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Reconstructing the History of Nutrient Loads and Sources in the Derwent Estuary, Tasmania, Australia, using Isotopic Fingerprinting Techniques

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Abstract

Carbon and nitrogen stable isotope analysis of estuarine sediment cores has proved useful for tracing nutrient sources and for assessing changes to nutrient loading through time. However, this technique has rarely been applied to estuaries in the Southern Hemisphere, despite the vulnerability of urban estuaries to excess nutrient loading and eutrophication because of mounting anthropogenic pressures. This study uses sediment core nutrient concentrations (total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP)) and stable isotope analysis (δ^{13}C, δ^{15}N, and δ^{34}S) in combination with lead-210 (^{210}Pb) dating, to reveal information about past and current nutrient loads and sources to various parts of the Derwent estuary, Tasmania, Australia. The upper estuary was found to experience periods of low dissolved oxygen levels and δ^{13}C and δ^{15}N values indicate that the nutrient sources to the upper estuary are predominantly riverine inputs and pulp and paper mill effluent. The middle estuary was found to have higher nutrient (TN and TP) concentrations than other Australian estuaries (Quibray Bay, Woolooware Bay, and Moreton Bay). Along the whole estuary there was a transition of predominantly terrestrial OM in upper estuary to predominantly marine OM in middle/lower estuary. However, there was a clear influence from a nitrogen source with an enriched δ^{15}N value, likely wastewater treatment plant (WWTP) effluent. 3-endmember mixing analysis between terrestrial OM, marine OM, and WWTP effluent shows that WWTP effluent has contributed to up to 30.9% of sediment composition in the past—highlighting the significance of anthropogenic nutrient inputs, such as waste-water treatment plant effluent, to an urban estuary.

Keywords Nutrients · Sediment · Estuary · Stable isotopes · Eutrophication

Introduction

Excess nutrient loading is a problem encountered by many populated coastal waters around the world. Nutrient enrichment can lead to increased primary productivity, eutrophication, and hypoxic events, which in turn can cause a loss of biodiversity, pose a threat to fisheries, and jeopardize drinking water treatment (Cloern 2001; Yang et al. 2008; Conley et al. 2009). The River Derwent and the upper Derwent estuary have recently experienced summer-time blue green algal blooms which are hypothesized to be the result of elevated nutrient levels (DEP 2018). The ability to trace and identify sources of nutrients and organic matter (OM) is therefore of great importance.

Stable isotope analysis (δ^{13}C, δ^{15}N, and δ^{34}S) of estuarine sediment can be utilized for tracing nutrient and OM sources in aquatic systems, provided that the sources have unique isotopic signatures. Stable carbon isotopes (δ^{13}C) have been used to distinguish between marine and terrestrial OM (Shultz and Calder 1976; Meyers 1994; Xiao et al. 2020). Marine OM is typically of phytoplankton origin and has a δ^{13}C signature between −22 and −20‰ (Gearing et al. 1984), and baseline values of sediment from the South-east coast of Australia range between −19.8 and −21.8‰ (Davenport and Bax 2002; Radke et al. 2017). In contrast, terrestrial OM is often derived from C_3 land plants that have more depleted δ^{13}C values between −28 and −26‰ (O'Leary 1988; Shultz and

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Calder 1976). Terrestrial OM is likely a large component of Derwent estuary sediment because of the Norske Skog pulp and paper mill (PPM) and the riverine/catchment inputs in the upper estuary (Fig. 1). The PPM effluent reflects the typical signature of C_3 plants, with $\delta^{13}C$ values of particulate organic carbon, as well as surface sediment at the outfall, between −25 and −29‰ (Oakes et al. 2010). In addition, stable nitrogen isotopes ($\delta^{15}N$) have been used to trace the origin of nitrogen sources entering a water body (Meyers 1997; Kendall 1998). Common nitrogen sources to estuaries include marine OM, terrestrial OM, urban runoff, agricultural runoff, aquaculture waste, and wastewater treatment plant (WWTP) effluent. Marine OM has reported $\delta^{15}N$ values ranging from −2 to 10‰, with many papers reporting values around 6 to 7‰ (Gearing 1988; Peters et al. 1978; Davenport and Bax 2002; Radke et al. 2017). The Huon estuary is a neighbouring estuary to the Derwent estuary, and it shares many similarities except for the fact that it is much less urbanised and less

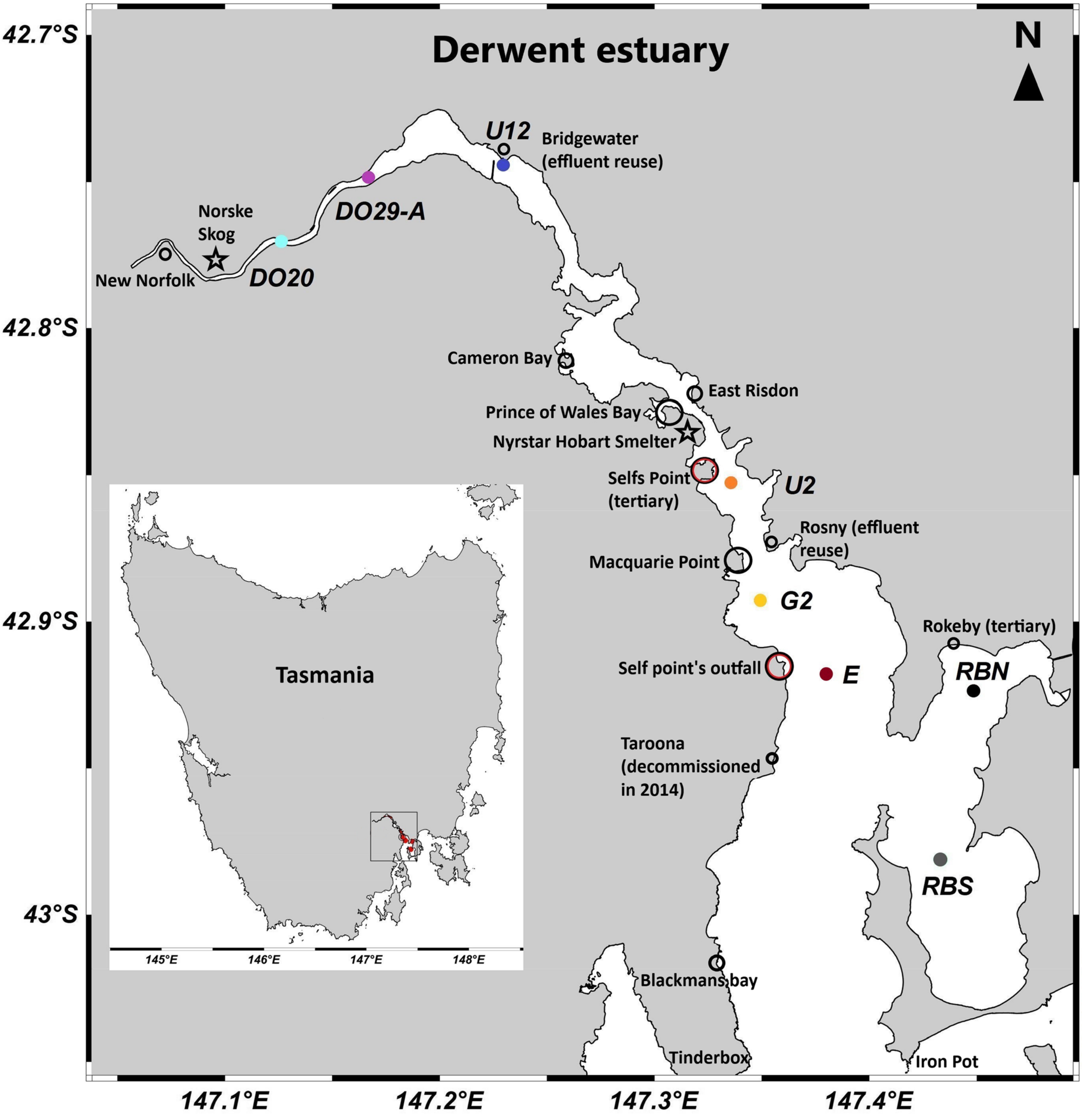


Fig. 1 Derwent estuary map: The eight sampling sites are indicated by filled, coloured circles; WWTPs are indicated by hollow, black circles of 3 various sizes representing effluent quantity in 2015 (< 1000 ML/year, 1000–2000 ML/year, and > 2000 ML/year) (DEP 2015); and major industries are indicated by black stars. Map produced using Ocean Data View (Schlitzer 2020)

impacted by industry. Average stable isotope values of sediment in the lower Huon estuary are −20.6‰ and 7.7‰ (δ^{13}C and δ^{15}N, respectively, $n = 9$) (Thomson 2008). Terrestrial OM has δ^{15}N values between −10 and 10‰, with an average of 2‰ (Gearing 1988). Unpublished data from Proemse (2015) shows particulate matter in the River Derwent having an average δ^{15}N value of 1.7‰ and average δ^{13}C value of −28.2‰ ($n = 4$). Anthropogenic nitrogen sources can have different δ^{15}N signatures. WWTP effluent is a major contributor to the Derwent estuary because of the twelve operating plants around the estuary's edges (Fig. 1) (DEP 2015). Secondary- or tertiary-treated WWTP effluent typically has total nitrogen (TN) δ^{15}N values above 10‰ because common treatment processes (e.g. ammonia volatilization and bacterial denitrification) have a tendency to favour the lighter nitrogen isotope (^{14}N) and leave the final effluent comparatively enriched in ^{15}N (Heaton 1986; Ruiz-Fernández et al. 2002; Sampaio et al. 2010; Vizzini and Mazzola 2004). Surface sediment δ^{34}S values can vary with source materials and provide a method of source determination (Rosenbauer et al. 2009). However, below the surface, δ^{34}S values are not a suitable source indicator because values often vary due to high rates of sulphate reduction which alters the isotopic composition (Kaplan et al. 1963).

Sediment cores contain a repository of information due to the nature of sediment accumulation, and when coupled with sediment dating techniques, the history about past nutrient inputs can be revealed. ^{210}Pb dating provides a reliable method of sediment dating in sediments deposited within the last 100 - 150 years (Krishnaswamy et al. 1971). Additionally, zinc (Zn) concentrations in the sediment core provide a method of estimating sediment age that is unique to the Derwent estuary, with Zn inputs, and therefore Zn concentrations in the sediment, peaking in 1970 (Townsend and Seen 2012; Hughes 2014). Stable isotope techniques combined with sediment dating have been successfully applied to certain estuaries (Voss et al. 2000; Ruiz-Fernández et al. 2002; Böttcher et al. 2010) but have yet to be applied to the Derwent estuary, Tasmania. The aim of this project was therefore to (1) reveal the history of nutrient loads entering the Derwent estuary and (2) identify and trace the potential sources of organic matter and nutrient loads entering the estuary using stable isotope techniques.

Methods

Study Site

The Derwent estuary is a temperate salt wedge estuary. It is the largest estuary in south eastern Tasmania, spanning an area of almost 200 square kilometres. The estuary extends 52 km from the freshwater inflow (River Derwent) at New Norfolk, to the mouth that lies between Tinderbox and the Iron Pot lighthouse (Fig. 1). There is a salt wedge at the New Norfolk end that moves back and forth depending on seasonal rainfall in the catchment and tide (DEP 2015).

Sediment Core Sampling

Eight sediment cores (DO20, DO29-A, U12, U2, G2, E, RBN, and RBS) were collected from eight different sampling sites spanning across the estuary (Fig. 1). The sites are visited monthly by the Derwent Estuary Program (DEP) for ambient water quality monitoring. Sediment cores were collected in polycarbonate tubes by either a Uwitec hammer corer or multicorer over summer 2019/2020. Care was taken when coring to ensure straight, undisturbed cores were collected. The sediment was sliced into 'pucks' and a homogenous portion of this sediment puck was put into a plastic bag for freeze drying, grinding, and analysis, whilst another portion of sediment puck was used to fill a pre-weighed plastic cube for bulk density analysis. The thickness of the slices was generally 1 cm for the top (surface) 10 cm of each core, and 2 cm for all depths below 10 cm. The shorter cores (DO20 and DO29-A) have samples of 0.5 cm thickness near the surface and 1 cm thickness further down. Not every sample was analysed—the longer cores (U12, U2, G2, E, RBN, RBS) had 13 samples analysed, DO20 had 9 samples analysed, and DO29-A had 6 samples analysed (Table 1).

Sediment bulk density from chosen samples was determined by filling plastic cubes of known weight and volume. The wet weight of the sediment was measured, before being dried to constant weight in an oven at 55 °C and weighed again. Wet-bulk density (g/cm^3) was calculated as the mass of wet sediment divided by the total volume of wet sediment. Dry-bulk density was calculated as the mass of dry sediment divided by the total volume of wet sediment as in Dadey and Klaus (1992).

Carbon ($\delta^{13}C_{TC}$), nitrogen (δ^{15}N), and sulphur (δ^{34}S) stable isotopic composition were analysed using flash combustion isotope ratio mass spectrometry (*varioPYRO cube* coupled to an *Isoprime100* mass spectrometer) at the Central Science Laboratory, University of Tasmania (Australia). Stable isotopic signatures are reported in the standard delta notation (Eq. 1) with respect to the international reference materials for carbon (Pee Dee Belemnite), nitrogen (atmospheric air), and sulphur (Vienna-Canyon Diablo Troilite). Values are reported in permil and instrumental precision was 0.03, 0.09, and 0.25% for nitrogen, carbon, and sulphur percentages, respectively, and 0.1, 0.1, and 0.2‰ for delta values, respectively.

$$\delta X\ (‰) = \left[\left(\left(\frac{R_{sample}}{R_{standard}}\right) - 1\right) \text{x } 1000\right] \tag{1}$$

Table 1 Sediment core characteristics, location, and indication of whether ^{210}Pb dating, sediment acidification for organic carbon determination, or sulphur analysis were applied. * indicates that the ^{210}Pb dating was applied but not successful

Core name	DO20	DO29-A	U12	U2	G2	E	RBN	RBS
Core length (cm)	33	10	34	48	66	82	32	32
Water depth (m)	11	6	6	17	21	26	6	3
Latitude	−42.7705	−42.7484	−42.7442	−42.8525	−42.8927	−42.9178	−42.9235	−42.9812
Longitude	147.1264	147.1668	147.2297	147.3357	147.3492	147.3802	147.4486	147.4331
^{210}Pb dating	N	N	Y*	N	Y	N	N	Y*
Acidification	Y	N	Y	Y	N	Y	N	N
^{34}S and S (%)	Y	Y	Y	Y	Y	Y	N	N

where X = ^{13}C, ^{15}N, or ^{34}S and R = the ratio ^{13}C/^{12}C, ^{15}N/^{14}N, or ^{34}S/^{32}S.

Additionally, 39 samples (out of the total 93) were acidified to remove inorganic carbon in the sample and isolate total organic carbon (TOC) for δ^{13}C analysis. Two 200 μL aliquots of 1 M HCl were added to 0.1 g of sample and dried on a hotplate at 40 °C. Between 2 and 20 mg of each sample was weighed into silver cups to be analysed by isotope-ratio mass spectrometry as described above.

Portable X-ray fluorescence spectroscopy (pXRF) analyses were performed using an *Olympus Vanta M Series* portable XRF analyser at University of Tasmania. Each sample was analysed twice: once in *soil-VMR* mode, which operates at a higher voltage and targets heavier elements within the sample, and once in *Geochem-RH* mode, which operates at a lower voltage and targets lighter elements within the sample. Two in-house standards, NIST2702 (marine sediment) and NIST2711A (soil powder), were analysed at the beginning of the run and again every hour after that. This is to assess for instrumental drift, as well as pXRF accuracy because the standards have been analysed using inductively coupled plasma mass spectrometry.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) sample preparation and analysis were conducted at the Isotope Tracing in Natural Systems facility at the Australian Nuclear Science and Technology Organisation (ANSTO), Sydney. Samples were acidified and digested in a microwave, according to ANSTO Method VI 2995. After digestion, samples were centrifuged before being analysed by ICP-AES for Zn, lead (Pb), and total phosphorus (TP) according to ANSTO Method VI 3775.

Three cores (RBS, U12, and G2) were dated at ANSTO Sydney, using the ^{210}Pb dating techniques. All samples were digested on a hot plate according to ANSTO Method I-3331 (Lead-210 dating sample preparation). Each sample was further prepared using Method I-3329 (Polonium Chemical Isolation) and I-3330 (Radium Chemical Isolation), polonium fractions were auto-deposited onto silver disks, radium fractions were co-precipitated with $BaSO_4$ and collected on fine resolution filter papers ready for spectroscopy analyses. The filter samples containing ^{133}Ba and ^{226}Ra were first analysed by gamma ray spectroscopy to measure ^{133}Ba activities and determine the ^{226}Ra recoveries. Finally, each prepared sample was analysed for ^{210}Po and ^{226}Ra activities using alpha particle spectroscopy. ^{210}Po is the granddaughter of ^{210}Pb and is in secular equilibrium with ^{210}Pb, allowing the activity of total ^{210}Pb to be determined. ^{226}Ra is the grandparent of ^{210}Pb which can be used as the proxy of supported ^{210}Pb. Unsupported ^{210}Pb activity was calculated by subtracting the supported from the total ^{210}Pb activity for each sample. Using the determined unsupported ^{210}Pb activities, two sediment dating models were applied: Constant Flux Constant Sedimentation (CFCS), which assumes a constant sedimentation accumulation rate (Krishnaswamy et al. 1971), and Constant Rate of Supply (CRS), which assumes a constant atmospheric flux of ^{210}Pb and variable influx rate of sediments (Appleby and Oldfield 1978).

For all applicable cores, Zn concentrations were used as a proxy for time. Most of the Zn within the Derwent estuary sediment is from a single source, the Nyrstar Hobart Smelter. Using key dates, such as 1917 (when the smelter began operating and sediment Zn concentrations began increasing) and 1970 (when sediment Zn concentrations were at their maximum), the age of the sediment can be estimated (Townsend and Seen 2012; Hughes 2014). Two different linear sedimentation rates were assumed between 1917–1970 and 1970–2020.

Results

Bulk density analysis revealed vast differences in physical characteristics between sediment cores of different sites within the estuary. Dry bulk density ranges from 0.27 (E) to 1.62 g/cm^3 (RBN) (Fig. S1). The bottom portion of U12, and all of U2, G2, and E, exhibit lower densities (0.25 to 0.55 g/cm^3), which indicate that the sediment is predominantly composed of muds and silts. RBN and RBS have the highest dry bulk densities (~ 1.55 g/cm^3), which is attributed to the high sand and shell content of sediment in this region.

Total carbon (TC) content varies greatly between sites, with values ranging from 0.31% (RBS) to 13.49% (G2) (Fig. 2a). DO20 has comparatively high levels of carbon, ranging from 3.34% in sediment at 26.5 cm, to 11.34% at 7.5 cm. DO29-A has much lower levels of TC, with values around 2.8% at every depth. U12 has low values in the top 14 cm of sediment (~ 1–3%) but much higher values below this depth (6–7%). U2 has values that range from 4.48% at

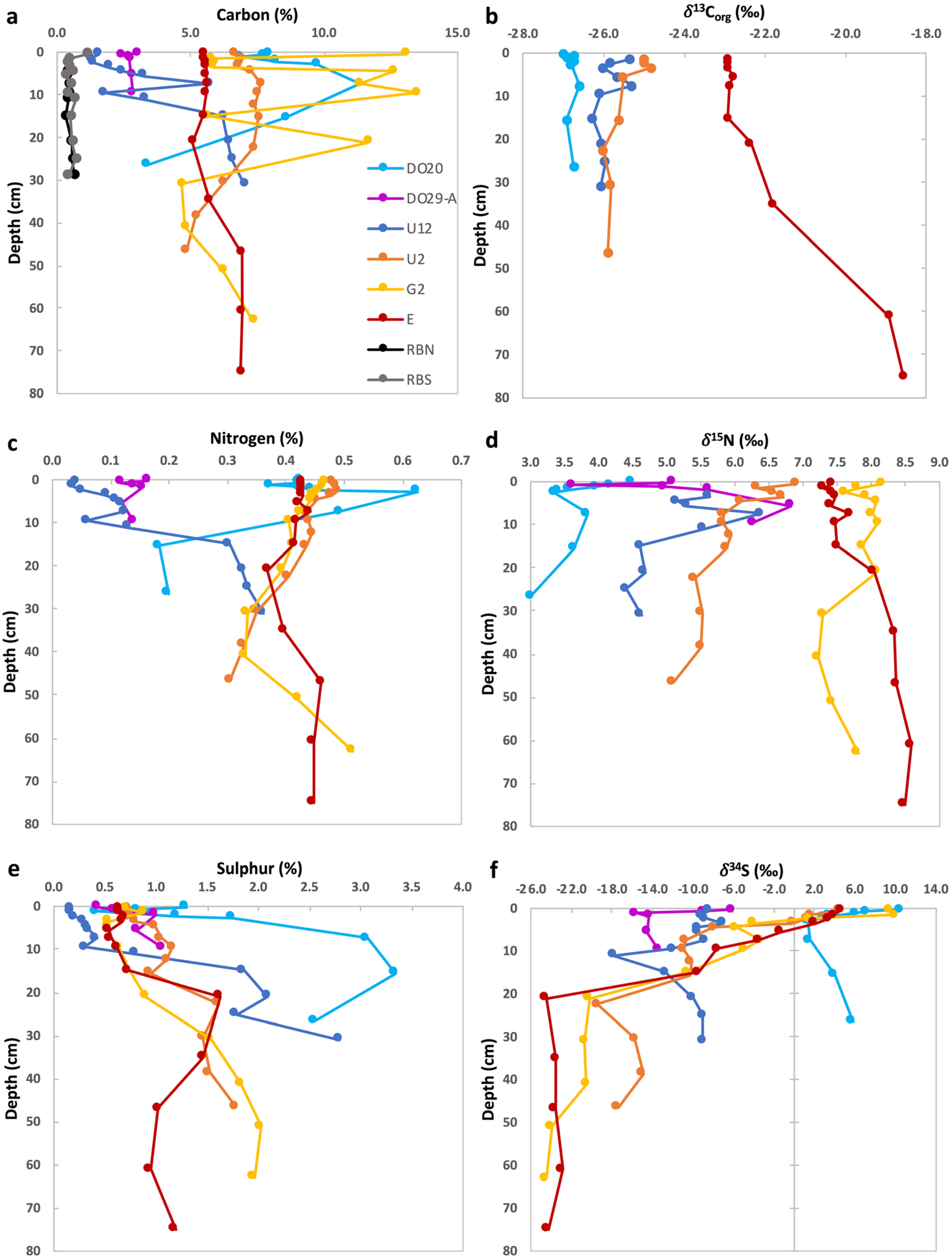


Fig. 2 Core locations are colour-coded and ordered from furthest up the estuary (DO20) to furthest down the estuary (RBS). Cool colours for upper estuary, warm colours for middle estuary, and neutral for Ralphs Bay. (**a**) total carbon content (%), (**b**) organic carbon δ^{13}C (‰), (**c**) total nitrogen content (%), (**d**) total nitrogen δ^{15}N (‰), (**e**) sulphur content (%), and (**f**) sulphur δ^{34}S (‰)

46.5 cm to 7.62% at 7.5 cm below the surface. G2 has large fluctuations between depths, with some values in the upper sediment reaching 13.49% TC, whilst some depths remain at around half that value, around 6% TC. Core E shows little variation between depths, with values ranging from 5.07 to 6.93%. Ralphs Bay cores (RBN and RBS) have much lower TC contents compared with other cores.

TOC $\delta^{13}C$ values range from -26.96‰ (DO20) to -18.56‰ (E) (Fig. 2b). DO20 $\delta^{13}C$ values are around -26.8‰ for the entirety of the core. U12 $\delta^{13}C$ values range from -26.27‰ to -25.28‰. U2 values range from -26.01‰ to -24.80‰. $\delta^{13}C$ values in core E begin at -18.56‰ in sediment at 75 cm depth and decrease towards the surface (-22.91‰). $\delta^{13}C$ values tend to be more depleted in the upper estuary cores (DO20 and U12) and more enriched in ^{13}C in the middle estuary cores (U2 and E) that are closer to the open ocean.

TN contents range from 0.04 (U12) to 0.63% (DO20) (Fig. 2c). DO20 has a highly variable TN content that experiences a minimum at 15.5 cm depth (0.18%) and a maximum at 2.75 cm depth (0.63%). Core DO29-A has a TN content around 0.13% for every depth sampled. U12 has a low nitrogen content (~ 0.09%) in the top 14 cm of sediment, but in the deeper sediment, nitrogen content increases to around 0.33%. The middle estuary cores (U2, G2, and E) exhibit similar profiles, particularly in the surface 20 cm of sediment. At the surface, nitrogen content ranges between 0.40 and 0.50%, but this decreases with depth. At ~ 23 cm, the TN content is below 0.40% for all middle estuary cores. Core U2 nitrogen content decreases with depth for the full profile of the core, whereas G2 and E show increasing nitrogen content below a certain depth. RBN and RBS TN contents were too low for analysis, and therefore TN (%) and $\delta^{15}N$ values are indicative only (Fig. S2).

Nitrogen isotopic compositions ($\delta^{15}N$) range from 3.00 (DO20) to 8.59‰ (E) (Fig. 2d). DO20 has low $\delta^{15}N$ values that range from 3.00‰ at 26.5 cm to 4.48‰ at the surface. DO29-A shows a large variation with depth, and values range from 3.61‰ at 0.75 cm to 6.82‰ at 5.5 cm. U12 has $\delta^{15}N$ values around 4.5‰ in the sediment deeper than 14 cm but increasing $\delta^{15}N$ values in the surface sediment. U2 has a minimum value of 5.10‰ in the deepest sediment sample (46.5 cm) and increasing values towards the surface, where the maximum is 6.90‰. G2 exhibits high $\delta^{15}N$ values that range between 7.22 and 8.16‰. Core E exhibits similarly high values that range from 7.30‰ in sediment close to the surface, and 8.59‰ in deep sediment. There is a general trend of $\delta^{15}N$ values increasing from the upper estuary towards the open ocean, although not every data point adheres to this trend. Many of the cores (DO20, U12, U2, and G2) also show an overall decrease in $\delta^{15}N$ values with depth.

Sulphur content varies from 0.16 (U12) to 3.34% (DO20) (Fig. 2e). DO20 has the highest sulphur content. The remaining cores all have similar sulphur contents—at the surface, values are below 1%, and generally increase slightly with depth.

$\delta^{34}S$ values range from −24.45‰ (G2) to 10.57‰ (DO20) (Fig. 2f). $\delta^{34}S$ values typically begin at a core maximum at the sediment surface and decrease with depth. This trend has exceptions, in which values increase with depth at a certain point (DO20, U12, and U2). There does not appear to be any significant spatial trends along the estuary.

At sites U12 and RBS, the unsupported ^{210}Pb activities were very low and did not exhibit a decreasing profile against depth as a result (Fig. S5). Therefore, both sites were not suitable for ^{210}Pb dating. Core G2 showed higher ^{210}Pb activities and showed a decreasing profile against depth, allowing for age dating. Sediment ages were calculated using the Constant Flux Constant Sedimentation (CFCS) and Constant Rate of Supply (CRS) ^{210}Pb dating models, and both models yielded comparable age approximations, apart from the deepest data point (51 cm) which had a discrepancy of ~ 72 years between the two models (age 147 ± 8 and 219 ± 31, respectively) (Fig. S6). The CFCS model age is used for all figures and discussion.

The change in Zn concentration tends to follow the same pattern in many of the cores (G2 shows a typical profile of the middle estuary cores (Fig. 3)), as a result of one major source (Nyrstar Hobart Smelter) being predominantly responsible for the concentration change throughout time. This allows the use of a Zn dating estimation. Zn concentrations can be used to approximately date sediment and calculate sedimentation rates because of three key dates: 1917, when Zn concentrations began increasing; 1970, when Zn concentrations were at their maximum (Hughes 2014; Townsend and Seen 2012); and 2019/2020, the surface sediment.

Cores from the middle estuary (U2, G2, and E) are the most applicable for the Zn concentration age estimation because of their close proximity to the Zn smelter and because they contain both pre-anthropogenic Zn levels (except U2) and post-anthropogenic levels (Fig. 3). The other cores either did not show Zn concentration peaks (DO29-A, RBN, and RBS) or only small Zn peaks (DO20 and U12) but the chronology of the core is uncertain because of the likely highly variable depositional environment (DO20 and U12) (Fig. S7 and Fig. S8).

^{210}Pb dating of core G2 supports the Zn dating estimation, because the peak in Zn concentration occurs around 1970 and the increasing of Zn concentration above background levels occurs around 1917 (Fig. 3).

Discussion

There are a wide range of nutrient concentrations and isotopic compositions throughout the estuary (Fig. 2). Various major carbon and nitrogen sources can be seen in the different sediment cores and there is an overall shift from predominantly

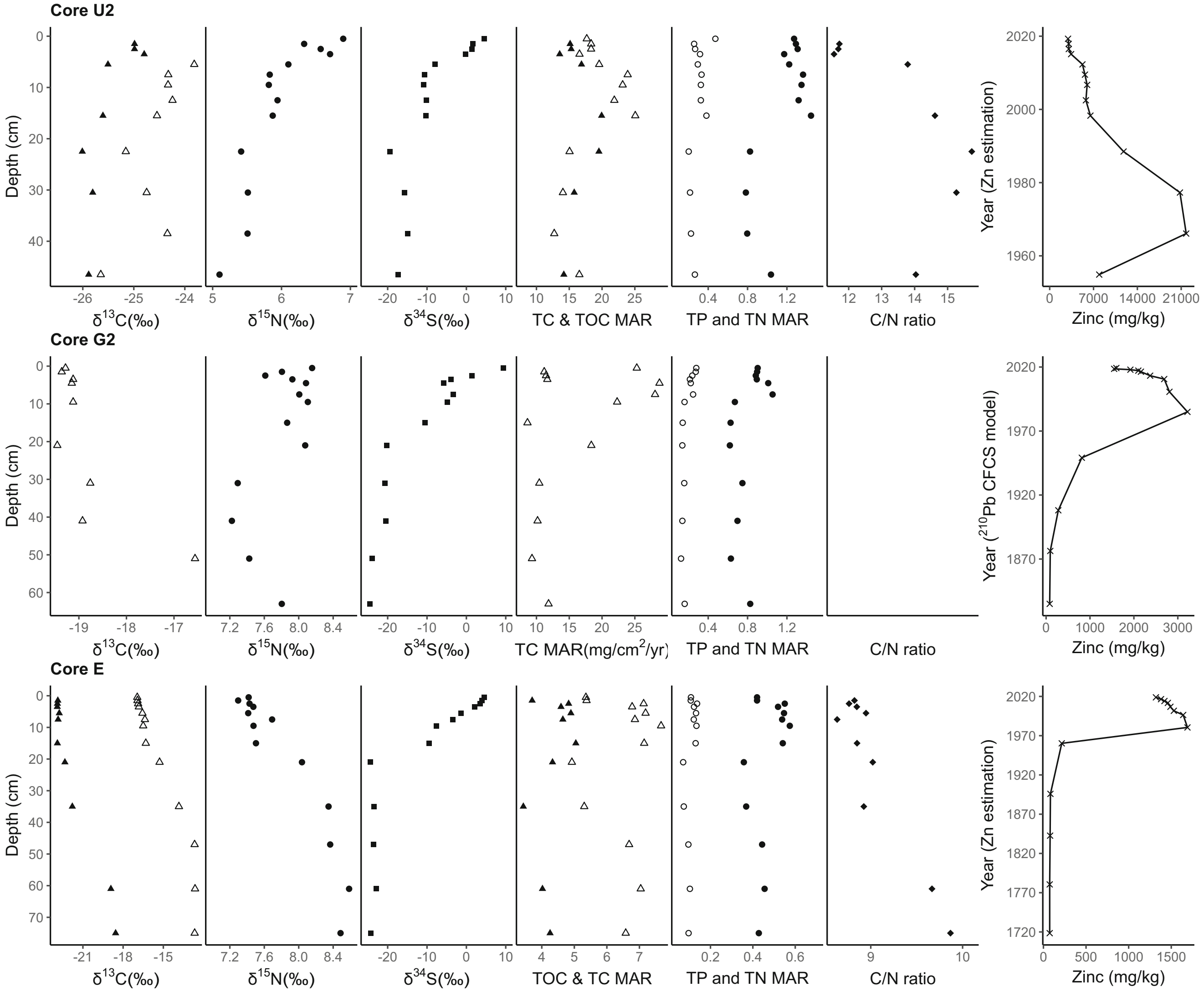
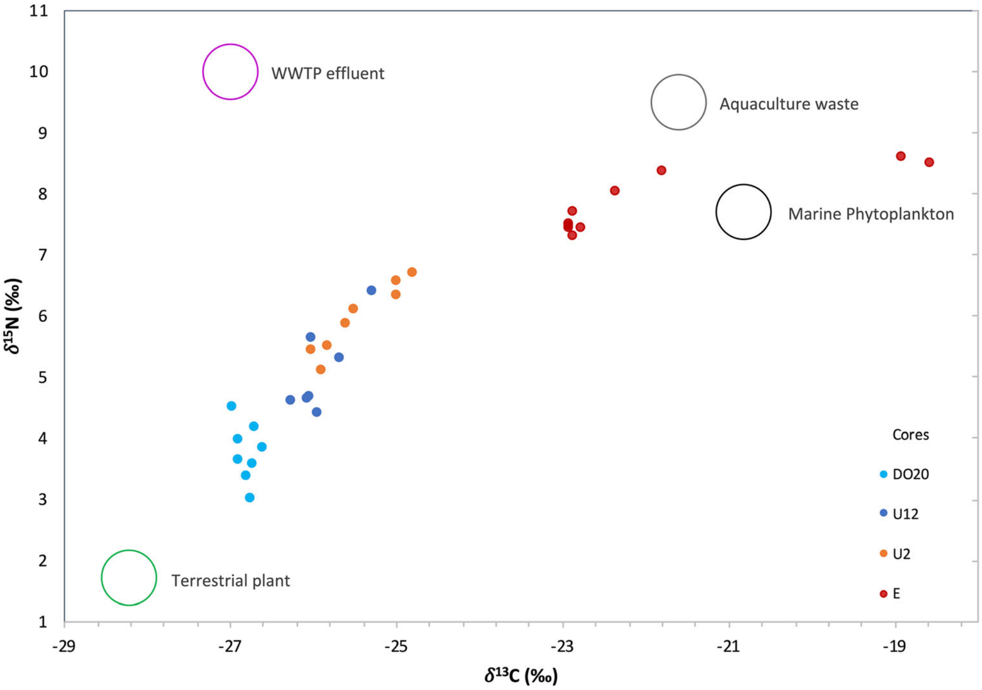


Fig. 3 Plot of stable isotope data and mass accumulation rates (MAR) (mg/cm^2/yr) for three middle estuary cores: U2 (top), G2 (middle), and E (bottom). MAR is calculated using linear sedimentation rate and dry bulk density. Reporting MAR instead of concentration has the advantage in that it is independent to variable dilution by other sediment components (e.g. inorganic matter). Open triangles represent TC $\delta^{13}C_{TC}$ and TC MAR, whereas filled triangles represent TOC $\delta^{13}C$ and TOC MAR. Open circles represent TP, whereas filled circles represent TN. Additionally, sediment age is provided on the Y axis of the Zn concentration graphs (Core U2 and E have age estimations using Zn whilst G2 ages were determined by ^{210}Pb dating techniques). Figure created with R studio using the ggplot2 package (R Core Team 2014; Wickham 2009)

terrestrial OM in the upper estuary to predominantly marine OM towards the open ocean (Fig. 4). All data points in the figure fall between the signatures of the main sources, apart from two samples in core E, which have a $\delta^{13}C$ value more positive than marine OM. These two samples are at 60 – 62 cm and 74 – 76 cm – the deepest analysed samples from this core. Two possible explanations for this increase are early diagenesis, which may have played a role in altering $\delta^{13}C$ values above the marine OM expected range; or, the dominant phytoplankton species in the past may have had a different signature to the dominant species of the present, meaning that the two points may have indeed fallen between the bounds of the major sources in the past.

The observed ranges of C and N isotopes, and the shift from terrestrial OM to marine OM, are similar to that observed in many other estuary studies (Shultz and Calder 1976; Sherr 1982; Cifuentes et al. 1988; Peterson et al. 1994; Graham et al. 2001; Hu et al. 2006; Zhang et al. 2014), including the Huon estuary, which is a smaller estuary located in south-eastern Tasmania (Thomson 2008). Overall, the observed ranges of TC and TN concentrations are comparable to other Australian bays and estuaries such as Quibray Bay and Woolooware Bay in NSW (Macreadie et al. 2012), Moreton Bay in Queensland (Sanders et al. 2016), and the Huon estuary (Thomson 2008). However, middle estuary TN concentrations (~ 0.40 to ~ 0.50% (Fig. 2c)) are higher than the concentrations found in

Fig. 4 δ^{15}N versus δ^{13}C values for the analysed sediment samples. The depth of each sample is not indicated in any way. The isotopic signature of four end-members are also shown - WWTP effluent (Heaton 1986), Terrestrial plants (Proemse 2015), estuarine-marine phytoplankton (Thomson 2008), and aquaculture waste (Ye et al. 1991; Sarà et al. 2004)



Quibray Bay, Woolooware Bay, and Moreton Bay (maximum concentrations are ~ 0.16, ~ 0.42, and ~ 0.22%, respectively), and middle estuary TP concentrations (~1000 to ~1400 ppm (Fig. S3)) are considerably higher than the TP concentrations found in the Moreton Bay core (~300 to ~520 ppm). However, it is difficult to confidently compare the nutrient concentrations of the Derwent estuary to other Australian estuaries/bays because the studies mentioned above have data from only a single site within a bay, and not the bay as a whole, meaning that other parts of the bay may have higher or lower nutrient concentrations. Also, physical sediment parameters (e.g., grain size) are not compared between locations and may alter nutrient concentrations. Contrarily, this study only looked at eight locations within the Derwent estuary and locations existing with even higher nutrient concentrations are highly probable.

Figure 4 highlights the influence of an anthropogenic nutrient source contributing to the sediment in the estuary, because the transition from predominantly terrestrial OM in the upper estuary to predominantly marine OM in the lower estuary is not a straight line and is skewed upwards throughout the whole figure. To expand on this further, 3-endmember mixing analysis was applied to the applicable, dated cores—U2 and E. The three endmembers selected were the three major sources to the estuary—terrestrial OM, marine OM, and WWTP effluent (Fig. 5). Aquaculture waste is not included in the 3-endmember mixing because of a few reasons: firstly, it has not been a possible source until recently (post 2000); secondly, the nitrogen reaching the Derwent estuary from aquaculture is in the dissolved form and is not likely to enter the sediment without being assimilated by phytoplankton first and the affect that this process has on the stable isotope composition is not well documented. Core U2 shows a strong contribution from each of the three sources, whereas core E shows a dominance of marine OM, highlighting the change that can occur from the 'centre' of the estuary (U2) to just ~8 km downstream towards the open ocean (Fig. 5). WWTP effluent appears to be a significant source at both sites—with a maximum contribution of 30.9% in 2016 at site U2 and a maximum of 22.6% in 2002 at site E. This emphasizes the importance of WWTP effluent treatment and management because it is a significant nutrient source to the estuary.

Stark differences in nutrient concentrations and isotopic compositions can be seen between upper estuary cores (DO20, DO29-A, and U12), middle estuary cores (U2, G2, and E), and Ralphs Bay cores (RBN and RBS). In the following, we discuss the overall sources of nutrients to Ralphs Bay, the upper estuary, and the middle estuary, and we discuss evidence for changes in nutrient sources and loads over time.

Ralphs Bay

Ralphs Bay is a wide shallow bay that contains salt marsh vegetation communities and tidal sandflats. It is partially sheltered from the main part of the Derwent estuary and cores show different physical and chemical sediment properties compared with cores from other sites. Sediment has higher wet bulk density and much higher dry bulk density compared to the upper and middle estuary (Fig. S1). This relates to the higher sand and shell content that was apparent upon visual inspection of the sediment, especially apparent in RBS. The sheltered nature of the bay, as well as the distance away from

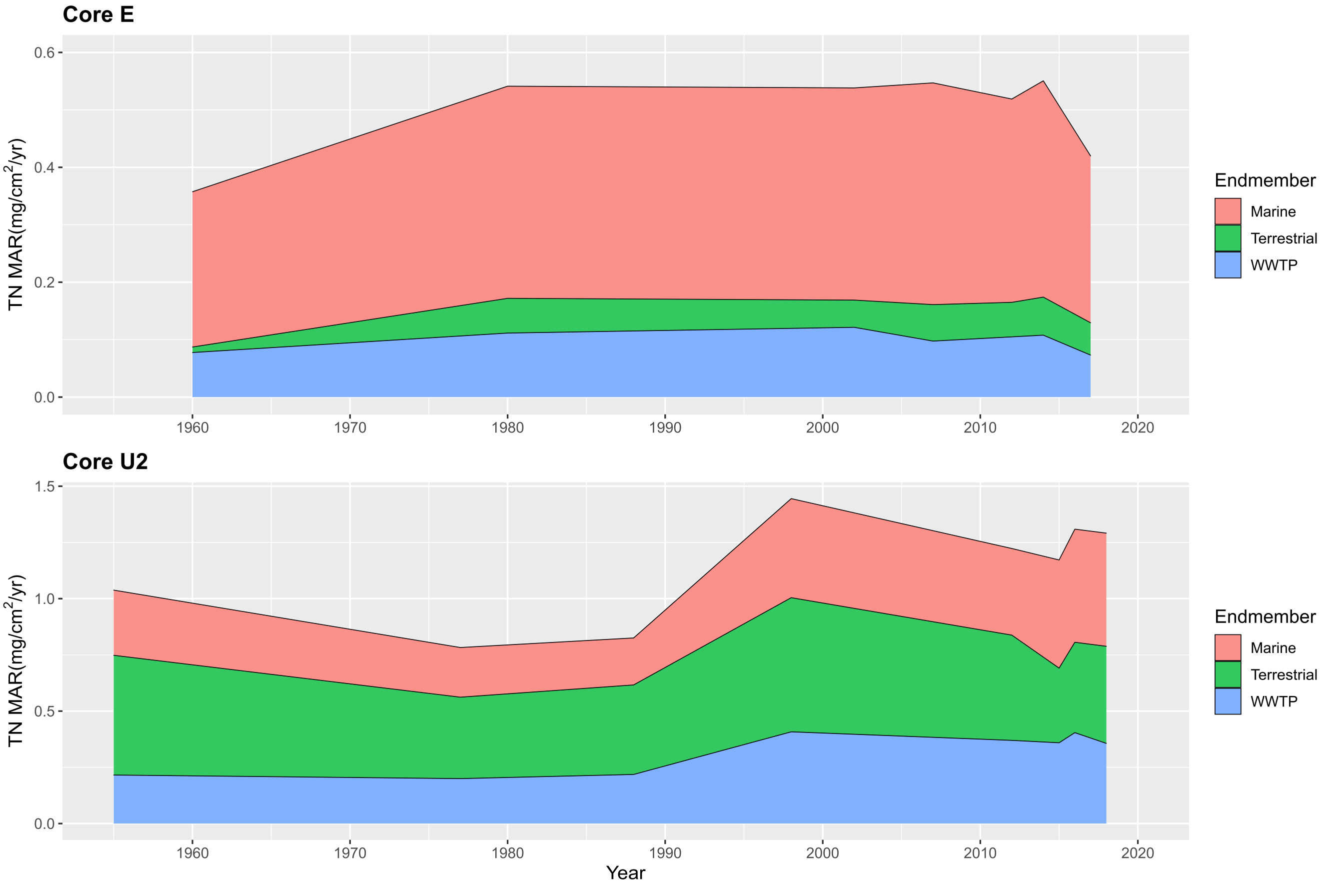


Fig. 5 3-endmember mixing analysis on cores E and U2 (n = 7 and n = 8, respectively). The three endmembers are terrestrial OM (δ^{13}C -28.2‰, δ^{15}N 1.7‰, Proemse 2015), marine OM (δ^{13}C -20.8‰, δ^{15}N 7.7‰, (Thomson 2008)), and WWTP effluent (δ^{13}C -27.0‰, δ^{15}N 10.0‰, (Heaton 1986; Vizzini and Mazzola 2004)

the major anthropogenic inputs, means that industry and WWTP effluent is less prevalent than in the middle estuary. Zn and Pb concentrations remain relatively low at both RBN and RBS, indicating that only small amounts of contaminants from the Zn smelter reach the bay and remain in the sediment (Fig. S9). Sediment from Ralphs Bay has low levels of carbon, nitrogen, and phosphorus, especially compared with sediment from the middle and upper estuary (Fig. 2a, Fig. 2c, and Fig. S3). Nitrogen levels were below detection limits on the isotope-ratio mass spectrometer despite the mass of the sample nearing the upper limits for this instrument (20 mg). The low concentration of nutrients and Zn in the sediment is partially related to the large grain size of the sediment in this area, as OM has a lower affinity for large-grained sediment (Mayer 1995). Additionally, the low levels of nutrients may be attributed to water flow patterns, and the inability for many of the major anthropogenic nutrient inputs from the middle estuary, to penetrate the bay and remain in the sediment.

Upper Estuary

The major OM and nutrient sources to the upper estuary appear to be PPM effluent and catchment/riverine inputs. Unfortunately, these two sources cannot be differentiated using NCS stable isotope techniques because their signatures overlap. Multiple parameters indicate that terrestrial OM (including PPM effluent) dominates OM in the sediment from the three upper estuary cores— DO20, DO29-A, and U12. δ^{13}C values in DO20 OM ranged from −27.0 to −26.5‰, indicating that the sediment is dominated by OM of terrestrial origin (Fig. 2b). δ^{13}C values in U12 OM ranged from −26.5 to −25.0‰, demonstrating that terrestrially derived OM still dominates OM composition but to a lesser extent than DO20—which is closer to the PPM. δ^{15}N values also indicate a strong influence from terrestrial OM. DO20 shows δ^{15}N values that vary from 4.5‰ at the surface, to 3.0‰ in sediment 26.5 cm deep (Fig. 2d). Core U12 δ^{15}N values are around 4.5‰ between 15 and 31 cm depth and increase in the surface 15 cm to around 5.5‰ with a maximum of 6.4‰ at 7.5 cm depth. As δ^{15}N values increase towards the surface sediment, TN and TOC content decreases. TN decreases from 0.36% at 31 cm to 0.04% at 0.5 cm and TOC decreases from a maximum of 5.53% at 21 cm to 0.82% at 1.5 cm.

The Bridgewater WWTP outfall is less than 1 km away from site U12, and in 1996, an effluent reuse scheme was commissioned. Since 2006, the majority of the secondary treated effluent is reused for agricultural purposes (DEP 2015). Another major nutrient source in the upper estuary is the pulp and paper mill. In 2007, the PPM shifted from primary treatment of effluent to secondary treatment, and in 2009 shifted to pine-only processing. Both of these changes contributed to drastically decreased biochemical oxygen demand loads (~ 9000 tonnes/yr pre 2007 to < 1000 tonnes/yr post 2007), decreased particulate OM, decreased the C/N ratio of particulates from ~ 50 in primary effluent to ~ 8.5 in secondary effluent, and increased nitrogen levels because nutrients were added to 'feed' the microbes needed for secondary treatment (Oakes et al. 2010; DEP 2015). The increase to δ^{15}N values, and decline in TN, TOC, and TS concentrations in the surface 5 cm of DO20 and 15 cm of U12 sediment, may be related to the PPM and the Bridgewater WWTP upgrades, although due to the inability to date the sediment, it is difficult to be certain.

Furthermore, C/N ratios in DO20 and U12 indicate that the OM is of terrestrial origin. Land plants have C/N ratios of around 20 or above, whereas plankton and algae have C/N ratio signatures of around 4–10 (Meyers 1994). Core DO20 and U12 have C/N ratios around 16 and 20, respectively (Fig. 6). Some variation is seen throughout time, but the C/N ratio remains consistently high in both regions. The lower average C/N ratio of DO20 compared with U12 (that goes against the trend of further up the estuary yielding stronger terrestrial signatures) might be explained by DO20's close proximity to the PPM. Since 2007, the PPM is further treating effluent, decreasing the C/N ratio of effluent and particulates, whereas U12 is closer in proximity to the Jordan River, which is likely carrying terrestrial OM with a high C/N ratio.

The upper estuary is susceptible to low oxygen conditions from sustained low flow during summer and long periods of stratification. The dissolved oxygen levels in the water column have been reported to be very low, nearing anoxia, particularly in late summer and early autumn (DEP 2015). Multiple lines of evidence from the sediment geochemistry support the finding of low oxygen bottom water in the upper estuary. First, the occurrence of TOC:TS ratios below 5 in subsurface sediments (Fig. S10) is consistent with periodic anoxia (Berner 1984). Second, the low δ^{34}S of surface sediment at DO29-A and U12 (−6.11 and −8.34‰, respectively) is consistent with sulphate reduction (Rudnicki et al. 2001), although it might also reflect input of lighter S from terrestrial sources such as terrestrial plants, marsh plants, and soils, which have δ^{34}S ranges of −3 to 7, −10 to 5, and -5 to 22‰, respectively (Peterson and Fry 1987; Krouse 1991). Finally, the lack of phosphorus enrichment in the surface layers of DO20 and U12 provides further support for poor oxygenation in the upper estuary. Phosphorus concentrations are known to increase in surface sediment because phosphorus is released at depth in the sediment by sulphate reduction and then becomes trapped/bound to iron oxyhydroxides that exist in the surface oxygenated layer of sediment (Ee and Edmonds 1997). This phenomenon is apparent in the sediment cores taken from the middle estuary and Ralphs Bay, but it is not apparent in DO20 or U12 (Fig. S3).

The significant reductions in biochemical oxygen demand from the PPM is an important step for reducing the risk of future hypoxia, particularly in the highly stratified upper estuary. Extended periods of low dissolved oxygen can cause ecological disruption,− and acute stress and death for aquatic life (Pollock et al. 2007). Furthermore, low dissolved oxygen can reduce the redox status of the sediment, accelerating the desorption of heavy metal contaminants and increasing their

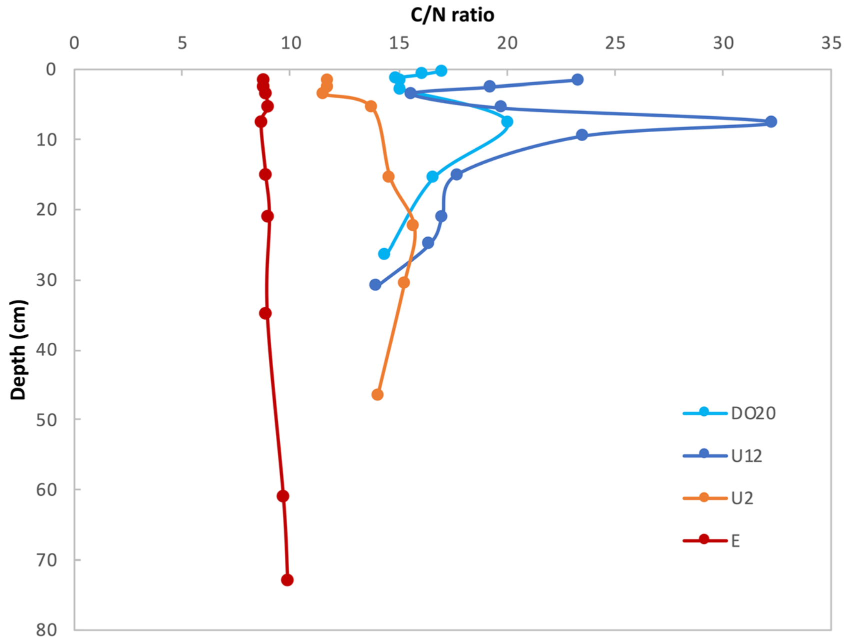


Fig. 6 Total organic carbon to total nitrogen ratio down-core comparison

bioavailability (Eggleton and Thomas 2004). The Derwent estuary, like many other urbanised estuaries around the world, has high levels of metal contamination that can be toxic to organisms if bioavailable. A previous study on Derwent estuary sediment indicates that low dissolved oxygen levels can slightly increase the bioavailability of metals such as As, Cd, Cu, and Zn, due to the dissolution of manganese oxyhydroxides and iron oxyhydroxides (Banks et al. 2012). The minor increase of bioavailable metals to the overlying water column may exacerbate already high contamination or result in localised toxicity, thus warranting consideration in estuary management.

Middle Estuary

The major OM and nutrient sources to the middle estuary appear to be a combination of catchment/riverine inputs, PPM effluent, autochthonous phytoplankton, WWTP effluent, and possibly aquaculture waste. This is to be expected because the major terrestrial OM inputs, which are in the upper estuary, are settled out and/or heavily diluted by the time they reach the lower middle estuary. Core U2 is located in the centre of the estuary and is likely impacted by most of the nutrient inputs into the Derwent. TP and TN MARs are generally higher than any of the other middle estuary cores as a result (Fig. 3).

All three middle estuary cores show increases in TN MAR after ~ 1990—possibly related to increasing nutrients from WWTPs (associated with the increasing population) and/or from nearby aquaculture operations—that have rapidly increased in scale since the late 1990s (Leith et al. 2014). Major aquaculture operations are carried out in the Huon estuary and D'Entrecasteaux Channel, which are located along the coast south-west of the Derwent estuary. In 2002, 3D biogeochemical models showed that the Huon and D'Entrecasteaux Channel are substantial net exporters of nutrients, sending ~ 1197 tonnes of N into neighbouring marine environments (Storm Bay and Derwent estuary) each year (Volkman et al. 2009). The majority of the exported N is related to aquaculture operations, and as a result, the nitrogen is in a labile form. In 2009, total permissible dissolved nitrogen output limits were set for the aquaculture companies in the Huon estuary and D'Entrecasteaux Channel region to minimise environmental impact. The D'Entrecasteaux Channel marine farming development plan area currently has a limit of 1140.67 tonnes/yr and recent production levels have remained fairly close to these targets (DPIPWE 2011; Bell et al. 2017).

TN MAR values in the three cores all show declines from their maximum value over the 2015 to 2020 period, roughly in agreement with the decline in reported WWTP nitrogen loads for the Derwent area (Fig. 3) (DEP 2020). Similarly, 3-endmember mixing analysis shows that WWTP contributions in the surface-most sediment analysed (2018 and 2017, respectively) are at their minimum for the past 32 years in core U2 and past 60 years in core E (Fig. 5). The reason for the decline in WWTP nitrogen loads is not entirely clear as there were no significant treatment upgrades to any of the major WWTPs during this time period. Effluent reuse initiatives may have played a part in the reduced nitrogen loads as the volume of effluent reused can vary dramatically year-to-year depending on climatic conditions, user demand, storage capacity, and effluent quality (DEP 2015). Effluent of 3300 ML (18% of sewage generated in the Hobart area) was reused over the 2013/14 period, which is double the volume reused in 2009/10. The increase was partly due to improved storage capacity with the commissioning of the Duck Hole storage dam in 2013. Improved storage capacity, along with new reuse initiatives, may have continued to increase effluent reuse over the 2015 to 2020 period, contributing to the decline in reported nitrogen load.

Despite being approximately 31 km downstream of the PPM, core U2 appears to have changed in composition as a result of the improvements to effluent treatment in 2007 and the shift to pine-only processing in 2009. Terrestrial OM in the 3-endmember mixing analysis has an average contribution of 46.8% between 1955 and 1998 (n = 4), but it decreases to 32.7% between the 2012 and 2018 period (n = 4) (Fig. 5). The organic carbon mass accumulation rate has decreased post 2010 (~150 g/cm^2/yr) from elevated levels occurring from 1998 to 2009 (~200 g/cm^2/yr) (Fig. 3). δ^{13}C values have shifted from ~−25.8‰ to ~−25‰ in surface sediment, indicating a weakened terrestrial OM contribution. δ^{15}N values have gradually become more enriched, from 5.1‰ in deep sediment to 6.9‰ in surface sediment, noting a rapid increase since ~2009 (5.83‰). C/N ratios have decreased from ~ 14 in deep sediment to 11.7 in surface sediment (Fig. 6). These sediment composition changes indicate that marine OM is contributing to a larger proportion of OM because of the decreased terrestrial OM contribution since 2007 and 2009 when PPM improvements were implemented and increased primary production from increasing labile nutrient loads since ~ 1990.

Core E was taken from a location approximately 1500 m from the outfall of Selfs Point WWTP, and temporal variations in nutrient MAR likely reflect changes in treatment at the plant. The plant was commissioned in 1927 and began pumping untreated effluent into the water. After this date, core E shows increases to TOC, TP, and TN MAR, possibly associated with increased primary production stimulated from increased nutrient inputs, as well as particulates directly from the effluent. The plant implemented primary treatment in 1973 and secondary treatment in 1977 but nutrient mass accumulation rates remain high. In 1997, Selfs Point upgraded to tertiary treatment and also implemented infrastructure to redirect raw sewage from Sandy Bay to Selfs Point for treatment. The impact of these upgrades are evident in Core E, where TN

MAR reaches a maximum of 0.574 mg/cm^2/yr in ~ 1996, after which it begins to decline and values are at 0.420 mg/cm^2/yr in 2019 (Fig. 3). Also, a decrease in WWTP contribution is evident post ~2002 in the 3-endmember mixing analysis (Fig. 5). In 2014, Selfs Point was reported to contribute to only 3% of biochemical oxygen demand/yr and 2% dissolved inorganic nitrogen/yr of the total inputs into the Derwent from WWTPs, despite contributing 21% of wastewater by volume, highlighting the efficacy of tertiary treatment (DEP 2015).

Overall, the middle estuary has higher concentrations of carbon, nitrogen, and phosphorus compared with the upper estuary and Ralphs Bay sites (Fig. 2). Carbon, nitrogen, and phosphorus inputs have all increased to the middle estuary over the past 30–40 years, with mass accumulation rates showing spikes at all three middle estuary sites (Fig. 3). These increases are most likely due to all of the anthropogenic inputs associated with the continuously growing population around the middle estuary, primarily WWTP effluent.

Conclusion

Isotopic fingerprinting reveals a clear trend between terrestrially derived OM, which dominates in the upper estuary, to marine-derived OM, which dominates towards the open ocean. Along the whole estuary, there appears to be a constant influence from anthropogenic nutrient sources, likely WWTP effluent. Terrestrial OM is supplied by river and catchment inputs, as well as the PPM in the upper estuary. Terrestrial OM is either settled out and/or heavily diluted by the time water reaches the middle estuary. The middle estuary isotopic signature arises mainly from marine sources of OM, such as in situ phytoplankton production, which coincide with increased nutrient concentrations in this region. Despite being primarily marine-derived OM in the middle estuary, WWTP effluent appears to contribute to almost one third of sediment OM at site U2. Nitrogen and phosphorus mass accumulation rates have been increasing in the middle estuary for the past ~ 30 years, likely due to the pressures associated with a rapidly increasing population, such as wastewater treatment and disposal, and the recent surge in aquaculture operations. Overall, the observed trends highlight the need for nutrient management and monitoring in urban estuaries, particularly those with increasing pressures from population growth, agriculture expansion, growing aquaculture operations, or any major nutrient source. This study highlights the importance of wastewater treatment, in particular tertiary treatment, which can drastically limit nutrient input to the estuary. The implementation of initiatives such as effluent reuse can further reduce nutrient loads entering an estuary. Due to the numerous invaluable ecosystem services that estuaries provide, the continued monitoring and management is crucial to ensuring the health of the Derwent estuary, and every other urban estuary worldwide, in the future.

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