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ORIGINAL PAPER

Changes in the chemistry of sedimentary organic matter within the Coorong over space and time

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Abstract Like many other coastal systems across the world, the Coorong lagoonal ecosystem (South Australia) has degraded over the last 100 years; in this case as a result of extensive regulation and diversions of water across the Murray-Darling Basin following European settlement. To evaluate whether the sources of organic matter (OM) supporting its food-web have changed since the inception of water management and barrage construction, sedimentary OM was characterised in cores spanning the Coorong's salinity gradient at depths representative of the last 100 years over which the management alterations to river and estuarine flow were most marked. Detailed ^{210}Pb, ^{137}Cs and Pu dating in conjunction with palaeolimnological data (*Pinus* pollen) allowed for the reconstruction of the timing of substantial changes observed in the composition of the OM, most of which occur during the early 1950s, concurrent with management-related variations in water flow and salinity. Negative shifts in δ^{13}C of up to 8.3‰ in the 2–10 and <2 μm fractions after the 1950s suggest a pronounced alteration in biogeochemical cycling or in the origin of OM. Elemental ratios and δ^{13}C values of potential sources are inconclusive as to the cause of these biogeochemical changes. However, ^{13}C-NMR spectra of the sediments suggest that degraded phytoplankton constitutes a large proportion of today's OM and also reveal that an OM source rich in lignin was present prior to the 1950s. The high δ^{13}C (−18.3‰) and low C/N (7.5) signatures of the lignin-bearing sediments are inconsistent with a C3 terrestrial OM source and instead suggest that the lignin-bearing seagrass *Ruppia megacarpa* (δ^{13}C of −13‰) contributed to a large degree to the sediment of the North Lagoon. *R. megacarpa* once was abundant in the North Lagoon but today has all but vanished from the system. Thus, only through a combination of isotopic and spectroscopic techniques was it possible to effectively decipher the changes in the composition of OM deposited throughout the Coorong over space and time. These results have important implications for research in estuarine OM dynamics in other geographic locations. Specifically, utilising complementary analytical techniques may sometimes be essential in reliably determining OM sources and processes in estuaries and lagoons.

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Introduction

Stable isotopic analyses of organic carbon (δ^{13}C), often in conjunction with C/N ratios and/or nitrogen isotopic values (δ^{15}N) measured from sedimentary OM, have frequently been used to assess the relative contributions of terrestrial and marine biota to aquatic settings. Estuarine systems in particular have become the focus of isotopic applications because of the complexity arising from multiple OM sources (e.g. Haines 1976; Torgersen and Chivas 1985; Ember et al. 1987; Chmura and Aharon 1995; Middelburg and Nieuwenhuize 1998). Isotopic techniques also appear suitable for palaeoecological studies. In fact, the reconstruction of past environments and chemical conditions from core records is commonly done through the joint use of δ^{13}C and C/N analyses (summarised in Lamb et al. 2006), due to the apparent ease of distinguishing different OM sources through such analyses (e.g. Wilson et al. 2005). Fry and Sherr (1984), however, urge caution by stating that "carbon isotopic measurements are often of limited value in their usefulness for deciphering the complex carbon flows that occur in estuaries". Thus, particularly in estuarine systems, there is an inherent complexity in the biota and processes that control the production of sedimentary OM, which needs to be taken into account when using isotopes for reconstructing past environments. Specifically, determining the sources of organic matter (OM) is often hampered by variability in δ^{13}C of the different potential sources. For example, marine macro-algae can vary by over 30‰, freshwater plants and seagrasses by over 10‰ and sometimes seagrasses can vary by over 4‰ within one location (Fry and Sherr 1984). The reasons for these large variations among the primary producers are mainly due to the δ^{13}C of the dissolved inorganic carbon pool, concentrations of CO_2 or HCO_3^- as well as the degree of enzymatic fractionation. Enzymatic fractionation depends on the photosynthetic pathway with the RuBP enzyme of the C3 photosynthetic pathway fractionating the source C to a greater degree (between −23 and −41‰) than the PEP enzyme of the C4 photosynthetic pathway (between −0.5 and −3.6‰). However, due to the rate-limiting step of diffusion in the aquatic environment of CO_2 or HCO_3^- across the leaf boundary, actual δ^{13}C values of some seagrasses may vary only between −10 and −14.5‰.

Changes in flow regime of various systems have been known to result in complex and often dramatic declines in ecological diversity (Kowalski et al. 2000; Borman et al. 2002), similar to those seen in the Coorong today (Shuttleworth et al. 2005). Decreased riverine inflows can either diminish the supply of OM and nutrients or alter the salinity gradients, biogeochemical cycles, and primary production of estuaries (Gillanders and Kingsford 2002). The application of stable isotopic analyses to systems that have undergone rapid changes due to human-induced factors is a commonly used tool to assess the changes in the ecological status of an ecosystem (e.g. Shalovenkov 2006; Voss et al. 2000; Vizzini and Mazzola 2006; Banaru et al. 2007).

The Coorong is one of the most important wetland systems in Australia, covering 467 km² and consisting of ocean beach, the mouth of the River Murray, the lakes and estuary. Like many other estuaries that have experienced degradation over the last decades, the Coorong has been the subject of little previous work on the geographic and secular variation in the composition of its sedimentary OM. To date, the only studies attempting palaeoenvironmental reconstruction based on change in geochemistry were conducted in ephemeral lakes adjacent to the Coorong, using episodes of sapropel formation, identification of kerogen types, elemental and isotopic (C, N) compositions, biomarker hydrocarbon signatures and microfossil (diatom, ostracod) assemblages (e.g. Hayball et al. 1991; McKirdy et al. 1995, 2007; Mee et al. 2004, 2007; Edwards et al. 2006). Analyses of sediment cores from the southern Coorong lagoon using micropalaeontological and dating techniques were used to infer changes in water quality, but much of the resulting data are contained in unpublished reports (summarized in Gell and Haynes 2005). To date, the most comprehensive and detailed palaeolimnological study of the Coorong was carried out by Gell and Haynes (2005), utilising cores that span the entire length of the two Coorong lagoons for sedimentological assessment and reconstruction of water condition based on diatom assemblages. Their data suggest that substantial changes in water quality, such as increased turbidity and reduced flushing by marine and fresh water, occurred in the early to mid-1900s (coinciding with an expansion of European settlement). These were

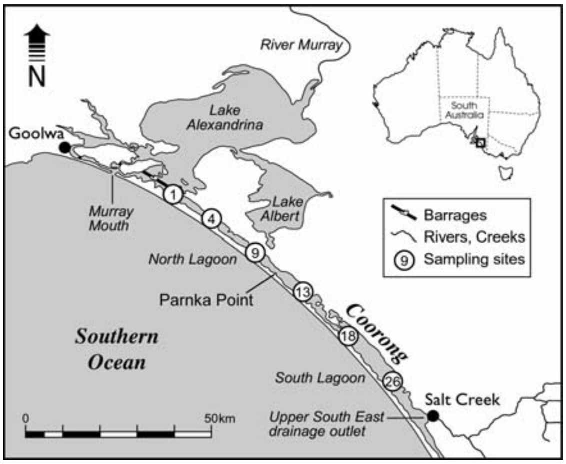


Fig. 1 Location of the Coorong lagoons and sampling sites

followed by further deterioration in the 1940s, 1950s and 1980s, associated with the construction of barrages (Fig. 1), increased water extractions upstream and the periodic closure of the Murray Mouth, respectively. Although barrage construction was completed in the 1940s, connectivity with the lower lakes was maintained until the 1950s as the barrages were regularly opened to prevent flooding of the surrounding farmland. Since then, salinities within the Coorong have been increasing steadily and the South Lagoon is now permanently hypersaline.

In this study, we have attempted to identify the recent changes (i.e. those over the last 100 years, established by radionuclide dating) in the sources of OM deposited in the Coorong lagoons of the Murray-Darling Basin (Australia). It is suspected that such changes may be fundamental to this environmental decline. To evaluate if the chemical properties of OM supporting the Coorong food-web have indeed varied over the last century, we used a combination of stable isotopic, radionuclide, spectroscopic, elemental and palaeoecological data on shallow organic-rich sediments dating from prior to European settlement until the present day, as well as its contemporary biota.

Materials and methods

Site description

The Coorong is a narrow neck of water on the landward side of a Holocene barrier dune (Younghusband Peninsula) that extends southeast from the mouth of the River Murray for approximately 150 km. Tenuously connected to the ocean at its northern end via the Murray Mouth, it effectively comprises two shallow lagoons separated by a shoal at Parnka Point (Fig. 1). Climate in the region is semiarid, with long hot summers and cool winters. The ecological significance of the Coorong is highlighted by its classification as a Ramsar site in 1985 (Ramsar Convention on Wetlands: http://www.ramsar.org/). Historically, this region had very high biological productivity and diversity, particularly with regard to populations of fish and migratory waterbirds. More recently, major ecological changes have been observed within the two lagoons of the Coorong, particularly the rapid decline of bird and fish populations, which have been attributed to increasing salinity, a consequence of major changes in the flow regime.

A reduction of two thirds in river flows, a consequence of regulation structures being built along the length of the River Murray since European settlement, has caused the river mouth to close, requiring permanent dredging (Phillips and Muller 2006). In addition, the frequency of drought is now ten times higher than prior to European settlement (Shuttleworth et al. 2005). Barrages separating the Lower Lakes from the Coorong were constructed in the 1940s to minimise tidal incursions into the lakes and thus ensure fresh water supplies for metropolitan consumption and agriculture (Phillips and Muller 2006). It was not until the 1950s that the lakes remained fresh as barrages were regularly opened prior to that date. Thus, extensive regulation and diversions across the Murray-Darling Basin over the last 80 years have drastically altered the flow regime of the river at the Murray Mouth (Jensen et al. 2000; Shuttleworth et al. 2005). Considerable ecological changes have accompanied these modifications to the water regime of the region, including the loss of key species, the hypersalinisation of the South Lagoon, and the siltation of the Murray Mouth (Jensen et al. 2000; Shuttleworth et al. 2005; Phillips and Muller 2006).

Collection of samples and preparation for analysis

Sediment samples were obtained from cores collected in 2005 by a group from the 'Discipline of Geographical and Environmental Studies' at the University of Adelaide, under the direction of Dr Peter Gell, a project commissioned by the Department of Water, Land and Biodiversity Conservation (DWL&BC) for the Upper South East (USE) Program. Thirty sites had been selected over the length of the Coorong for sediment coring to document trends of changing water quality within and between the two lagoons, using diatom analysis and various dating techniques. All cores used in the current study were extracted using a field piston corer and 3 m lengths of 50 mm PVC pipe. They were sliced vertically using a circular saw and 'dustless' diamond blade, wrapped in multiple layers of cling film, and stored at the University of Adelaide in a cold room at 4°C until further analysis. Sediment samples for this study were taken from cores C1, C4, C9, C13 (North Lagoon) and C18 and C26(2) (South Lagoon), spanning the entire length of the Coorong (Fig. 1). Sediment samples for isotopic and spectroscopic analyses were taken from one half of the core in 7 cm intervals, kept cold during transfer from Adelaide University to CSIRO Land and Water, immediately frozen upon arrival and subsequently freeze dried. To determine the chemical and isotopic compositions of the potential sources of sedimentary OM in the Coorong, samples of local aquatic and terrestrial plants, phyto- and zooplankton were collected in March and November 2006. Aquatic and terrestrial plant samples were collected by hand and placed in plastic containers at 6 sites along the long axis of the North Lagoon; no shoreline plants or aquatic plants were present in the South Lagoon. Plankton samples were recovered with a 200 μm net at several sites along the long axis of the North Lagoon and in the northern and central portion of the South Lagoon. Samples of the seagrass *Ruppia megacarpa* (now extinct in the Coorong) were made available to us through J. Dick's collection of *Ruppia* leaves and seeds, extracted from Coorong cores. In preparation for isotopic and spectroscopic analyses, the plants were washed in deionized water, dried at 60°C and finely ground, while the plankton samples were freeze dried and finely ground.

Chronology

Chronologies were determined on cores collected in close vicinity to those used for OM assessments. These include: core C3 in the upper North Lagoon (near cores C1 and C4), core C12 in the lower North Lagoon (near cores C9 and C13), core C19 in the South Lagoon (near core C18), and core C23, also in the South Lagoon (near core C26). Although the chronological analysis of these cores shows that there is spatial variation in sedimentation throughout the Coorong, we were able to correlate the chronologies of the different cores from each region using the first appearance of *Pinus* pollen as a common marker. In each region, the depth of inception of *Pinus* showed good agreement between cores and we therefore contend that the chronology for each region is established to within ±5 years.

Radionuclide activities were determined using a combination of gamma and alpha spectrometry. Excess ^{210}Pb and ^{137}Cs were measured by gamma spectrometry (Murray et al. 1987). In some cases, where sample mass was limited, ^{210}Po was measured by alpha spectrometry (Martin and Hancock 2004) and used as a surrogate for ^{210}Pb. The sediment was homogenized by grinding in a ring mill, and compressed into a sealed perspex container. Excess ^{210}Pb was determined from the difference between ^{210}Pb and ^{226}Ra activity of the sample. The count time was 1–2 days. ^{210}Po analysis by alpha spectrometry entailed acid digestion of the sample and autoplating onto a silver disc for counting. A known activity of a tracer isotope (^{209}Po) was added to determine the chemical yield. If required, a subsample was taken for Pu analysis, also measured by alpha spectrometry. Radiochemical separation procedures were employed involving the addition of a ^{242}Pu yield tracer to the sediment, leaching of Pu with nitric acid, radiochemical purification by ion-exchange techniques, and electroplating procedures (Wong 1971).

Sub-samples for diatom analysis were taken from the cores at 0.5–1 cm intervals, prepared and mounted on slides for identification and quantification (see Gell and Haynes 2005, for the complete methodology); whereas those for pollen analysis were collected from the upper 50 cm of the core over sections displaying obvious lithological changes, following the bulk method of Ogden (2000). The first appearance of *Pinus* pollen (an exotic species introduced by Europeans primarily by the establishment of pine plantations), based on calibration with radionuclide data, is used as an approximate marker for the 1950s.

Leco analyses

Unfractionated (bulk) sediment samples from the Coorong cores were analysed for total carbon (TC) and total organic carbon (TOC) content on a LECO CR12 Carbon Analyser as described by Merry and Spouncer (1988). For TOC determination, each sample was pre-treated with sulphurous acid in ceramic boats containing a nickel liner to remove carbonates prior to Leco analysis. Total inorganic carbon (TIC) content was calculated by subtraction of TOC from TC. Total N was measured by a Leco CNS 2000.

Particle size separation

Freeze-dried sediments (5 g) were treated with 1 M HCl to remove any calcareous material. They were then separated by wet sieving and settling into >53, 10–53, 2–10 and <2 µm fractions, followed by freeze drying. Losses from size separation were <5%.

Stable isotopic analysis

Each freeze-dried and acidified fraction was analysed for δ^{13}C by weighing samples containing between 300 and 800 µg of carbon into ultra-clean tin capsules. After sealing, the capsules were combusted and analysed on a 20–20 Europa Scientific Automated Nitrogen Carbon Analysis-Mass Spectrometer (ANCA-MS). ANU-EDTA was used as an internal standard. Standard deviation from replicate samples was 0.1‰ for bulk sediments and 0.3‰ for size separated samples; internal precision of the mass-spectrometer is 0.02‰.

^{13}C-NMR spectroscopy

Prior to their analysis, carbonate-free sediment samples were treated with 2% hydrofluoric acid (HF) to remove paramagnetic materials and concentrate the organic fraction in order to reduce interference and increase peak resolution (Skjemstad et al. 1994).The HF-treated sediment was then washed with deionised water and freeze dried. All cross-polarized with magic-angle spinning (CP/MAS) ^{13}C-NMR spectra were obtained at 50.309 MHz on a Varian Unity 200 spectrometer with a 4.7 wide-bore Oxford superconducting magnet. Samples were spun at 5 kHz in 7 mm- diameter zirconia rotors with Kel-F caps in a Doty Scientific MAS probe. Spectra were accumulated with a 1-ms contact time, a 1-s recycle time, 2-k zero filling, 50-Hz Lorentzian line broadening and a 0.01-s Gaussian broadening. Spectral distributions were calculated by integrating the proportional contribution of the functional groups in the seven chemical shift regions: carbonyl (210–165 ppm), O-aromatic (165–145 ppm), aromatic (145–110 ppm), O_2-alkyl (110–95 ppm), O-alkyl (95–60 ppm), *N*-alkyl/methoxy (60–45 ppm), and alkyl (45–10 ppm) (Baldock and Smernik 2002).

A more quantitative and detailed analysis of ^{13}C-NMR data can be achieved by applying a molecular mixing model which is described in Baldock et al. (2004). The modelling approach is based on the assumptions that natural organic materials can be represented by a mixture of different organic components (e.g. carbohydrate, lignin, protein, lipid and charcoal) and that each class of organic component can be assigned a representative distribution of ^{13}C-NMR signal intensity.

Total phosphorus by acid digestion

Total phosphorous was determined by US EPA method 3051A (US Environmental Protection Agency, Washington, DC). The finely ground sample was digested in a microwave oven using a mixture of nitric acid and hydrochloric acid. The solution was then analysed for P by inductively coupled plasma optical emission spectrometry (ICPOES).

Results and discussion

Chronology from radionuclide and pollen analyses

A combination of ^{210}Pb, ^{137}Cs and Pu isotopes was used to obtain core chronologies covering the last 50–60 years (Figs. 2 and 3). The use of ^{210}Pb, or more strictly, "excess" ^{210}Pb as a chronometer for 100-year periods of sedimentation is well known (e.g. Robbins 1978); however, problems and uncertainties exist as discussed in Robbins and Herche (1993) and Appleby (2001). Use of the anthropogenic "bomb" fallout nuclide ^{137}Cs can alleviate some of these uncertainties by providing a known time horizon, thus enabling a check of the modelled ^{210}Pb dates (Appleby 2001). Where ^{137}Cs is immobile in the sediment column, the first detection of ^{137}Cs in the southern hemisphere sediment can be confidently dated at 1955 ± 2 years (Leslie and Hancock 2008). However, there is evidence that ^{137}Cs is mobile in anoxic organic-rich

Fig. 2 Radionuclide profiles of core C3 showing (**a**) excess ^{210}Pb (assuming a surface mixed layer of 4 cm); (**b**) fallout ^{137}Cs and Pu (neither are detected below 31 cm); (**c**) dated horizons determined from Pu isotopes. The dotted vertical line represents the ratio of ^{238}Pu/$^{239+240}$Pu (0.12). Ratios above this value indicate sediment deposition post 1964

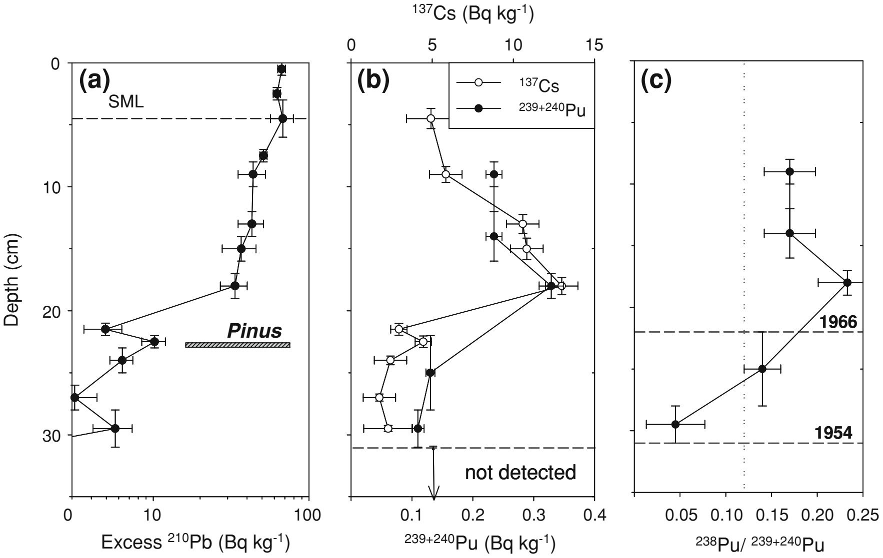
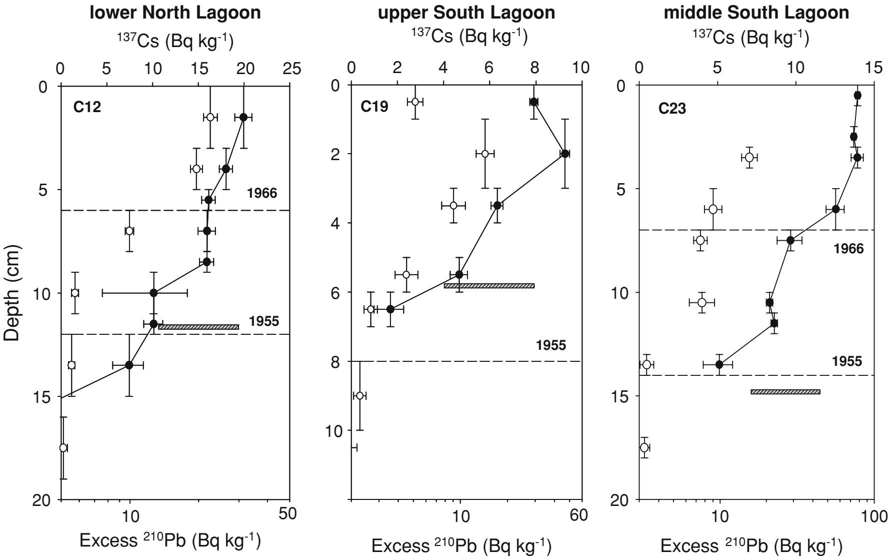


Fig. 3 Excess ^{210}Pb and ^{137}Cs profiles for three cores (C12, C19 and C23). First-appearance *Pinus* horizons are indicated by the horizontal bar. The dated horizons (dashed lines) are determined from ^{137}Cs and Pu



sediment (Davis et al. 1984) and in near-shore saline sediment (Sholkovitz and Mann 1984) such as that found in the Coorong. We have therefore also measured Pu at selected depths in all cores. Pu is a bomb product with a similar fallout history to ^{137}Cs, but it possesses greater particle reactivity and is believed to be essentially immobile in marine sediments (Carpenter and Beasley 1981; Sholkovitz and Mann 1984). In addition, Pu has three isotopes that can be used to provide another dated horizon. The fallout Pu isotopic signature in the southern hemisphere changed significantly in the mid 1960s due to the failed SNAP-9A satellite launch in 1964 (Koide et al. 1979). Thus, for some of our cores Pu was able to provide two dated horizons, the mid-1950s and the mid-1960s. These dates are of considerable importance given the poor agreement between the ^{210}Pb and ^{137}Cs chronologies in some of the cores.

Figure 2 illustrates the utility of the three tracers as exemplified in core C3. The log-linear profile of excess ^{210}Pb (Fig. 2a) shows a flat section of constant excess ^{210}Pb activity near the surface (the upper ~5 cm), a section of lower activity below (5–20 cm), and a section of rapid decline (20–30 cm). Using a conventional approach to modelling these data we assumed that the surface layer of constant excess

^{210}Pb activity represents rapid mixing in the upper 3–5 cm. Applying the constant initial concentration approach (CIC: Appleby and Oldfield 1992) yielded ages of 60 to 100 years for sediment between 23 and 28 cm depth, ages inconsistent with the presence of ^{137}Cs at 31 cm (Fig. 2b); i.e. the first detection of ^{137}Cs in 1954–1956 should yield an age of no more than 50 years. Overall, the CIC modelling of the excess ^{210}Pb chronologies did not provide a good match with the ^{137}Cs and Pu horizons, and therefore we have elected not to use conventional ^{210}Pb dating to obtain a high-resolution chronology. Instead, a combination of ^{137}Cs and Pu data is used to estimate bulk accumulation rate over the last 40–50 years. Overall, the veracity of the ^{137}Cs data is confirmed by the presence of Pu at 31 cm, indicating that the ^{137}Cs profile has not been notably distorted as a result of chemical mobility and vertical diffusion of ^{137}Cs in the saline sediments (Fig. 2b).

As shown by the ^{238}Pu/$^{239+240}$Pu ratio (Fig. 2c), a notable shift in the Pu isotope signature occurs above 28 cm, shifting the ratios from <0.08 to >0.12. This increase is from an episodic ^{238}Pu fallout due to the disintegration of the SNAP-9A satellite in 1964. By contrast, the $^{239+240}$Pu activity of the sediment is almost entirely from bomb fallout. Based on these data, the sediment at 22 cm depth can now be dated as 1966 ± 2 years. In general, the Pu measurements in all of the analysed cores corroborate the ^{137}Cs-onset horizons, indicating that ^{137}Cs was not subject to vertical diffusion in the sediment profiles. The first appearance of *Pinus* in these cores coincides with the period of the mid-1950s to 1960s (Fig. 3).

Using the ^{137}Cs and Pu data the sedimentation rate was able to be calculated for the last 50 years for all four Coorong cores. The rate of sediment accumulation was highest at the site of core C3 (0.56 cm year^{-1}), decreasing southward through core site C12 (0.16 cm year^{-1}) to a minimum at core C19 (0.10 cm year^{-1}) before increasing again to 0.22 cm year^{-1} at core C23.

Element concentrations and ratios

Elemental analyses (TOC and TIC, total N and P) of bulk (i.e. unfractionated) sediment in the uppermost layer (0–7 cm) revealed a southward increase in the concentrations of N and P as well as TOC and TIC within the North Lagoon (Table 1), which parallels increasing salinity levels (Fig. 4). N/P and C/P ratios (wt%) both increase along the NW-SE axis of the North Lagoon and remain high (C/P) or increase further (N/P) in the South Lagoon, indicating a reduced availability of P. In the OM that was deposited before the 1950s, C/P and N/P ratios also rise southward within the North Lagoon; however, the rate of increase is not as pronounced as in the uppermost sediment layer, suggesting a greater degree of P limitation under the current conditions.

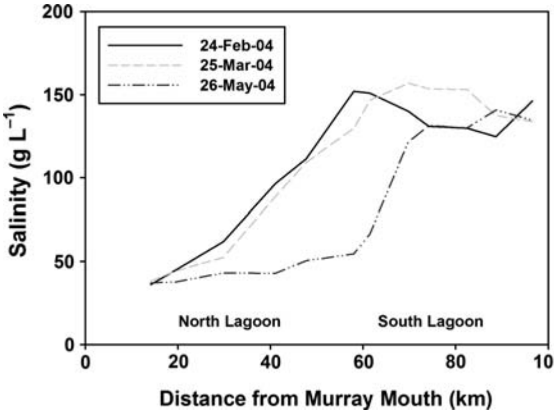


Fig. 4 Seasonal variations in salinity during 2004 in the Coorong. Data collected by the South Australian Environment Protection Authority and the Department of Environment and Heritage

C/N ratios of the bulk OM from the uppermost sediment layer do not vary much throughout the North Lagoon, averaging 8.6 ± 0.1 (Table 1). In the clay fraction (<2 μm), however, C/N ratios decrease along the major axis of the North Lagoon (Table 2). Given that C/N ratios of marine plankton vary around 6, the observed decline may indicate a greater contribution from plankton-derived OM in the southernmost parts of the North Lagoon and in the South Lagoon today. Similarly, prior to the 1950s, the C/N ratios in the clay fraction also decreased southward within the North Lagoon, but like the C/P and N/P ratios, their rate of decline is slower than that in the topmost sediments. These trends suggest that there is a spatial gradient in the ecology and biogeochemical cycling of the North Lagoon. Moreover, this gradient has been accentuated in recent times, resulting in limitations of nutrients, possibly due to declining inputs. The data also imply that, even prior to the mid-1950s, the nutrient status of the South Lagoon was more impoverished than that of the North Lagoon, albeit not to the same degree as today.

Table 1 Elemental analysis and nutrient ratios (weight %) in bulk sedimentary OM in the Coorong

Sample/depth (cm)	TC (%)	TOC (%)	TIC (%)	TN (%)	TP (mg kg^{-1})	C/N	N/P	C/P
North Lagoon								
C1 0–6	0.87	0.78	0.1	0.10	224	7.6	4.55	34.82
C1 6–12	0.63	0.64	0.0	0.07	169	9.7	3.90	37.78
C1 12–18	1.04	1.03	0.0	0.11	194	9.4	5.68	53.20
C1 18–24	0.69	0.73	0.0	0.07	163	10.0	4.48	44.94
C1 24–30	0.54	0.52	0.0	0.06	94	8.8	6.26	54.93
C1 30–36	1.6	1.47	0.1	0.17	268	8.5	6.45	54.92
C1 36–40	1.7	1.69	0.0	0.20	615	8.7	3.17	27.50
C4 0–6	3.0	2.98	0.0	0.32	425	9.3	7.55	70.13
C4 6–12	2.7	2.87	0.0	0.31	440	9.3	7.02	65.21
C4 12–18	2.6	2.78	0.0	0.29	413	9.5	7.07	67.33
C4 18–24	2.2	2.23	0.0	0.26	393	8.6	6.62	56.76
C4 24–30	1.9	1.93	0.0	0.23	323	8.4	7.11	59.52
C4 30–36	2.2	2.15	0.1	0.25	284	8.5	8.90	75.46
C4 36–42	1.1	1.28	0.0	0.13	162	10.1	7.83	79.05
C9 0–6	4.9	5.11	0.0	0.64	625	8.0	10.28	81.83
C9 6–12	3.3	3.48	0.0	0.39	481	8.9	8.12	72.35
C9 12–18	2.9	2.98	0.0	0.33	437	8.9	7.64	68.10
C9 18–24	2.7	2.51	0.2	0.30	457	8.3	6.60	54.78
C9 24–30	2.4	2.31	0.1	0.28	431	8.2	6.50	53.54
C13 0–6	5.4	5.61	0.0	0.59	543	9.5	10.89	103.28
C13 6–12	3.9	4.07	0.0	0.45	445	9.0	10.20	91.33
C13 12–18	3.0	2.81	0.1	0.32	390	8.7	8.25	72.01
C13 18–24	5.3	2.86	2.4	0.31	326	9.2	9.54	87.80
C13 24–30	6.2	2.69	3.5	0.30	261	9.1	11.30	103.14
South Lagoon								
C18 0–7	7.7	5.82	1.9	0.65	695	8.9	9.39	83.78
C18 7–13	5.4	1.57	3.9	0.16	175	10.1	8.86	89.77
C18 13–20	7.3	2.19	5.1	0.23	197	9.3	11.85	110.74
C26 0–6	9.6	5.30	4.3	1.04	527	5.1	19.81	100.51
C26 6–12	8.5	4.78	3.7	0.53	512	9.1	10.30	93.43
C26 12–18	8.9	6.83	2.1	0.77	574	8.8	13.47	118.97
C26 18–24	9.2	6.85	2.3	0.78	567	8.8	13.80	120.97
C26 24–30	10.2	7.42	2.8	0.84	651	8.9	12.87	113.93
C26 30–36	10.1	6.52	3.5	0.74	659	8.8	11.29	99.01
C26 36–42	8.7	5.23	3.4	0.61	576	8.6	10.51	90.78
C26 42–50	9.5	5.99	3.5	0.72	659	8.3	10.90	90.92

Stable carbon isotopic analyses

With the exception of core C4, the average δ^{13}C values of the bulk OM and its three size fractions in the uppermost sediment layer (0–7 cm) of both lagoons are -22.0 ± 1.2‰ (Fig. 5). The finer fractions are more depleted in ^{13}C in the northern part of the North Lagoon but show no notable difference elsewhere. OM from core C4 is consistently lighter than the corresponding fractions in the other cores, and this

Table 2 C/N ratios (wt%) in size fractions of sedimentary OM in the Coorong

Sample/depth (cm)	C/N		
	10–53 µm	2–10 µm	<2 µm
North Lagoon			
C1 0–6	9	11	14
C1 6–12	9	11	14
C1 12–18	10	12	15
C1 18–24	15	12	8
C1 24–30	13	12	8
C1 30–36	11	9	8
C1 36–40	13	9	9
C4 0–6	9	10	11
C4 6–12	8	9	11
C4 12–18	8	10	11
C4 18–24	8	10	13
C4 24–30	10	8	8
C4 30–36	10	8	8
C4 36–42	11	9	6
C9 0–6	8	7	5
C9 6–12	9	8	5
C9 12–18	9	9	5
C9 18–24	8	8	4
C9 24–30	8	8	4
C13 0–6	9	9	4
C13 6–12	9	9	4
C13 12–18	9	8	4
C13 18–24	9	9	5
C13 24–30	9	9	5
South Lagoon			
C18 0–7	8	9	9
C18 7–13	9	9	5
C18 13–20	10	9	6
C26 0–6	9	9	6
C26 6–12	9	9	6
C26 12–18	9	9	ND
C26 18–24	9	8	ND
C26 24–30	9	8	ND
C26 30–36	9	ND	ND
C26 36–42	9	ND	ND
C26 42–50	9	ND	ND

ND, Not determined

deviation is most likely due to freshwater influx, as suggested by a greater abundance of riverine diatom taxa (D. Haynes, unpublished data).

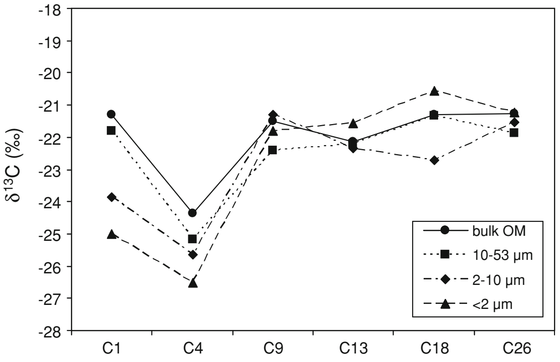


Fig. 5 δ^{13}C variations in bulk and size separated OM from the uppermost (0–7 cm) sediments in the Coorong's North and South lagoons

In comparison with the δ^{13}C values of the top sediment layer, the bulk and size-separated OM fractions that predate the first occurrence of *Pinus* (i.e. pre 1950s) are significantly ^{13}C-enriched. This may be due to various factors, including changes in ecology or different physicochemical constraints on carbon fixation. The secular variation in the C-isotopic compositions of the bulk OM and the fine sand to silt fraction (10–53 µm) in both lagoons shows concurrent changes in the fine silt and clay fractions (2–10 and <2 µm, respectively) (Figs. 6 and 7). The arrows in each figure indicate the first appearance of *Pinus,* corresponding to the mid 1950s to 1960s in the respective cores. Negative shifts in the δ^{13}C profiles of the bulk OM and the 10–53 µm fraction coincide with the first appearance of *Pinus* in cores C4 and C13 in the North Lagoon and cores C18 and C26 in the South Lagoon. No *Pinus* pollen have been detected in core C1, which is likely due to a lack of influx of *Pinus* pollen in this part of the estuary. It is worth noting that palynological analysis of sediment cores from nearby Lake Alexandrina (Fig. 1) also failed to reveal *Pinus* pollen (J. Fluin, pers. commun.), despite the fact that their chronology spanned the last few centuries.

Analyses of the 2–10 and <2 µm size fractions proved to be more informative with regard to isotopic changes following the first appearance of *Pinus* (i.e. post the mid-1950s). The δ^{13}C shifts that are evident in the bulk OM of cores C4, C13 and C18 are even more pronounced in the fine fractions (Fig. 7). Especially in core C1, where there is no apparent isotopic change in the bulk OM, the fine fractions exhibit a >4‰ negative isotopic shift. In core C9, however, there is no abrupt isotopic excursion coincident with

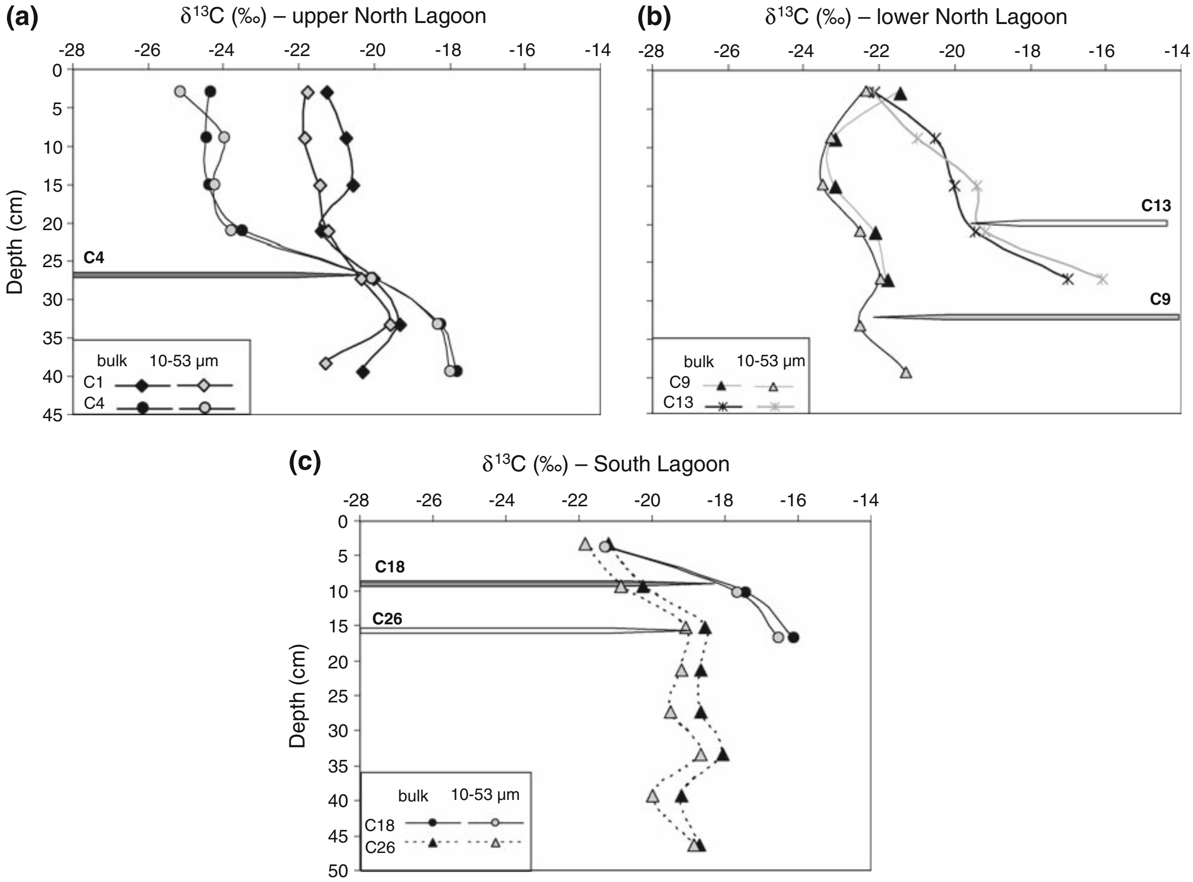


Fig. 6 $\delta^{13}C$ variation with depth of bulk and silt-sized (10–53 μm) OM in the Coorong's upper North (**a**), lower North (**b**) and South (**c**) lagoons. Arrows indicate the first occurrence of *Pinus* pollen (i.e. below which dates as pre-1950s) in the respective cores. No *Pinus* pollen are preserved in core C1

the first appearance of *Pinus* at 24 cm. Instead, the secular increase in $\delta^{13}C$ is more gradual as indicated by the analyses of deeper samples (Fig. 8), suggesting a greater degree of mixing in this part of the lagoon.

It is possible that diagenesis may have been responsible for the observed shifts in $\delta^{13}C$ (making their coincidence with the first appearance of *Pinus* purely fortuitous), since the original isotopic signatures of dead biomass are known to change during its sedimentation and early burial (e.g. Henrichs 1992; Meyers and Ishiwatari 1993; Spiker and Hatcher 1987; Prahl et al. 1997 and Freudenthal et al. 2001; summarised in Fan et al. 2007). During its initial burial, microbial degradation of OM in sediments may lead to small changes in $\delta^{13}C$, reported to be less than 2‰. Continued degradation of OM during early diagenesis may result in a negative shift of up to 4‰ through the preferential removal of ^{13}C-enriched moieties such as carboxyl groups. Lehmann et al. (2002) reported that in lacustrine settings sedimentary OM is ^{13}C-depleted by about 1.5‰ relative to sinking biomass. These isotopic changes are in agreement with the 1.6‰ decrease observed during a three-month, incubation-based simulation of diagenesis (Lehmann et al. 2002). Thus, the negative isotopic shift from the pre-1950s to the conditions characterising the Coorong today occurs in the opposite direction of that typically observed during initial burial and early diagenesis. Accordingly, we are confident that the C- isotopic profiles of the Coorong cores record primary features of the sedimentary OM and are not a result of post-burial alteration.

In temperate (C3-dominated) environments, such as the Coorong, a shift from isotopically heavier to lighter OM in aquatic sediments is commonly interpreted as a change from lower to higher inputs of

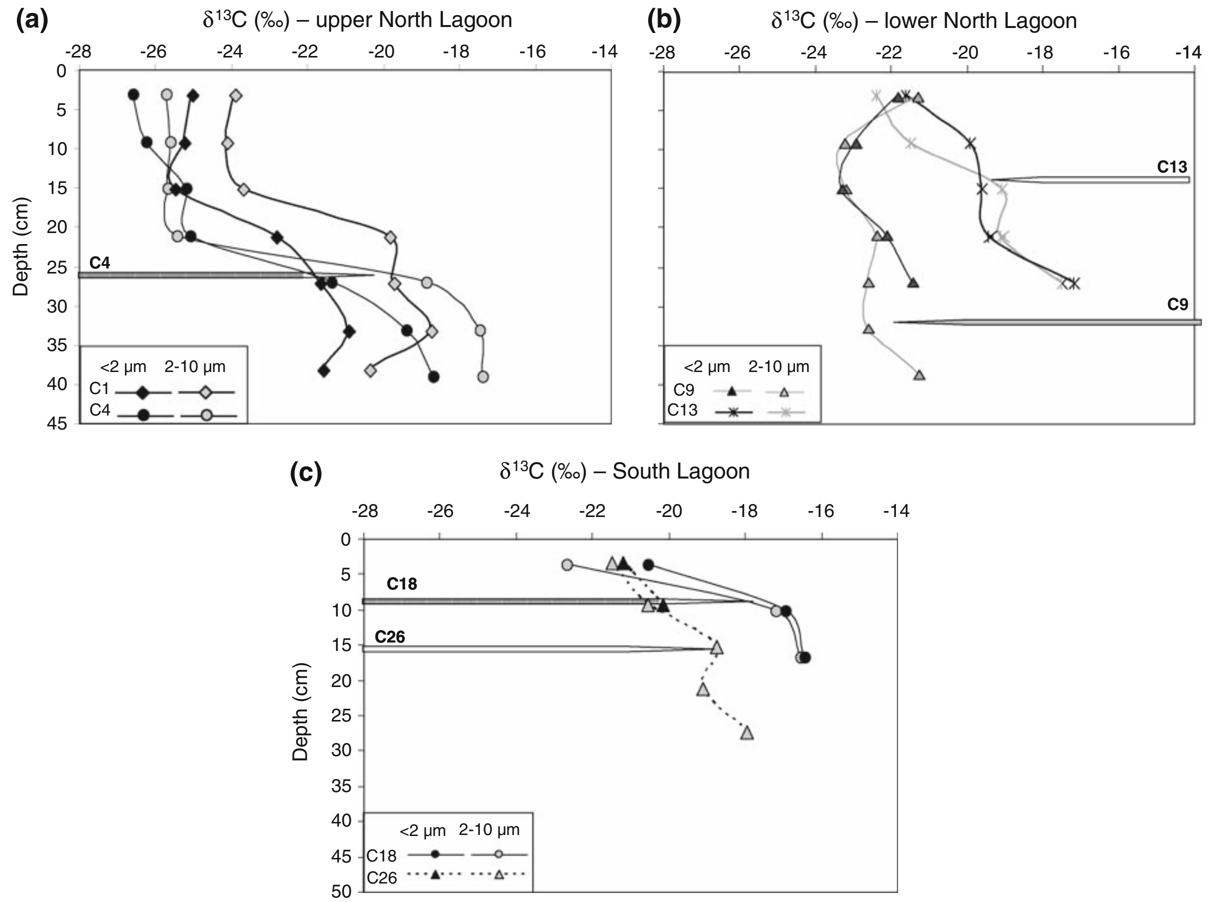


Fig. 7 δ^{13}C variation with depth of fine silt and clay-sized (2–10 and <2 μm) OM in the Coorong's upper North (**a**), lower North (**b**) and South (**c**) lagoons. *Pinus* occurrence as for Fig. 6

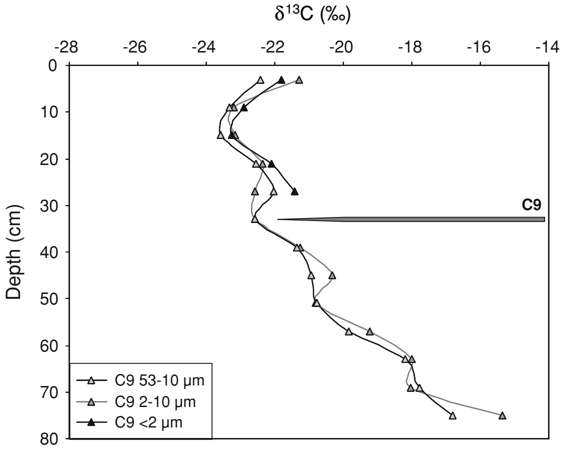


Fig. 8 δ^{13}C variation with depth in core C9. The more gradual shift to heavier values with increasing depth possibly reflects greater bioturbation

terrestrial OM (more ^{13}C depleted), or from more to less autochthonous OM. Thus, in order to understand whether the causes of the marked ^{13}C-depletion were indeed related to changes in the sources of OM, we examined the δ^{13}C signatures and C/N ratios of potential source biota which are currently found in the Coorong. These include macro-algae (*Gracilaria,*), flowering aquatic plants (*Myriophyllum, Lepilaena*), reeds, (*Typha, Phragmites*), filamentous algae, halophytes (*Samphire*) and plankton (phyto- and zoo-) as well as a terrestrial grass (Table 3).

However, there was no clear indication as to an obvious change from one source to another. The greatest degree of overlap occurred between sedimentary OM and phytoplankton but no distinction was possible between pre- and post-1950s sediment (Fig. 9). In addition, given that shifts in C/N ratios

Fig. 9 Plot of δ^{13}C versus C/N illustrating the relationship between sedimentary OM in the Coorong and some of its potential sources

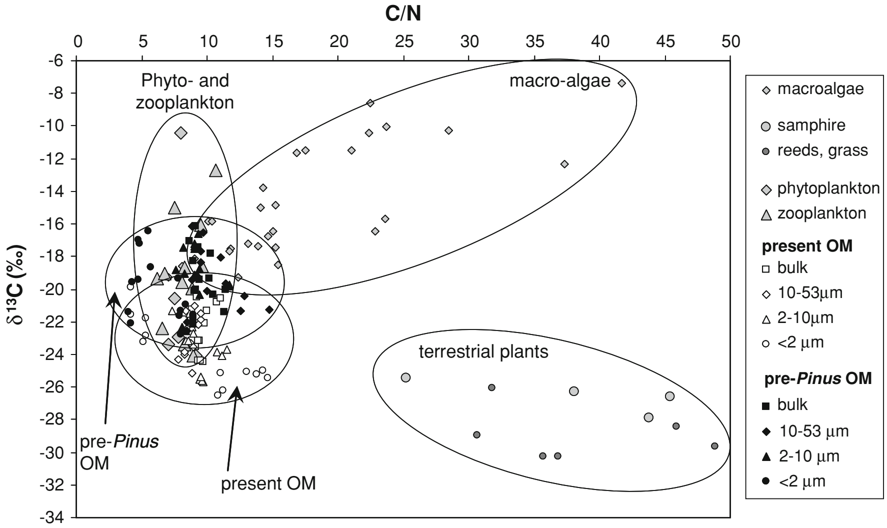


Table 3 Aquatic and terrestrial biota from the Coorong lagoon and surrounding environs

Species	δ^{13}C‰	C/N
Gracelleria (*n* = 6)	−17.5	11.5
Ulva (*n* = 2)	−16.1	23.2
Brown algae (*n* = 2)	−17.3	13.5
Myriophyllum (*n* = 4)	−10.0	30.6
Lepileaena (*n* = 3)	−10.3	24.9
Phragmites (*n* = 2)	−27.8	40.3
Typha (*n* = 3)	−29.8	34.4
Terrestrial grass (*n* = 1)	−28.4	45.9
Filamentous algae (*n* = 6)	−13.9	15.5
Samphire (*n* = 4)	−26.5	38.1
Phytoplankton (*n* = 4)	−22.7	7.9
Zooplankton (*n* = 4)	−18.7	8.2
Ruppia megacarpa (*n* = 10)	−13.2	34.8

from higher to lower values have been observed during burial and decomposition (Meyers and Ishiwatari 1993; Meyers 1997; Lehmann et al. 2002), it is difficult to estimate what the contribution of reeds or macro-algae to sedimentary OM in the Coorong may have been.

^{13}C-NMR spectroscopy

In the absence of a clear indication of source changes based on isotopic and elemental data, we employed ^{13}C-NMR spectroscopy to verify whether the isotopic shift indeed correlates with an increase in terrestrial-derived OM in the post-1950s. ^{13}C-NMR spectroscopy and subsequent application of the molecular mixing model developed by Baldock et al. (2004) provided information as to the major C-associated functional groups present (alkyl, O-alkyl, aryl, O-aryl, carbonyl, ketones) and the proportional representation of major biomolecules.

Figure 10a shows the results of applying the molecular mixing model to NMR data obtained from the surface sediments of both lagoons. The data reveal that the OM comprises lipid, carbohydrate and protein in roughly equal proportions, with lipids rising to dominance in cores C13, C18 and C26. The increasing proportion of lipids appears to correspond with increasing salinity (Fig. 4). Also evident is the presence of a small proportion of aromatic C in the sediments proximal to the Murray Mouth (in C1), the amount declining southward, again in association with higher salinities. Although not as pronounced, similar decreasing trends are observed for the proportion of carbohydrates and proteins. Most of the aforementioned compositional variation occurs in the North Lagoon. OM in the surface sediments of the South Lagoon is much more uniform. The southward increase in lipidic material may be a reflection of an increased proportion of lipid-rich plankton (e.g. Hedges et al., 2002; Sannigrahi et al. 2005).

Comparison of the NMR spectra from the top sediment layer with potential sources (e.g. macro-algae, aquatic plants, reeds, halophytes, plankton and soil) revealed that soil OM, macro-algae and aquatic plants

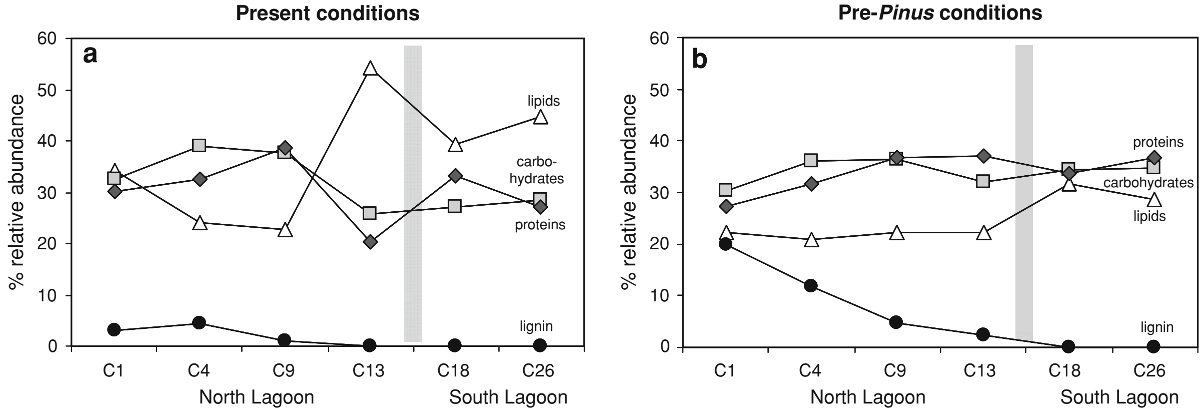


Fig. 10 Spatial variation of major biochemical entities (based on ^{13}C-NMR data) within the Coorong's sedimentary OM (**a**) pre- and (**b**) post-1950s. The grey line represents the boundary between the North and South Lagoons

bore little resemblance, whereas the NMR spectra from phytoplankton exhibited the greatest similarity (Fig. 11). Whether this is evidence for plankton dominating the system from an ecological point of view cannot be determined from these data, as it is possible that biomass with a greater degree of decomposability than plankton was subjected to a faster turnover rate and consequently would have had a lower proportion preserved in the sedimentary record. However, plankton is usually regarded as one of the most bio-available materials (Hedges et al. 2001) and it is therefore reasonable to assume that the OM composition recorded in the sediment is a valid indication of plankton being the major source of the Coorong's OM.

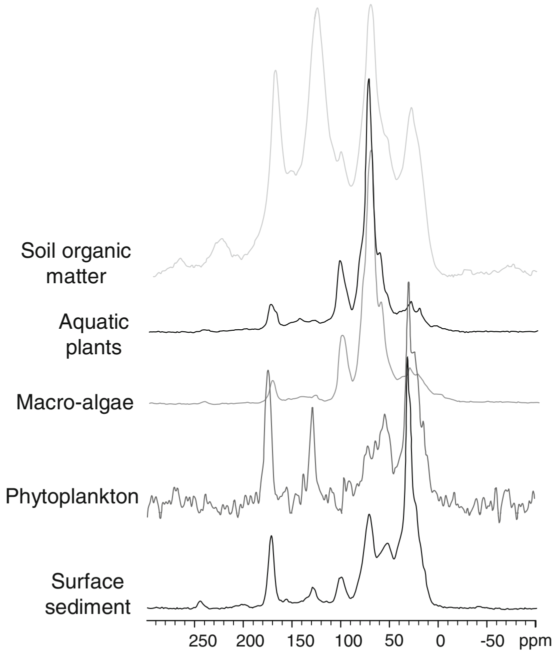


Fig. 11 ^{13}C-NMR spectra of the OM in the uppermost sediment in the Coorong and combination with selected potential sources

Results of the application of the molecular mixing model to the NMR data do not support the interpretation that the post-1950s sediment carries a large proportion of terrestrial-derived material (as suggested by its lighter δ^{13}C signatures). If the small terrestrial component, represented by aromatic C (lignin) in Fig. 10a, is responsible for this isotopic signal, the enhanced ^{13}C-depletion should be more apparent in cores C1 and C4 (5% of OM) and absent in core C13, as there is no evidence for aromatic C in the southern part of the North Lagoon or in the South Lagoon. In addition, even lower amounts of aromatic C are to be expected in the pre-1950s sediments as suggested by their heavier C-isotopic composition. However, while NMR data of the pre-1950s sediments reveal a similar decline in the contribution of aromatic C (lignin) with increasing salinity, the total proportion of aromatic C in the sediments of the North Lagoon is much greater (up to 20%) than in those deposited under the post-1950s conditions (Fig. 10a). As in the post-1950s sediments, there is no contribution from aromatic C in the South Lagoon and the compositional differences between the different biomolecules are not as pronounced as in the North Lagoon.

Thus, these findings appear to be at odds with the interpretation suggested by the isotopic results, namely a higher proportion of autochthonous material in pre-1950s sedimentary OM. Instead, the results from the NMR-based molecular mixing model suggest a greater (not lesser) contribution of aromatic C (lignin), which is customarily assumed to be of terrestrial origin and therefore more ^{13}C-depleted.

In order to resolve this apparent conundrum and determine the possible source of isotopically heavy (δ^{13}C >−20‰), lignin-rich OM in the pre-1950s sediments of the North Lagoon, we extended the pool of possible OM sources to those that once were present in the Coorong but are now extinct, namely the seagrass *Ruppia megacarpa* (Nicol 2005). Figure 12 illustrates the differences in composition between other aquatic species (phytoplankton and zooplankton) and *R. megacarpa*. Phytoplankton and zooplankton are characterised by low amounts of aromatic C of which most is likely associated with the aromatic side chains of some amino acid residues in proteins rather than lignin (J. Baldock, pers. commun.). By way of contrast, aromatic C is the dominant constituent of *R. megacarpa* which can be explained by its evolution from terrestrial angiosperms and, as such, having maintained its original lignin content (Klap et al. 2000). Thus, in this case, most of the aromatic C is indeed associated with lignin. However, due to the fact that its photosynthetic fixation of carbon is carried out in the aquatic environment, *R. megacarpa* is accordingly ^{13}C-enriched relative to C3 terrestrial land plants (δ^{13}C = −13‰; see also Boyce et al. 2001). By comparison, some phytoplankton (e.g. diatoms) use a different form of carbon fixation and tend to be isotopically lighter ($\delta^{13}C = -22$ to −26‰: Raven et al. 2002). Thus, the apparent contradiction of OM that is both lignin- and ^{13}C-enriched can be explained by a larger contribution of seagrasses, such as *R. megacarpa*, to the Coorong's sedimentary OM prior to the changes associated with barrage construction and extraction of water upstream.

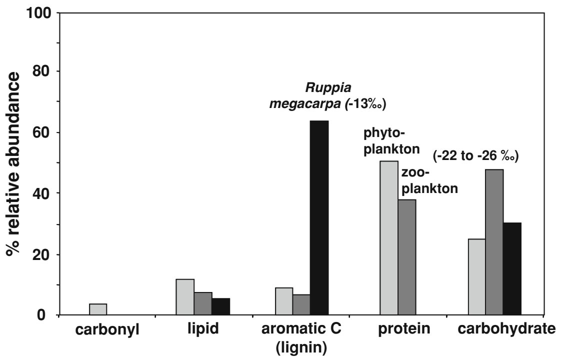


Fig. 12 Comparison of the chemical and isotopic compositions of the lignin-containing seagrass *Ruppia megacarpa*, phytoplankton and zooplankton

Correlation with palynology

The biogeochemical changes occurring across the narrow time period of the mid-1950s to the mid-1960s, evident from C-isotopic and NMR analyses of its sedimentary OM, appear to be mirrored by changes in the Coorong's aquatic ecology, as reflected in diatom abundance and composition (Gell and Haynes 2005; Haynes et al. 2007). Diatom assemblages of the Coorong lagoons prior to the first occurrence of *Pinus* (i.e. pre-1950s) are dominated by marine-estuarine or thalassic taxa (e.g. *Paralia sulcata*), reflecting a strong marine influence and salinities varying between 5 and >35 g/l. River-borne flora (e.g. *Aulacoseira* spp.), which are abundant in the River Murray and Lake Alexandrina, are rare (or absent) in all cores southeast of site C12, suggesting that the direct influence of river-water was limited to the northern end of the North Lagoon. By comparison, the pre-*Pinus* flora of the South Lagoon are brackish and saline taxa, supporting the geochemical indications that the South Lagoon tended to be different from the North Lagoon with regard to its salinity, ecology and associated biogeochemistry.

Across both lagoons, however, the most substantial change in diatom assemblage occurred shortly after the first appearance of *Pinus* when thalassic species were replaced by tychoplanktic taxa, which are adapted to turbid and low light environments (Gell et al. 2007a; Haynes et al. 2007). Of particular importance was the appearance in the post-1950s of small diatoms (Fragilariaceae), some of which are facultative planktonic and as such have a competitive advantage in turbid waters. Their abundance in post-1950s sediments across the Coorong has been suggested to be an indicator of increased turbidity, as well as the development of a semi-closed system (Gell and Haynes 2005). Isolation of the Coorong from the Lower Lakes through barrage construction reduced the estuarine size and degree of mixing of the lagoonal system. Simultaneously, increased sedimentation around the Murray Mouth decreased marine water inflow via tidal action. The increased proportion of taxa, able to tolerate hypersaline conditions, towards the south-east of the North Lagoon indicates a salinity gradient similar to that observed today, and one that parallels the biogeochemical trends observed in the sediments.

Conclusions

The combined application of stable isotopic, radionuclide, elemental, spectroscopic and palaeoecological techniques to its sediments and biota has revealed pronounced biogeochemical changes along the Coorong, both today and in the recent past. These data indicate that the present condition of the Coorong lagoons differs very much from that of the pre-1950s. The period from the 1950s onward was associated with significant changes to the water level and salinity regimes of the Coorong as a result of the presence of the barrages and changes in the timing and magnitude of inflows from the River Murray. This resulted in subsequent isolation from the Lower Lakes, increased sedimentation and constriction of the Murray Mouth and reduced mixing with the ocean. Consequently, the Coorong is now in a condition that is unprecedented in its 6000-year history (Gell et al. 2007b).

The combination of high-resolution radionuclide dating with palaeolimological analyses and stable isotopic, elemental and ^{13}C-NMR analyses provided the means to identify when and how the Coorong lagoons started to deteriorate. The use of multiple organic matter tracing techniques suggest that a significant change in the primary producer community has occurred in this system since the 1950s. The loss of the *Ruppia* seagrass community in the last 30 years has been a significant factor in the ongoing decline of this ecosystem as indicated by the observation that increases in turbidity were coincident with a decline in sediment stabilising seagrasses (e.g. *Ruppia*) enabling phytoplankton to become the main primary producer. These findings have important implications for other degraded or degrading coastal systems worldwide, as it is the complexity of these systems that necessitates a range of techniques in order to fully understand the changes in their biogeochemistry. The biogeochemical and palaeolimnological trends evident in the upper sediments of the Coorong point towards a system wherein the ecological degradation is migrating inexorably northward. If the current state of the Coorong persists, i.e. a heavily-regulated system that does not receive major freshwater and marine, it is likely that the North Lagoon will develop conditions that are observed today in the areas more distal to the Murray Mouth.

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