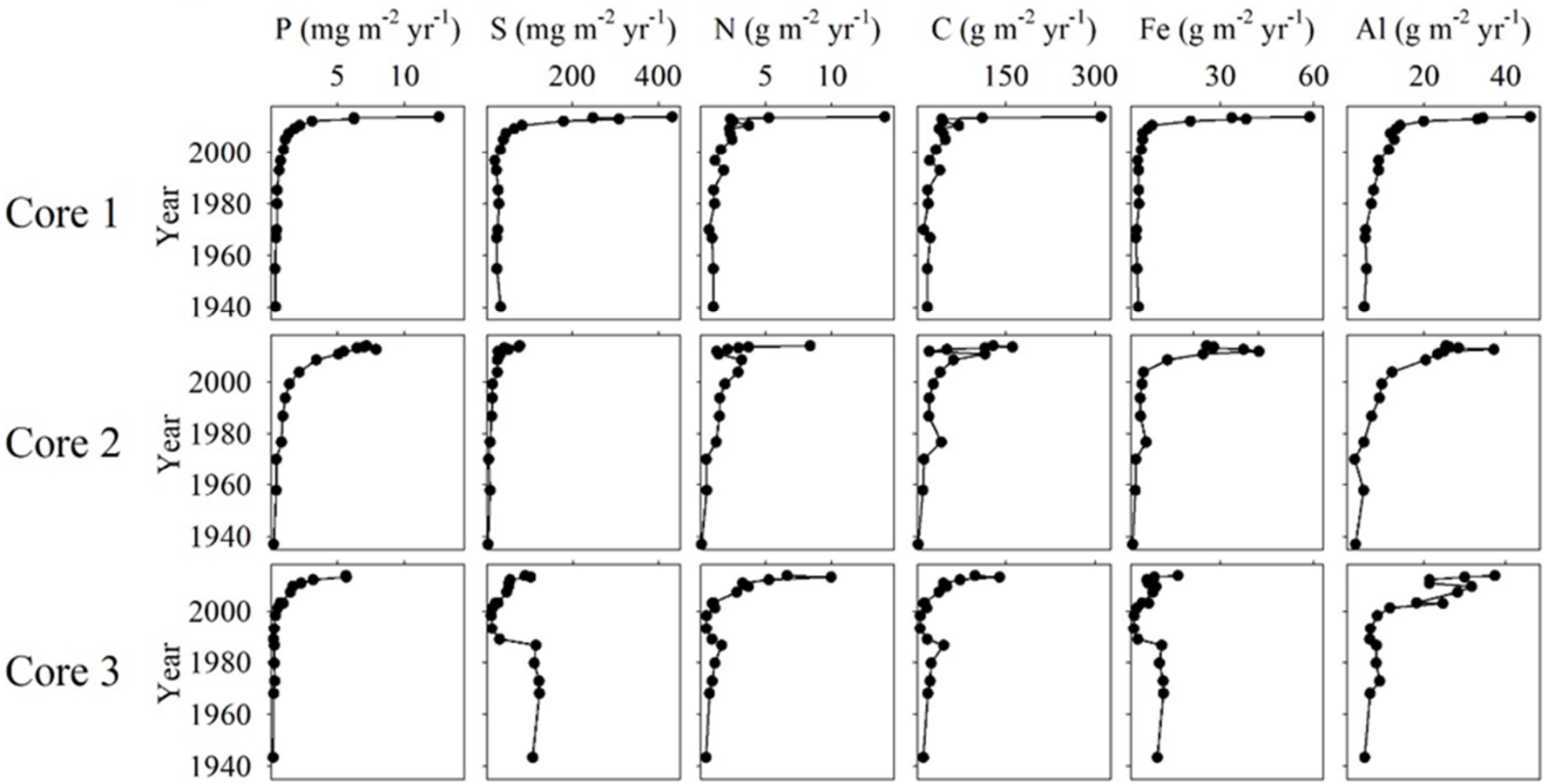

Figure 7 (cont.). Sediment flux of all elements compared with sediment ages from Hearnes Lake sediment cores. Flux calculated as amount of contaminant present in sediment times sediment mass accumulation rate calculated using ^{210}Pb radionuclide counting. Flux values represent amount of contaminant entering sediment per area per time (mg m^{-2} yr^{-1} or g m^{-2} yr^{-1} as denoted).

4. Discussion

4.1 Nutrients

The results of P enrichment and flux calculations imply anthropogenic alterations in the sediment quality of Hearnes Lake. The P EF in all cores exceeded 4 in the upper layers, with Core 3 showing the greatest enrichment (EF = 8.9). Average surface sediment sample (using bottom core interval means as baseline content, which are determined to be before agricultural activity in the basin) P enrichment was 3.5. Overall, surface sediments range from not enriched (EF < 1) to severe (EF > 5) (Yongming et al. 2006). Furthermore, the enrichment of Cd and Zn along the same timescale is a strong indication of a fertiliser source because P fertilisers often have high concentrations of Cd and Zn (Molina et al. 2009, Tang et al. 2010).

The dated sediment cores are useful when comparing P sediment accumulations to land use history. For example, all P fluxes and enrichments reached maxima post 2002, congruent with the timescale in the change of agricultural practices from banana to blueberry cultivation (Figure 8). Banana farm areal extent decreased in area after 1985, when P flux begins to elevate. Blueberry farm areal extent increased rapidly from 0.5 % in 2002 to 11 % in 2017, congruent with a rapid increase in P flux to younger sediments. The change in land use is the most likely explanation for the increased P flux to recent sediments of the estuary. The clearing of the steep, historically intensely fertilized banana farmland to blueberry farms beginning ~2002 may have promoted surface sediment erosion and subsequent downstream sediment transport and deposition in Hearnes Lake. This hypothesis is supported by the observed increase in sediment mass accumulation rate and general trend of rapidly increasing trace metal and nutrient fluxes in our sediment cores after 2004. Because the recent mass accumulation rates found in Hearnes Lake far surpass pre-agricultural rates, 1 g cm^{-2} yr^{-1} to over 5 g cm^{-2} yr^{-1}, respectively, siltation of this estuary has apparently increased as a result of the agricultural runoff as observed elsewhere (Hinderer 2012). The dated sediment cores in this study reveal a reasonable chronology of the trapping of P enriched sediments by the wetlands.

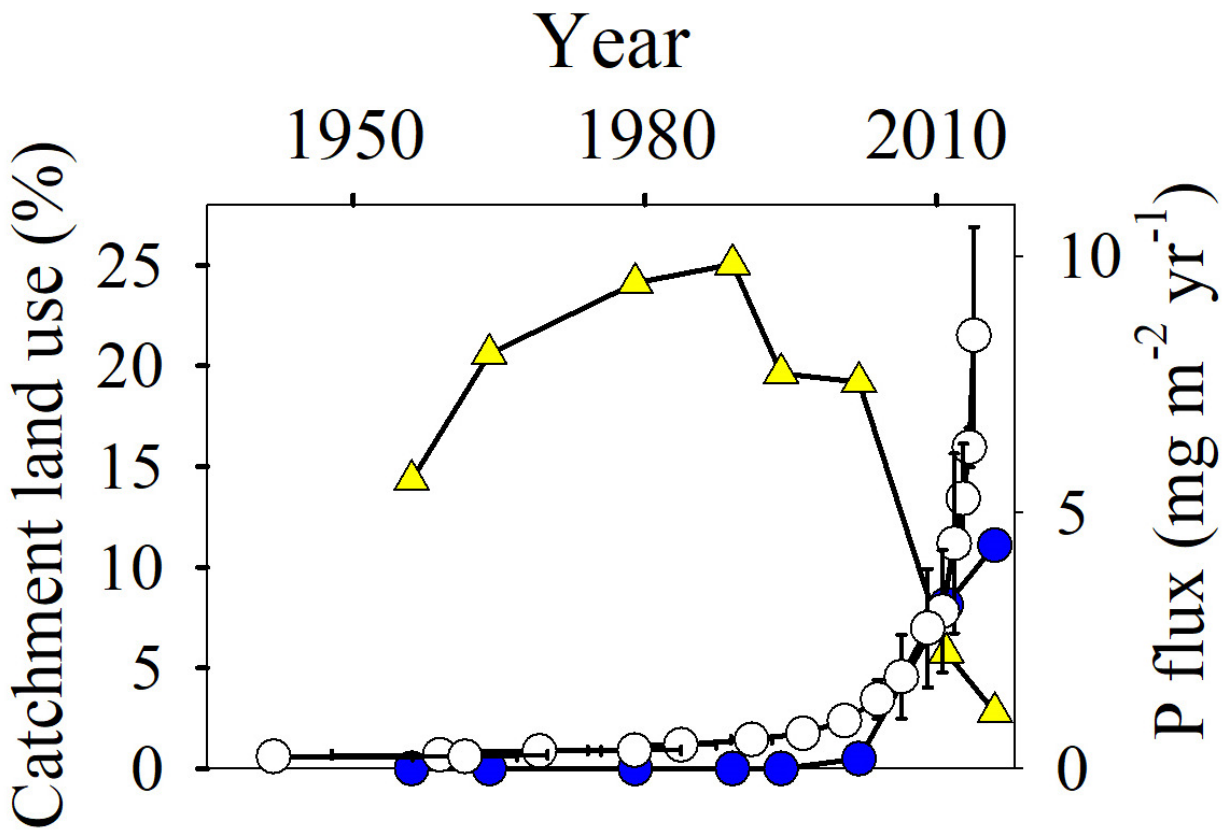

Figure 8. Catchment land use (%) from banana farms (yellow triangles) and blueberry farms (blue circles) from 1956 until 2017 compared with mean phosphorus (P) flux from 3 Hearnes Lake sediment cores. Farm area data was obtained from GIS layers from Coffs Harbour City Council and New South Wales Department of Primary Industries. Vertical error bars represent standard error in P flux. Horizontal errors represent standard error in ages of sediment.

By comparing the recommended fertiliser dosage (83 kg ha^{-2} yr^{-1}, Doughty et al. (1988)) to the accumulation rate of P in the estuary we can estimate the capability of the estuarine system to sequester P lost from agricultural practices. The spatial extent of blueberry cultivation in the basin increased from 56 ha in 2011 to 77 ha in 2017 (Figure 8). Assuming a constant rate of the suggested P fertiliser dosage, we estimate that there was between 4,648 – 6,391 kg P yr^{-1} applied to blueberry farms within the catchment for the years 2011 to 2017. Extrapolating our mean flux rates from the three sediment cores from 2011 (1.1 mg m^{-2} yr^{-1}) and 2017 (2.1 mg m^{-2} yr^{-1}) to the areal extent of wetlands (81 ha) yields estimates P burial estimates between 891 – 1,701 g yr^{-1} in Hearnes Lake wetlands. This sequestration by wetlands is equivalent to < 1 % of the estimated P applied to farms over this time. This may be an underestimation of the total estuarine systems capacity to sequester P as bare sediments can also be a sink for P (Pant and Reddy 2001). If we include the areal extent of the lake (bare sediments and wetlands, 197 ha) our burial rate estimate increases to 2.1 – 4.1 kg yr^{-1} P burial, which remains < 1 % of the total P fertiliser rate presumably applied to farms in the catchment. These calculations are based upon extreme assumptions that illustrate minimum and maximum scenarios and imply that most of the P from fertilization is retained in agricultural soils or taken up by the biota, with a relatively small fraction of P exported into the estuary being sequestered by the sediments or alternatively exported to the ocean.

Despite only a small fraction of fertilisers being lost to Hearnes Lake, the enrichment factor and flux rate estimates suggest that the sediment quality in Hearnes Lake has been anthropogenically modified from agricultural activity. The extent of contamination differs from that of other urban and more developed estuaries. The enrichments and fluxes of P reported in this work are greater than sediments from a geologically similar sampling location in coastal wetlands of Coffs Creek (~20 km south of Hearnes Lake, P EF = 2.2, Conrad et. al 2017). Phosphorus flux from Conrad et al. (2017) reached a maximum in surface sediments at 110 µg m^{-2} yr^{-1}. Furthermore, Borges et al. (2009) reported sediment P fluxes reaching maxima of 192 µg cm^{-2} $year^{-1}$ in a highly polluted estuary of Rio de Janeiro, Brazil and Surratt et al. (2008) reported sediment P accumulation ranged from 3 to 600 µg m^{-2} yr^{-1} in a eutrophic estuary of the southeastern United States. The P fluxes estimated for Hearnes Lake are orders of magnitude greater (mg compared to µg) than all these other impacted systems, reaching maxima of 13, 8, and 6 mg m^{-2} yr^{-1} in cores 1, 2, and 3, respectively. The intense agricultural use of this small basin has resulted in greater sediment P flux than reported in these other studies which, in some cases, were in highly polluted estuaries.

What are the implications of high P fluxes into Hearnes Lake sediments? Even though the wetland sediments here are shown to be a major sink for P, these systems may contribute to a P flow back to surface waters (Carpenter 2005), which could promote a persistent eutrophic state in Hearnes Lake. Half of sediment bound P buried in estuarine sediments may be recycled to surface waters as inorganic P, as observed in the Gulf of Saint Lawrence estuary, Canada (Sundby et al. 1992). When sediments saturate with P, porewater will release inorganic P into surface waters (Sundby et al. 1992), potentially driving dissolved P to exceed natural levels (Carpenter 2005). The recycling of P from sediments into surface waters can propagate a long term eutrophic state, even after input of P into the system has ceased (Carpenter 2005). Indeed, Rémi et al. (2015) found that wetland soils in an intensely cultivated catchment contributed more soluble P to surface waters than surface runoff in times of low flow. Therefore, the severely P enriched sediments of Hearnes Lake may continue to contribute to decreased water quality, even when allochthonous P inputs to the lake are decreased, although our study did not measure if this is currently occurring within Hearnes Lake.

While it is uncertain from our results whether sediments of Hearnes Lake are contributing to persistently degraded water quality, comparisons to the literature may be useful. For instance, other examples from the literature report much higher sediment P contents in persistently eutrophic lakes. For example, Ding et al. (2015) and Nürnberg et al. (2018) found average P sediment contents of 567 mg kg^{-1} and 1,471 mg kg^{-1}, respectively, in eutrophic lakes where sediment P contributed to decreased surface water quality. These contents are much greater than our mean P surface sediment content (including top interval of 3 cores) of 145 mg kg^{-1}. We note, however, that the P concentrations, enrichment factors and fluxes increased rapidly in the last decade and the blueberry industry is also predicted to continue expanding. Despite the uncertainty in whether the P sediment contents will contribute to decreased water quality in Hearnes Lake, these findings of large P burial in coastal wetlands are important as there are global trends of coastal agricultural development and estuarine eutrophication (Bennett et al. 2001, Tilman et al. 2001, Smith 2003).

While sediments are shown here to be a sink for anthropogenic P, the results suggest that these wetland sediments are not as efficient in sequestering N. Overall sediment cores were enriched with P (mean EF = 2.6) however, no overall enrichment of N was observed (mean EF = 1.5). This is likely because the interactions of groundwater and estuarine sediments

promote removal of N through denitrification (Xiao et al. 2018). Indeed, Xiao et al. (2018) estimated 2.07 g day^{-1} N loss from one cubic meter of mangrove sediments of an agriculturally impacted catchment, attributed to microbial denitrification and ammonium oxidation processes within the sediments. Our sediment flux rate of N (mean 2.44 mg m^{-2} yr^{-1} for three sediment cores) is considerably lower than the estimated sediment loss from Xiao et al. (2018). While our results agree with others that demonstrate the efficiency of wetland sediments as sinks for contaminants, especially P (Tam and Wong 1993, Dorioz et al. 1998), they also imply the removal of N from the sediment. Here, the sediment P contents indicate the affinity for P to bind to sediments rather than to stay dissolved in surface waters, and transferal of sediments enriched with P downstream of the source (Holtan et al. 1988, Baldwin et al. 2002). Earlier work showed significant fluxes of dissolved nitrate from blueberry farms on the Bucca Bucca catchment (White and Santos 2018). However, here the sediment N contents are lower than other anthropogenically affected wetland areas (Jennerjahn and Ittekkot 1997, Middelburg et al. 1997, Marchand et al. 2003), suggesting that N discharge into this basin is displaced into the atmosphere, exported to the coastal ocean, or incorporated into the biota (Herbert 1999).

4.2 Heavy metals

The grain size and Al content of Core 3 near Site 5 show this is an area of preferential deposition within this estuary. This may explain the enrichments of five metals noted along the sediment cores taken in this region of the estuary (Figure 6). Mild Zn enrichments were observed in Cores 1 and 2 (EF between 2 and 3.5). The timeline of Zn enrichments and flux increases are congruent with the increase in blueberry farming beginning ~2002. These observed increases in Zn enrichments may be from Zn polymer fungicides applied on berry farms of Australia (Simpson 2017) and/or from Zn associated with P fertilisers (Lambert et al. 2007). However, while there is evidence of increasing anthropogenic Zn in surficial sediments of Hearnes Lake estuary, the contents are low, especially when compared to other more urban estuaries. All samples (both core and surface) from Hearnes Lake contained less Zn than the mean Zn content of 79 mg kg^{-1} at the nearby (~20 km away), more urban influenced Coffs Creek wetlands (Conrad et al. 2017).

Elevated accumulation rates and moderate to severe enrichments of Cd were observed in sediment Cores 1 and 2 after year 2000 (Figures 6 and 7), congruent with blueberry horticulture expansion. Cadmium in surface sediments may be an indicator of the application

of P fertilisers (Lambert et al. 2007, Molina et al. 2009). Core 3 has Cd enrichment further down core (25 cm depth) and occurs with high content of S (Figure 4). This Cd enrichment at the deeper intervals along with S, likely driven by the mobility of S bound Cd in reduced (anoxic) layers of the sediment column (Rosenthal et al. 1995). While overall Cd accumulation has increased in the more recent intervals of Hearnes Lake estuary, the contents are not present in toxic amounts (Simpson et al. 2013).

Sediment Core 3, nearest to the depositional hotspot, as indicated by the lateral grain size distribution, provides evidence of fine grain sediments transported from along the drainage basin high in Cr and Cu. This is evidenced by an increase in Al flux rate from 2001 until 2011 at this site (Figure 7). On this same timescale there is a similar pattern in the increase of Cr and Cu flux. Because increased Al deposition can indicate downstream transport of sediments (Upadhyay and Gupta 1995, Sanders et al. 2010, Conrad and Sanders 2017), the increased Al, Cu, and Cr deposition detected along this sediment profile are likely from erosion of lithogenic material from the quarry or possibly soils contaminated with wood treatment products (chromated copper arsenic) from the sawmills that operated in the basin.

Contents of As are above SQG values in surface samples at Sites 12 and 13, but only mild enrichment was observed in sediment Core 3 (EF = 2.4, Figure 6) at 25 cm depth. This As may be from earlier anthropogenic activities in the basin, such as As pesticide use. Decrease of As occurs post 1987, congruent with global decreases in the use of As pesticides in the 1980s (Smith et al. 1998, Mandal and Suzuki 2002). However, this result may also be evidence of As mobility along the sediment, as As is influenced by changing geochemical conditions. For example, under anoxic conditions the chemical charge of As is reduced and As can desorb from sediments and enter porewater (Burton et al. 2008). Arsenic from more surficial sediments may have entered surface waters or migrated down the sediment column (Nikolaidis et al. 2004). Increased contents of Fe and S also occur with As at 25 cm depth in Core 3 (Figure 4). Fe and S together in anoxic (reducing) sediment conditions indicates pyrite (FeS) formation (Berner 1985). In anoxic sedimentary conditions when FeS is formed, reduced As may be incorporated into the FeS mineral matrix (Burton et al. 2014). These results demonstrate sulphate reduction and possible formation of arsenopyrite. Zn and Cd also occur at this depth in of Core 3 and are likely incorporated as pyritization of trace metals is common in mangrove sediments (Figure 4, Andrade et al. (2012), Kumar and Ramanathan

(2015)). However, re-oxidation of this layer may result in the release of As, Zn, Cd and acid volatile sulphate into surface waters if disturbed (Burton et al. 2008, Keene et al. 2010).

5. Conclusions

1) Sediment accumulation rates increased rapidly from 2004 to present, surpassing pre-agricultural rates by over five-fold and increasing the probability of estuarine siltation as an apparent result of the agricultural runoff.
2) Sediments were enriched in P up to 8 times greater than the natural values. Sediment accumulation of P has increased ~40-fold since the expansion of horticulture industry in the basin and is greater than nearby Coffs Creek urban estuary.
3) Two of sixty nine samples exceeded ANZECC SQG low range values for As, while no other samples exceeded ANZECC SQG values. Sediment trace metal observations indicated minor or moderate enrichment in As, Zn, and Cd. No trace metals analysed present a notable risk to estuary ecosystem health at this time.
4) Even though surface water N from blueberry farms was found to be high in our companion report (White et al. 2018), the sediment N did not reach similar enrichment, suggesting that N discharge from the basin is lost to the biota, ocean, or to the atmosphere.

   The major risk identified in this report relates to the release of sediment P to surface waters. Combined with dissolved nitrogen, the release of P from the sediment would enhance productivity and potentially drive eutrophication. Although no local data are available on how ecological communities are responding to P enrichments in sediments and dissolved N inputs, enclosed systems such as Hearnes Lakes are particularly vulnerable to eutrophication.

   We recommend catchment scale erosion control and nutrient management to retain particulate phosphorus and dissolved nitrogen on the farms.

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7. Appendices

Abbreviations:
ANZECC- Australian and New Zealand Environment Conservation Council
CRS- Constant rate of supply ^{210}Pb dating model
DBD- dry bulk density
SQG- soil quality guidelines
MAR- mass accumulation rate

Elements:
^{210}Pb- Lead-210 radioisotope
^{226}Ra- Radium-226 radioisotope
^{238}U- Uranium-238 radioisotope
Al- Aluminium
As- Arsenic
C- Carbon
Cd- Cadmium
Cr- Chromium
Cu-Copper
Fe- Iron
N- Nitrogen
P- Phosphorus
Pb-Lead
S- Sulphur
Zn-Zinc

Units:
Bq- Becquerel (measure of radioactivity; 1 decay per second)

Table A1- Sediment characteristics and trace metal and nutrient contents for Hearnes Lake sediment cores.

Sample ID and depth	DBD ($g\ cm^{-3}$)	Sand %	^{226}Ra ($Bq\ kg^{-1}$)	^{210}Pb ($Bq\ kg^{-1}$)	MAR ($g\ cm^{-2}\ yr^{-1}$)	As	Pb	Cd	Cr	Cu	Zn	S	P	Fe	Al	N	C
						($mg\ kg^{-1}$)								(%)			
Core 1 0-2	0.51	2.74	31.92	93.12	3.65	11.36	16.38	0.07	8.45	15.82	59.89	11815.11	344.42	1.61	1.26	0.38	8.48
Core 1 2-4	0.51	27.34	28.71	82.98	2.99	13.58	17.08	0.07	8.29	15.31	37.88	8283.47	207.80	1.12	1.15	0.17	3.69
Core 1 4-6	1.15	68.74	19.53	37.58	5.80	9.20	8.58	0.03	4.93	6.71	23.58	5315.27	107.34	0.66	0.57	0.04	0.73
Core 1 6-8	0.66	43.36	24.01	63.43	2.51	8.07	10.77	0.04	5.87	9.29	25.76	7154.42	122.17	0.81	0.79	0.10	1.74
Core 1 8-10	0.48	16.04	25.34	104.26	1.24	4.38	14.05	0.01	7.51	15.23	21.10	6713.54	172.99	0.64	1.13	0.30	5.71
Core 1 10-12	0.49	18.54	25.54	72.70	1.13	3.65	15.76	0.01	7.85	15.03	22.03	5764.90	153.48	0.58	1.16	0.20	3.34
Core 1 12-14	0.52	31.22	27.47	76.69	1.03	2.54	16.78	0.01	8.04	13.64	21.41	4486.06	128.27	0.48	1.14	0.22	4.38
Core 1 14-16	0.72	36.92	27.82	66.34	1.20	2.09	15.27	0.01	7.03	10.25	16.78	3353.73	88.21	0.41	1.05	0.20	4.00
Core 1 16-18	0.76	29.39	24.30	73.57	1.00	3.14	21.17	0.01	7.89	12.05	19.69	3330.43	93.44	0.45	1.12	0.16	3.24
Core 1 18-20	0.83	35.34	14.36	52.95	0.91	3.57	12.78	0.01	6.90	8.70	14.87	2244.31	76.24	0.36	0.97	0.13	2.38
Core 1 20-22	1.00	35.80	22.62	44.64	1.00	3.40	11.46	0.00	6.31	8.20	15.00	2348.24	59.67	0.35	0.87	0.18	3.88
Core 1 22-24	1.08	39.38	28.03	59.81	0.87	3.72	12.10	0.01	5.93	7.74	17.44	3265.74	51.80	0.42	0.87	0.12	2.12
Core 1 24-26	1.30	36.28	25.18	38.89	0.96	3.89	11.58	0.01	5.60	7.22	16.17	3104.42	47.77	0.39	0.73	0.12	2.02
Core 1 26-28	1.23	43.99	29.66	50.04	0.75	3.52	12.44	0.01	5.64	7.86	18.36	3605.23	55.18	0.39	0.75	0.09	1.54
Core 1 28-30	1.23	42.71	29.14	33.84	0.76	3.67	11.03	0.02	5.67	7.80	16.34	3223.59	48.02	0.35	0.73	0.12	3.01
Core 1 30-32	1.34	39.40	23.47	35.92	0.70	4.82	12.65	0.03	7.92	7.64	26.07	3611.67	41.39	0.44	0.83	0.15	2.55
Core 1 32-34	1.38	62.46	24.33	33.57	0.62	6.08	11.72	0.02	5.90	7.36	25.14	5499.25	53.71	0.57	0.85	0.17	2.89
Core 1 34-36	1.35	76.92	34.62	49.93	-	8.50	10.61	0.03	5.86	7.35	18.30	7069.27	46.59	0.68	0.86	0.13	2.40
Core 2 0-2	0.46	17.01	28.23	93.43	3.24	10.13	10.38	0.02	5.81	9.82	26.41	2419.15	220.92	1.11	0.78	0.26	3.97
Core 2 2-4	0.64	50.51	24.76	75.49	3.17	14.67	16.40	0.03	6.75	12.22	31.40	2374.09	219.41	1.24	0.82	0.12	5.08
Core 2 4-6	1.11	70.25	20.25	34.70	5.56	6.22	10.82	0.01	5.19	6.93	26.11	749.63	115.88	0.70	0.51	0.05	2.07
Core 2 6-8	1.15	58.20	20.89	35.40	5.10	7.64	15.02	0.03	6.01	10.27	39.04	1018.75	154.28	1.04	0.73	0.04	1.00
Core 2 8-10	1.17	75.20	24.59	38.48	4.56	9.47	11.96	0.02	5.80	7.09	34.73	615.50	119.27	1.32	0.54	0.03	0.46
Core 2 10-12	1.29	63.39	24.78	39.00	4.24	6.15	12.00	0.01	5.12	8.03	25.60	786.71	119.07	0.81	0.55	0.03	2.71
Core 2 12-14	0.90	39.82	29.38	64.67	2.09	7.53	16.92	0.02	7.27	11.48	29.66	1250.93	162.29	0.86	0.97	0.15	2.95
Core 2 14-16	0.70	27.33	25.28	99.69	1.02	6.66	16.25	0.02	7.92	14.13	27.15	2565.12	207.08	0.68	1.19	0.29	3.88
Core 2 16-18	0.97	22.04	18.54	58.22	1.11	4.21	14.13	0.01	6.37	9.43	20.04	1357.07	124.12	0.57	0.87	0.17	2.52
Core 2 18-20	1.03	23.18	18.84	52.67	0.97	4.20	15.39	0.01	7.03	10.53	20.54	1509.86	109.79	0.56	0.93	0.16	2.15
Core 2 20-22	0.98	26.01	20.23	54.51	0.75	7.74	15.53	0.00	7.32	11.86	24.43	1743.03	116.43	0.73	0.94	0.20	2.69
Core 2 22-24	1.22	53.15	24.25	51.81	0.76	16.54	17.64	0.00	6.30	8.31	21.18	1233.80	102.33	1.08	0.68	0.16	5.46
Core 2 24-26	1.09	37.88	23.90	38.60	0.62	6.84	10.77	0.00	4.93	6.52	12.85	948.34	61.97	0.55	0.47	0.08	1.97
Core 2 26-28	1.37	56.22	21.51	36.45	0.66	6.71	19.24	0.00	6.29	9.37	17.57	1426.61	58.89	0.48	0.78	0.08	1.59
Core 2 28-30	1.37	75.24	28.37	42.55	0.52	3.56	11.14	0.00	4.96	5.21	12.23	872.60	36.03	0.39	0.61	0.03	0.49
Core 2 30-32	1.51	57.91	30.67	43.91	-	4.09	11.98	0.00	4.91	5.98	12.35	786.91	37.34	0.42	0.63	0.04	0.87
Core 3 0-2	0.56	Lost	19.20	88.83	2.77	5.05	14.60	0.01	8.66	10.52	24.67	3200.50	202.40	0.59	1.35	0.24	3.53
Core 3 2-4	0.52	15.99	24.61	92.91	2.05	4.89	16.94	0.02	8.81	11.66	17.63	4975.12	275.21	0.42	1.46	0.49	6.80
Core 3 4-6	0.56	18.06	25.17	94.36	1.55	3.84	15.18	0.00	8.98	11.54	17.48	3490.05	202.82	0.40	1.37	0.34	4.70
Core 3 6-8	0.98	25.44	18.69	53.62	2.19	2.82	10.94	0.00	7.16	7.31	10.88	2339.47	102.46	0.31	0.97	0.15	2.06
Core 3 8-10	1.15	32.19	22.95	43.87	2.35	3.39	14.02	0.00	9.08	6.90	11.40	2151.74	69.27	0.39	1.34	0.16	2.15
Core 3 10-12	1.19	20.94	23.51	50.53	1.99	4.26	17.23	0.00	11.27	12.34	11.31	2305.10	72.36	0.41	1.42	0.14	1.88
Core 3 12-14	1.38	39.26	24.16	58.08	1.68	2.62	11.61	0.00	7.39	4.93	8.09	1558.60	40.54	0.28	1.08	0.06	0.77
Core 3 14-16	1.58	61.35	40.82	42.23	2.18	3.01	12.86	0.00	8.00	4.94	8.44	893.97	41.44	0.31	1.13	0.04	0.54
Core 3 16-18	1.80	56.87	45.91	53.59	2.42	1.13	5.56	0.00	4.01	2.00	4.20	552.23	20.73	0.13	0.48	0.05	0.69
Core 3 18-20	1.80	61.04	44.20	55.20	2.18	0.94	4.39	0.00	3.67	1.85	4.05	460.20	14.57	0.10	0.39	0.02	0.28
Core 3 20-22	1.85	54.40	44.32	58.81	1.87	0.91	4.10	0.00	3.81	1.38	4.27	615.21	12.72	0.11	0.36	0.03	0.31
Core 3 22-24	1.57	67.39	43.52	54.48	1.45	4.50	6.28	0.01	4.04	2.84	4.42	2045.00	11.95	0.23	0.46	0.06	1.23
Core 3 24-26	1.56	51.27	33.80	39.10	1.42	19.29	11.21	0.06	4.62	4.41	11.52	8028.56	16.76	0.78	0.58	0.12	3.19
Core 3 26-28	1.39	44.33	30.58	44.25	1.09	17.81	9.46	0.06	5.86	5.77	22.70	10098.55	21.69	0.94	0.75	0.10	2.22
Core 3 28-30	1.56	44.82	30.92	40.06	1.10	17.86	8.40	0.04	5.90	5.44	17.71	11066.19	0.09	1.05	0.83	2.05	2.05
Core 3 30-32	1.28	45.31	30.07	36.04	0.87	14.14	9.13	0.02	5.75	5.27	16.35	14142.00	0.09	1.34	0.77	2.17	2.17
Core 3 32-34	1.63	53.92	31.18	46.03	0.76	11.89	8.43	0.02	5.49	4.79	16.37	13969.30	0.06	1.26	0.70	1.45	1.45
Core 3 34-36	1.76	54.99	34.91	46.13	-	10.44	7.55	0.02	4.69	3.88	12.56	11550.47	0.07	1.13	0.57	1.42	1.42

Table A2- Sediment mass accumulation rate with trace metal and nutrient fluxes for Hearnes Lake sediment cores.

Sample ID and depth	MAR ($g\ cm^{-2}\ yr^{-1}$)	As	Pb	Cd	Cr	Cu	Zn	S	P	Fe	Al	N	C
		($\mu g\ m^{-2}\ yr^{-1}$)					($mg\ m^{-2}\ yr^{-1}$)			($g\ m^{-2}\ yr^{-1}$)			
Core 1 0-2	3.65	415.06	598.37	2.61	308.89	577.87	2.19	431.72	12.58	58.69	46.01	14.01	309.86
Core 1 2-4	2.99	406.20	510.81	2.24	247.96	457.98	1.13	247.74	6.21	33.55	34.41	5.23	110.27
Core 1 4-6	5.80	533.48	497.78	1.89	285.82	389.32	1.37	308.37	6.23	38.21	33.04	2.32	42.17
Core 1 6-8	2.51	202.58	270.29	1.05	147.23	233.19	0.65	179.59	3.07	20.28	19.82	2.50	43.56
Core 1 8-10	1.24	54.37	174.48	0.14	93.29	189.12	0.26	83.38	2.15	7.90	14.02	3.71	70.86
Core 1 10-12	1.13	41.32	178.17	0.13	88.80	169.97	0.25	65.19	1.74	6.51	13.11	2.25	37.74
Core 1 12-14	1.03	26.07	172.10	0.11	82.41	139.87	0.22	46.00	1.32	4.93	11.70	2.30	44.92
Core 1 14-16	1.20	25.10	183.57	0.10	84.55	123.22	0.20	40.33	1.06	4.91	12.61	2.44	48.13
Core 1 16-18	1.00	31.55	212.63	0.09	79.24	121.09	0.20	33.46	0.94	4.48	11.28	1.60	32.57
Core 1 18-20	0.91	32.46	116.31	0.05	62.77	79.21	0.14	20.43	0.69	3.31	8.80	1.16	21.67
Core 1 20-22	1.00	34.13	114.96	0.04	63.28	82.22	0.15	23.55	0.60	3.53	8.77	1.82	38.96
Core 1 22-24	0.87	32.30	104.99	0.11	51.49	67.18	0.15	28.34	0.45	3.63	7.53	1.05	18.37
Core 1 24-26	0.96	37.31	111.00	0.10	53.71	69.16	0.16	29.76	0.46	3.72	7.02	1.13	19.37
Core 1 26-28	0.75	26.41	93.48	0.10	42.35	59.03	0.14	27.09	0.41	2.95	5.61	0.70	11.54
Core 1 28-30	0.76	27.70	83.26	0.14	42.84	58.92	0.12	24.34	0.36	2.68	5.51	0.93	22.72
Core 1 30-32	0.70	33.76	88.68	0.20	55.49	53.54	0.18	25.32	0.29	3.08	5.85	1.03	17.89
Core 1 32-34	0.62	37.50	72.36	0.15	36.44	45.42	0.16	33.94	0.33	3.51	5.25	1.02	17.87
Core 2 0-2	3.24	328.14	336.02	0.56	188.17	318.16	0.86	78.34	7.15	36.02	25.29	8.37	128.69
Core 2 2-4	3.17	465.12	520.10	1.07	214.11	387.54	1.00	75.28	6.96	39.32	26.10	3.69	160.96
Core 2 4-6	5.56	345.73	601.77	0.76	288.61	385.16	1.45	41.68	6.44	38.90	28.39	2.93	114.95
Core 2 6-8	5.10	389.60	766.19	1.34	306.46	523.93	1.99	51.97	7.87	53.09	37.08	2.11	50.83
Core 2 8-10	4.56	431.63	545.37	0.75	264.58	323.14	1.58	28.07	5.44	60.16	24.80	1.29	21.03
Core 2 10-12	4.24	260.85	509.19	0.59	217.26	340.81	1.09	33.38	5.05	34.44	23.27	1.43	114.80
Core 2 12-14	2.09	157.44	353.72	0.52	151.89	239.90	0.62	26.15	3.39	18.01	20.33	3.17	61.67
Core 2 14-16	1.02	67.81	165.47	0.17	80.64	143.87	0.28	26.12	2.11	6.97	12.08	2.91	39.52
Core 2 16-18	1.11	46.62	156.27	0.09	70.43	104.32	0.22	15.01	1.37	6.29	9.57	1.92	27.87
Core 2 18-20	0.97	40.58	148.82	0.09	67.99	101.85	0.20	14.60	1.06	5.43	8.95	1.51	20.80
Core 2 20-22	0.75	58.24	116.94	0.02	55.10	89.29	0.18	13.12	0.88	5.52	7.06	1.49	20.29
Core 2 22-24	0.76	125.13	133.47	0.00	47.65	62.88	0.16	9.33	0.77	8.18	5.16	1.25	41.34
Core 2 24-26	0.62	42.30	66.62	0.01	30.47	40.36	0.08	5.87	0.38	3.42	2.90	0.49	12.18
Core 2 26-28	0.66	44.14	126.54	0.01	41.36	61.62	0.12	9.38	0.39	3.18	5.11	0.53	10.44
Core 2 28-30	0.52	18.36	57.46	-0.01	25.57	26.86	0.06	4.50	0.19	1.99	3.12	0.13	2.51
Core 3 0-2	2.77	140.05	404.97	0.27	240.24	291.92	0.68	88.78	5.61	16.27	37.32	6.62	97.93
Core 3 2-4	2.05	100.17	347.29	0.32	180.63	238.99	0.36	102.00	5.64	8.66	29.90	9.94	139.41
Core 3 4-6	1.55	59.50	235.30	0.06	139.16	178.91	0.27	54.10	3.14	6.23	21.24	5.24	72.90
Core 3 6-8	2.19	61.78	240.11	0.00	157.01	160.34	0.24	51.33	2.25	6.72	21.26	3.24	45.13
Core 3 8-10	2.35	79.57	329.16	0.03	213.23	162.05	0.27	50.53	1.63	9.17	31.57	3.68	50.59
Core 3 10-12	1.99	84.80	342.93	0.00	224.32	245.60	0.23	45.89	1.44	8.16	28.19	2.80	37.33
Core 3 12-14	1.68	44.10	195.59	0.04	124.46	83.08	0.14	26.25	0.68	4.75	18.12	1.03	13.03
Core 3 14-16	2.18	65.52	280.15	0.03	174.44	107.59	0.18	19.48	0.90	6.86	24.53	0.94	11.80
Core 3 16-18	2.42	27.27	134.63	-0.06	97.05	48.44	0.10	13.38	0.50	3.03	11.54	1.14	16.80
Core 3 18-20	2.18	20.51	95.89	-0.04	80.18	40.41	0.09	10.05	0.32	2.18	8.47	0.52	6.11
Core 3 20-22	1.87	17.07	76.63	0.00	71.15	25.80	0.08	11.49	0.24	2.07	6.78	0.51	5.74
Core 3 22-24	1.45	65.13	90.83	0.09	58.41	41.13	0.06	29.59	0.17	3.31	6.61	0.93	17.75
Core 3 24-26	1.42	274.24	159.37	0.89	65.68	62.68	0.16	114.15	0.24	11.03	8.25	1.66	45.31
Core 3 26-28	1.09	194.41	103.28	0.62	63.94	62.97	0.25	110.21	0.24	10.31	8.17	1.14	24.25
Core 3 28-30	1.10	196.03	92.22	0.40	64.78	59.72	0.19	121.43	0.27	11.52	9.06	0.94	22.55
Core 3 30-32	0.87	122.48	79.11	0.17	49.79	45.65	0.14	122.52	0.19	11.59	6.68	0.74	18.77
Core 3 32-34	0.76	90.61	64.23	0.16	41.85	36.47	0.12	106.43	0.15	9.62	5.35	0.48	11.01

Table A3- Trace metal and nutrient enrichment factors from Hearnes Lake sediment cores. Metals normalized to Al contents from bottom of sediment core.

Sample ID and depth	As	Pb	Cd	Cr	Cu	Zn	S	P	Fe	N	C
Core 1 0-2	0.92	1.06	1.92	0.99	1.48	2.25	1.15	5.07	1.63	1.98	2.42
Core 1 2-4	1.20	1.21	2.21	1.06	1.56	1.55	0.88	3.35	1.25	0.99	1.15
Core 1 4-6	1.64	1.23	1.94	1.28	1.38	1.96	1.14	3.50	1.48	0.46	0.46
Core 1 6-8	1.04	1.11	1.79	1.10	1.38	1.54	1.11	2.87	1.31	0.82	0.79
Core 1 8-10	0.39	1.01	0.34	0.98	1.59	0.88	0.73	2.84	0.72	1.72	1.82
Core 1 10-12	0.32	1.11	0.35	1.00	1.52	0.90	0.61	2.46	0.64	1.12	1.03
Core 1 12-14	0.23	1.20	0.31	1.04	1.40	0.89	0.48	2.09	0.54	1.28	1.38
Core 1 14-16	0.20	1.19	0.26	0.99	1.15	0.76	0.39	1.56	0.50	1.26	1.37
Core 1 16-18	0.28	1.53	0.26	1.04	1.26	0.83	0.36	1.54	0.51	0.92	1.04
Core 1 18-20	0.38	1.08	0.18	1.05	1.06	0.73	0.28	1.46	0.48	0.86	0.89
Core 1 20-22	0.40	1.07	0.17	1.06	1.10	0.81	0.33	1.27	0.51	1.35	1.60
Core 1 22-24	0.44	1.14	0.49	1.01	1.05	0.95	0.46	1.11	0.62	0.91	0.88
Core 1 24-26	0.54	1.29	0.51	1.13	1.16	1.04	0.52	1.21	0.68	1.04	0.99
Core 1 26-28	0.48	1.36	0.63	1.11	1.24	1.16	0.59	1.37	0.67	0.81	0.74
Core 1 28-30	0.51	1.23	0.84	1.15	1.26	1.06	0.54	1.22	0.62	1.10	1.48
Core 1 30-32	0.59	1.23	1.15	1.40	1.08	1.48	0.53	0.92	0.67	1.14	1.10
Core 1 32-34	0.73	1.12	0.95	1.03	1.02	1.40	0.79	1.17	0.86	1.26	1.22
Core 1 34-36	1	1	1	1	1	1	1	1	1	1	1
Core 2 0-2	1.99	0.70	3.55	0.95	1.32	1.72	2.47	4.75	2.12	5.46	3.66
Core 2 2-4	2.74	1.04	6.54	1.05	1.56	1.94	2.30	4.48	2.24	2.33	4.44
Core 2 4-6	1.87	1.11	4.28	1.30	1.42	2.60	1.17	3.81	2.03	1.70	2.92
Core 2 6-8	1.61	1.08	5.76	1.06	1.48	2.73	1.12	3.57	2.13	0.94	0.99
Core 2 8-10	2.67	1.15	4.80	1.36	1.37	3.24	0.90	3.69	3.60	0.86	0.61
Core 2 10-12	1.72	1.15	4.00	1.19	1.54	2.37	1.14	3.65	2.20	1.02	3.55
Core 2 12-14	1.19	0.91	4.07	0.96	1.24	1.55	1.03	2.80	1.32	2.57	2.18
Core 2 14-16	0.86	0.72	2.25	0.85	1.25	1.16	1.72	2.93	0.86	3.97	2.36
Core 2 16-18	0.75	0.86	1.57	0.94	1.14	1.18	1.25	2.41	0.98	3.31	2.10
Core 2 18-20	0.70	0.87	1.58	0.97	1.19	1.13	1.30	1.99	0.90	2.79	1.67
Core 2 20-22	1.27	0.87	0.56	1.00	1.33	1.32	1.48	2.08	1.16	3.47	2.07
Core 2 22-24	3.72	1.35	0.15	1.18	1.28	1.58	1.44	2.52	2.35	3.99	5.77
Core 2 24-26	2.24	1.20	0.45	1.34	1.46	1.39	1.61	2.22	1.75	2.79	3.03
Core 2 26-28	1.33	1.30	0.40	1.04	1.27	1.15	1.47	1.27	0.93	1.70	1.47
Core 2 28-30	0.90	0.96	-0.52	1.05	0.90	1.03	1.15	1.00	0.94	0.71	0.58
Core 2 30-32	1	1	1	1	1	1	1	1	1	1	1
Core 3 0-2	0.21	0.83	0.23	0.79	1.16	0.84	0.12	7.12	0.22	1.38	1.06
Core 3 2-4	0.18	0.88	0.34	0.74	1.18	0.55	0.17	8.93	0.15	2.58	1.89
Core 3 4-6	0.15	0.84	0.08	0.80	1.24	0.58	0.13	7.00	0.15	1.91	1.39
Core 3 6-8	0.16	0.86	0.00	0.90	1.11	0.51	0.12	5.00	0.16	1.18	0.86
Core 3 8-10	0.14	0.79	0.03	0.83	0.76	0.39	0.08	2.44	0.15	0.90	0.65
Core 3 10-12	0.17	0.92	0.00	0.97	1.29	0.37	0.08	2.42	0.15	0.77	0.54
Core 3 12-14	0.13	0.82	0.08	0.84	0.68	0.34	0.07	1.78	0.13	0.44	0.29
Core 3 14-16	0.15	0.87	0.04	0.87	0.65	0.34	0.04	1.74	0.14	0.30	0.19
Core 3 16-18	0.13	0.89	-0.17	1.03	0.62	0.40	0.06	2.06	0.13	0.77	0.59
Core 3 18-20	0.13	0.86	-0.16	1.16	0.71	0.48	0.06	1.78	0.13	0.48	0.29
Core 3 20-22	0.14	0.86	0.00	1.28	0.56	0.54	0.08	1.66	0.16	0.58	0.34
Core 3 22-24	0.54	1.04	0.45	1.08	0.92	0.44	0.22	1.24	0.25	1.09	1.09
Core 3 24-26	1.83	1.47	3.35	0.97	1.12	0.91	0.69	1.37	0.68	1.56	2.23
Core 3 26-28	1.31	0.96	2.35	0.96	1.14	1.39	0.67	1.37	0.64	1.09	1.20
Core 3 28-30	1.19	0.77	1.36	0.87	0.97	0.98	0.67	1.39	0.64	0.81	1.01
Core 3 30-32	1.01	0.90	0.80	0.91	1.01	0.97	0.91	1.36	0.88	0.86	1.14
Core 3 32-34	0.93	0.91	0.93	0.96	1.01	1.06	0.99	1.34	0.91	0.70	0.83
Core 3 34-36	1	1	1	1	1	1	1	1	1	1	1

Table A4- Location of Hearnes Lake surface sediment samples with sand, trace metal, and nutrient contents. Samples 1-3 are top layer of sediment cores.

Sample ID	Lat (°S)	Longitude (°E)	Sand %	As	Pb	Cd	Cr	Cu	Zn	S	P	Fe	Al	N	C
				(mg kg^{-1})								(%)			
1	-30.123888	153.195873	2.74	11.36	16.38	0.07	8.45	15.82	59.89	11815.11	344.42	1.61	1.26	0.38	8.48
2	-30.123600	153.195862	17.01	10.13	10.38	0.02	5.81	9.82	26.41	2419.15	220.92	1.11	0.78	0.26	3.97
3	-30.123471	153.197855	Lost	5.05	14.60	0.01	8.66	10.52	24.67	3200.50	202.40	0.59	1.35	0.24	3.53
4	-30.120257	153.115640	81.24	3.53	3.66	0.02	3.16	2.26	10.47	1551.21	89.95	0.33	0.28	0.07	0.91
5	-30.121387	153.197986	5.62	7.12	17.04	0.01	9.16	13.14	26.76	4972.51	351.64	0.70	1.43	0.55	8.31
6	-30.134722	153.198333	22.63	7.37	12.00	0.02	6.28	7.88	29.49	6037.07	165.95	0.89	0.85	0.19	2.66
7	-30.123471	153.197761	28.70	10.03	15.46	0.05	7.05	10.42	37.27	9953.65	220.60	1.26	1.01	0.28	4.73
8	-30.123724	153.197388	28.70	7.32	12.11	0.02	6.02	8.14	27.11	2560.43	184.14	0.93	0.84	0.25	4.71
9	-30.124519	153.190237	20.31	9.66	19.06	0.02	8.89	14.17	40.79	13834.68	287.52	2.00	1.01	0.06	5.36
10	-30.124569	153.192884	11.90	8.38	14.58	0.04	8.07	12.50	37.58	8262.34	261.97	1.30	1.03	0.30	6.53
11	-30.124071	153.194617	43.63	8.77	13.16	0.04	6.63	26.31	33.87	11434.11	107.66	1.25	0.80	0.15	3.22
12	-30.124636	153.196757	36.10	37.24	11.05	0.01	8.09	8.83	11.82	1192.84	50.14	4.07	1.03	0.06	0.56
13	-30.124502	153.195957	27.34	22.61	25.74	0.02	11.87	22.51	22.84	968.02	96.25	8.72	0.93	0.08	0.77
14	-30.125492	153.197350	56.62	5.48	8.85	0.01	5.10	4.80	14.03	3555.45	79.01	0.66	0.68	0.09	1.01
15	-30.126736	153.197799	44.01	3.38	10.46	0.01	7.90	8.40	16.71	4487.82	146.95	0.43	1.06	0.29	3.76
16	-30.130471	153.197485	84.66	0.54	3.85	0.00	2.41	0.47	3.38	671.64	12.24	0.06	0.33	0.03	0.20
17	-30.128551	153.196505	53.58	1.46	4.33	0.00	3.72	3.71	25.24	2482.53	70.44	0.16	0.45	0.12	1.51
18	-30.123922	153.197877	39.80	7.53	11.37	0.04	5.15	7.49	34.02	8128.42	143.21	1.12	0.68	0.11	1.46
19	-30.120224	153.197132	26.34	4.09	8.89	0.04	4.37	6.88	30.75	6939.92	150.68	0.80	0.63	0.16	2.55
20	-30.125123	153.197038	62.88	5.49	4.84	0.01	2.49	2.66	10.30	1512.88	49.53	0.79	0.28	0.05	0.44

Table A5- Land use history of Hearnes Lake catchment. Data supplied from Coffs Harbour City Council GIS files and NSW Department of Primary Industries aerial photography.

	Banana		Blueberry	
Year	ha^2	%	ha^2	%
1956	98.49	14.34	0.00	0.00
1964	141.49	20.59	0.00	0.00
1979	165.68	24.12	0.00	0.00
1989	172.12	25.05	0.00	0.00
1994	134.87	19.63	0.00	0.00
2002	131.86	19.19	3.44	0.50
2011	39.63	5.77	55.89	8.13
2016	18.98	2.80	76.55	11.10