Salinity variations in the Northern Coorong Lagoon, South Australia: Significant changes in the Ecosystem following human alteration to the natural water regime

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Abstract

European settlement and drought have significantly impacted the hydrology of the Coorong a shallow coastal lagoon complex in South Australia, which is part of a terminal wetland at the Mouth of the River Murray. An increased salinity associated with lower water levels and progressive isolation from ocean flushes contributed to a severe decline in ecological diversity over the past decades. Here we have conducted a molecular and stable isotopic study of a sedimentary core from the northern Coorong Lagoon spanning more than 5000 years to investigate the recent palaeoenvironmental history of the ecosystem. Major alterations were evident in many biogeochemical parameters in sediments deposited after the 1950s coinciding with the beginning of intensified water regulations. The most prominent shift occurred in $\delta^{13}C$ profiles of C_{21}-C_{33} *n*-alkanes from average values of -23.5 ‰ to an average of -28.2 ‰. Further changes included decreases in carbon preference index (CPI) and average chain length (ACL) of the *n*-alkane series as well as significant increases in algal (e.g. C_{20}HBI, long-chain alkenes and C_{29}-alkadiene) and bacterial (e.g. ^{13}C depleted short-chain *n*-alkanes and hopanoids, $\delta^{13}C$: -35.9 to -30.1 ‰) derived hydrocarbons. Long-chain *n*-alkanes with a strong odd-over-even predominance as observed here are typically attributed to terrestrial plants. In the Coorong however, terrestrial input to sedimentary OM is only minor. Therefore changes in the before mentioned parameters were

attributed to a source transition from a major contribution of macrophytes towards predominantly microalgae and bacteria.

δD values of C_{21}-C_{33} *n*-alkanes showed a general trend towards more enriched values in younger sediments, indicating an overall rising salinity. However, the most pronounced positive shift in these profiles again occurred after the 1950s. Altogether this study demonstrates that the recent human induced changes of the Coorong hydrology, compounded by a severe drought led to an increase in salinity and alterations of primary production which have been much more significant than natural variations occurring throughout the Holocene over several thousands of years.

1. Introduction

The Coorong is part of a terminal lake system in South Australia at the mouth of the River Murray. It consists of two narrow coastal lagoons (North and South Lagoon) which are connected through a small channel and together extend for more than 130 km in length (Fig. 1). The wetland is of great ecological significance, in particular for water birds (migratory and native; Paton et al., 2009), and is therefore listed under the Ramsar Convention on Wetlands and is protected as a national park. However, substantial water regulations imposed on the River Murray and the lake system in the second half of the 20th century, compounded by a severe drought from 2000-2010, have significantly altered the complex and dynamic hydrology of the ecosystem leading to a marked increase of salinity in the Coorong and a severe decline of ecological diversity over the past several decades (e.g. DEH, 2000; Shuttleworth et al., 2005; Paton et al., 2009; Dick et al., 2011). Although recent floods in 2010 temporarily improved the ecological state of the Lower Lakes and led to a short term recovery of the freshwater levels in the Coorong, the long term issue of providing continuous riverine input (especially under future drought conditions) has not been resolved and an extensive water management plan is required to further restore and maintain the diverse ecosystem of the Coorong (Kingsford et al., 2011).

Estuarine systems like the Coorong have multiple organic matter (OM) sources including *in situ* primary production by organisms such as phytoplankton, microbial mats, macroalgae or aquatic and benthic plants as well as allochthonous input from terrestrial plant debris and soil OM which enter the system mainly through riverine inflow (e.g. Shuttleworth et al., 2005; Volkman et al., 2008). Changes in the type of OM – for example caused by different flow regimes – can have a profound impact on the ecosystem since the base of the food-web is affected (Krull et al., 2009). Efficient remediation measures for the Coorong require a profound understanding of the effects of alterations in parameters such as water-level, salinity or quantity of riverine input (all of which have occurred as an immediate result of human water management) on the ecosystem. This also involves

gaining detailed knowledge about ecology and palaeoenvironmental conditions prior to human influence, and tracking changes in OM sources over time to establish their relationship with the key environmental parameters previously mentioned.

The analysis of sedimentary biomarkers in combination with compound specific stable isotope analysis (CSIA) is a powerful analytical tool for this purpose and has been frequently used to elucidate OM sources and/or environmental conditions at the time of deposition (e.g. Freeman et al., 1994; Grice et al. 1996, 2001, 2005; Volkman et al., 2008; McKirdy et al., 2010). Compound specific δD analysis has a great potential for reconstructions of climate and hydrological conditions in palaeoenvironments since D/H-ratios of biolipids in autotrophic organisms are strongly influenced by the composition of the utilized source water (Sessions et al., 1999; Andersen et al., 2001; Sauer et al., 2001; Dawson et al., 2004; Nabbefeld et al., 2010). δD signatures of biomarkers derived from aquatic or benthic organisms thus reflect D/H ratios in the lake or seawater (Sachse et al., 2006; Mügler et al., 2010) and therefore often strongly correlate with palaeosalinities (Andersen et al., 2001; McKirdy et al., 2010; Mügler et al., 2010). Salinity in estuarine systems such as the Coorong co-varies with δD signatures of lake water since it is largely determined by the balance of evaporation and seawater inflow (both leading to a D-enrichment in the reservoir) and the input of D-depleted meteoric waters from precipitation or riverine influx (Gat, 1996; Ingram et al., 1996).

A detailed investigation of OM sources in the recent Coorong was performed by Revill et al. (2009) who analysed abundances and stable isotopic compositions of pigment and lipid biomarkers in the water-column and surface sediments throughout both lagoons. McKirdy et al. (2010) carried out a comprehensive study which also included bulk and compound specific isotope analysis to reconstruct variations in environmental conditions and OM-sources in the Coorong from the mid to late Holocene. However, their main focus was a core from the South Lagoon and only some elemental and bulk isotope data from the North Lagoon was included. Nevertheless their data revealed significant differences between the ecosystems of the North and South Lagoon. Krull et al. (2009) combined elemental, bulk $\delta^{13}C$ and ^{13}C-NMR analyses with radionuclide dating in several cores from both lagoons spanning the past 100 years and found evidence for significant changes in sedimentary OM, which coincided with the beginning of substantial human impact on the water regime.

However, so far there have been no biomarker studies in sediments from the North Lagoon spanning the time periods before and after European settlement. Here we analysed bulk $\delta^{13}C_{OM}$ as well as abundances and stable isotopic compositions ($\delta^{13}C$ and δD) of lipid biomarkers in a core from the North Lagoon dating back more than 5000 years. The aim was to gain insight into the ecosystem of the North Lagoon in pre-European

times, reconstruct salinity variations over an extended timeframe and more robustly scrutinise the recent changes in OM sources observed by Krull et al. (2009). Pollen analysis and different dating techniques performed previously by Krull et al. (2009) and Fluin et al. (2007) in a core nearby allowed for a correlation of our data with recent events in the Coorong.

2. Experimental

2.1. Sampling location and core description

2.1.1. Environmental settings

Together with Lakes Alexandrina and Albert the Coorong forms a terminal wetland at the mouth of the River Murray (Fig. 1). The region experiences a Mediterranean climate, with comparatively cool and moist winters and long dry summers. The elongated Coorong covers an area between 150-240 km^2 depending on seasonal changes and features an average depth around 1 m with maximum depths of 4 m (Boon, 2000). In its natural state the North Lagoon used to be connected to Lake Alexandrina which receives freshwater input from the River Murray. The hydrology of the Coorong was determined by seawater exchange through the Murray Mouth and freshwater input from Lake Alexandrina as well as groundwater and surface runoff *via* Salt Creek at the southern end of the lagoons (Boon, 2000; Webster, 2005). Seasonal and tidal changes created various dynamic habitats in and around the lagoons, supporting a diverse range of bird, fish and plant species (DEH, 2000; Boon, 2000).

Human water management with an impact on the Coorong commenced approximately 100 years ago in the form of regulations and diversions from the River Murray for agricultural use and ship navigation (Maheshwari et al., 1995). In 1940 barrages were installed between the Coorong and Lake Alexandrina which largely prevented water exchange and reduced riverine input. However, there was still regular freshwater flow into the North Lagoon until the 1950s as the barrages were regularly opened to prevent flooding of the surrounding areas (Krull et al., 2009). After a major flood event in 1956 the inflow from the River Murray was reduced significantly due to increased abstraction for agricultural and domestic use. A severe drought between 2000 and 2010 has led to further decline in freshwater input (Webster, 2005, 2010; Kingsford et al., 2011). The reduced inflows contributed to siltation of the Murray Mouth limiting the seawater exchange with a temporary closure occurring in 1981. During the recent drought in the beginning of this century an open connection has only been maintained by regular dredging (Webster, 2005; Kingsford et al., 2011).

Depending on the amount of freshwater inflow through the barrages the salinities in the northern part of the lagoon close to the Murray Mouth can vary from values approaching zero to seawater levels. A salinity

gradient shows an increase with distance from the Murray Mouth and a constant hypersalinity prevails in the South Lagoon during periods of low freshwater inflow such as the drought from 2000 to2010 (e.g. Webster, 2005, 2010). The salinity increase is usually considered the main cause for the extinction of key species such as the macrophytes *Ruppia megacarpa* and other significant alterations to the ecosystem (Nicol, 2005; Dick et al., 2011). Increased freshwater inflows after 2010 have caused a slight and temporary improvement of the ecological state in the Coorong (Kingsford et al., 2011) but this is not addressed here since the presently analysed samples were collected in 2005.

2.1.2. Sample collection

The core analysed in this study was part of a suite of samples collected throughout the Coorong in 2005 by University of Adelaide researchers for a project commissioned by the Department of Water, Land and Biodiversity Conservation (DWL&BC) for the Upper South East (USE) Program. The sampling site was located in the middle of the North Lagoon slightly south of the Murray Mouth (Fig. 1) and is equivalent to core "C4" in Krull et al. (2009). Sample collection and preparation of the core are described elsewhere (e.g. Krull et al., 2009). For this study the core was sampled between the depths of 0 and 115 cm. 1 and5 cm intervals were homogenized for bulk analysis ($\delta^{13}C$ and TOC) and biomarker analysis, respectively.

2.1.3. Chronology

In the present study we used chronological data obtained by Krull et al. (2009) and Fluin et al. (2007) from a core referred to as "C3" (located in close vicinity to C4) to correlate observed alterations in biomarker parameters and their stable isotopic compositions with significant events in the Coorong. Krull et al. (2009) used a combination of *Pinus* pollen analysis (a species introduced by Europeans) and radionuclide-dating (^{137}Cs and Pu isotopes) in various cores collected throughout the Coorong to establish chronologies over the past 50-60 years. Sediment ages in more basal parts of some of these cores, obtained from ^{14}C-accelerator mass spectrometry (AMS), have been published by Fluin et al. (2007).

The first appearance of *Pinus* pollen in sediments from southeastern Australia is a common indicator for the evolution of European settlement and is often used in combination with other dating techniques (Tibby, 2003). In the Coorong its first occurrence roughly correlates with the 1950s (Krull et al., 2009). In core C3 and core C4 the first *Pinus* pollen were detected at depths of 23 and 27 cm, respectively (Krull et al., 2009). A detailed description of the principles of ^{137}Cs and Pu radionuclide dating can be found in Krull et al. (2009).

2.2. Analytical methods

2.2.1. Bulk stable isotope and TOC analysis

Sediment samples were dried at 55 °C overnight, ground, homogenised and weighed into tin cups for analysis. For carbonate removal sulfurous acid was added directly into the tin cups to prevent loss of acid-soluble organic carbon (Verardo et al., 1990). After re-drying the samples were analysed for C content and $\delta^{13}C$ using a Carlo Erba NA1500 CNS analyser interfaced via a Conflo II to a Finnigan Mat Delta S isotope ratio mass spectrometer operating in the continuous flow mode. Combustion and oxidation were achieved at 1090 ºC and reduction at 650 ºC. To ensure reproducibility, samples were analysed at least in duplicate. Results are presented in the standard delta (δ) notation relative to Vienna Pee Dee Belemnite (VPDB).

TOC (%) was calculated from mass spectrometer peak areas using standards with a known C content. The reproducibility of stable isotope measurements was ± 0.2 ‰.

2.2.2. Sample preparation and extraction for biomarker analysis

Samples were dried on a heated sandbath (55 °C) or in a cool oven (45 °C), powdered and extracted with a mixture of 9:1 dichloromethane (DCM): methanol by accelerated solvent extraction (ASE) using a Dionex ASE 200 (Dionex, Sunnyvale, CA, USA). The extracts were desulfurized overnight following addition of activated copper powder. The filtered extracts were successively fractionated by silica gel chromatography (column size: 20 cm x 0.9 cm I.D.) using approximately two column volumes of increasingly polar solvents. Aliphatic and aromatic fractions relevant for this study were eluted with *n*-hexane and 30% dichloromethane in *n*-hexane, respectively. An internal perdeuterated standard (*p*-terphenyl d^{14}) was added to the aromatic fraction to assist semi quantitative analysis. Abundances of hopanoids, sterenes and steranes were calculated from peak areas in *m/z* 191, *m\z* 215 and *m/z* 217 extracted ion chromatograms, respectively and reported relative to peak areas of C_{21}-C_{31} *n*-alkanes from total ion chromatograms (TIC) without the consideration of response factors.

2.2.3. Gas chromatography mass-spectrometry (GC-MS)

GC-MS analyses were performed on an Agilent 5973 Mass-Selective Detector (MSD) interfaced to an Agilent 6890 gas chromatograph (GC). For the separation of the analytes a capillary column (60 m x 0.25 mm) coated with a 0.25 µm 5% phenyl 95% methyl polysiloxane stationary phase (DB-5MS, J & W scientific) was used. The GC-oven was temperature programmed from 50 °C to 310 °C at a rate of 3 °C/min with initial and final hold times of 1 and 20 minutes, respectively. Samples were injected (split/splitless injector) with a HP 6890 auto-sampler operated in a pulsed-splitless mode at 280 °C. Helium was used as the carrier gas at a

constant flow rate of 1.1 mL/min. Full scan (50 - 550 Daltons) 70 *eV* mass spectra were acquired typically with an electron multiplier voltage of 1800 V and a source temperature of 230 °C.

2.2.4. Gas chromatography-isotope ratio mass-spectrometry (GC-irMS)

GC-irMS analyses were performed on a Micromass IsoPrime mass-spectrometer interfaced to either i) an Agilent 6890 GC equipped with a 6890 autosampler for carbon isotope analysis; or ii) an Agilent 6890N GC with 7683 autosampler for hydrogen isotope analysis. The GC- column, carrier gas, injector conditions and oven temperature program were identical to the settings described for GC-MS. For $\delta^{13}C$ analyses an interface consisting of a quartz tube packed with CuO-pellets (4 mm x 0.5 mm, isotope grade, Elemental Microanalysis LTD.) maintained at 850 °C was used to oxidize the organic analytes to CO_2 and H_2O. The latter was subsequently removed by a liquid nitrogen trap at -100 °C. Isotopic compositions were determined by integration of the *m/z* 44, 45 and 46 ion currents of CO_2 peaks from each analyte and reported relative to CO_2 reference gas pulses of known ^{13}C-content. Isotopic values are given in the delta (δ) notation relative to the international standard VPDB.

For hydrogen isotope (δD) analysis the gas chromatographically separated analytes were converted into hydrogen gas in a pyrolysis furnace packed with chromium catalyst at 1050 °C. δD values were determined by integration of the *m/z* 2 and 3 ion currents of H_2 peaks generated by the chromatographically separated analytes and reported relative to H_2 reference gas pulses of known D/H content relative to Vienna Standard Mean Ocean Water (VSMOW). A correction factor accounting for contributions from H_3^+ produced in the ion source was determined by *m/z* 3 analyses at two different H_2 gas pressures.

Each sample was analysed in duplicate and average values and standard deviations were reported. Standard deviations for C-CSIA in all reported results were < 0.5 ‰ and for H-CSIA always < 7 ‰ and in most cases < 5 ‰. In house standard solutions containing a mixture of *n*-alkanes with a known isotopic composition were regularly (after ~8 analyses) analysed to confirm accuracy of measured isotopic ratios.

Peaks of corresponding monoenes (if present) were included for the calculation of $\delta^{13}C$ and δD of *n*-alkanes since co-elution prevented baseline separations. A further separation of the aliphatic fraction by procedures such as 5A-molecular sieving (Grice et al., 2008a) or argentation-thin layer chromatography (TLC) was not possible due to the limited amounts of sample material.

3. Results

Fig. 2 displays depth profiles of selected biomarker and stable isotope parameters indicative of changing OM-sources in the North Lagoon in a chronological context. A pronounced excursion in the TOC profile shortly below a depth of 20 cm marks the increased input of terrestrial OM being flushed into the lagoon during a large flood event in 1956. A second excursion at ~ 50 cm might indicate an earlier and non-reported flood.

The first occurrence of *Pinus* pollen at a depth of 27 cm indicates the beginning of European influence in the Coorong region and roughly coincides with the beginning of a restricted freshwater inflow into the North Lagoon through the barrages (see section 2.1.1). Sediment ages also included in Fig. 2a were published by Krull et al. (2009) and Fluin et al. (2007). Sediments < 20 cm, deposited after drastic alterations of the Coorong water regime, are hereafter referred to as "recent sediments" and the remaining sediments deposited before a significant European influence as "older sediments".

3.1. Hydrocarbon abundances

3.1.1. n-Alkanes, n-alkenes and acyclic isoprenoids

The aliphatic fractions were dominated by a suite of mid- to long-chain *n*-alkanes (C_{21}-C_{33}) with a strong odd over even predominance, typically maximising at C_{27} (e.g. Fig. 3). In recent sediments (< 20 cm) their distribution profiles showed significant alterations evident in decreasing carbon preference indexes (CPI, Eq. 1) from an average of 6.13 (± 1.07 standard deviation) to 4.25 (± 0.43) and average chain length (ACL; Eq. 2) from an average of 26.12 (± 0.29) to 25.89 (± 0.52; Fig. 2a). P_{aq} values (Eq. 3), determined according to a proxy to distinguish input from terrestrial *vs*. aquatic plants (Ficken et al., 2000), varied between 0.37 and 0.61.

$$\mathrm{CPI} = \frac{\sum C_{odd}}{\sum C_{even}} \qquad \text{Eq. 1}$$

where "C_{odd}" and "C_{even}" are peak areas from TIC chromatograms of *n*-alkanes with odd and even numbered chain lengths, respectively over the range from C_{21}-C_{30}

$$\mathrm{ACL} = \frac{\sum (i \times C_i)}{\sum C_i} \qquad \text{Eq. 2}$$

where "C_i" is the peak area of the *n*-alkane with carbon number "i" over the range from C_{21}-C_{31}

$$P_{aq} = (C_{23} + C_{25}) / (C_{23} + C_{25} + C_{29} + C_{31}) \qquad \text{Eq. 3}$$

where "C" is the peak area of *n*-alkanes

Another notable difference in recent sediments of the North Lagoon deposited after the ~1950s was a significant increase in relative abundances of microalgal- and bacterial-derived hydrocarbons including the C_{20} highly branched isoprenoid (HBI; **I**, see Appendix for structures), and short-chain *n*-alkanes (C_{14}-C_{20}, Figs 2a and 3). Furthermore, the uppermost sediments (< 20 cm) contained high concentrations of unsaturated aliphatics, with C_{23}-C_{29} *n*-alkenes and a C_{29} *n*-alkadiene of notably high abundance (Fig. 3).

3.1.2. Hopanoids and steroids

Bacterial-derived hopanoids (C_{27}-C_{32}) were abundant in all samples (Fig. 4a) and showed distributions typical of immature sediments with a complex suite of hopenes (hop-17(21)-enes, *neo*hop-13(18)-enes and hop-22(29)-ene (diploptene)) and high abundances of 17β,21β-hopanes (biological configuration) relative to 17β,21α and 17α21β isomers. Most hopanoids exhibited highest abundances (*cf. n*-alkanes) in the uppermost 20 cm indicating an increased bacterial input (e.g. Fig. 4a). The molecular distribution of hopanoids showed slight variations throughout the core, however they were most pronounced in recent sediments.

The most abundant steroids in the aliphatic fractions were C_{27}-, C_{28}- and C_{29}-5α,14α,17α-20R-ster-2-enes, which are early diagenetic products of biological steroids (e.g. Mackenzie et al., 1982). We also detected low abundances of 5α,14α,17α-20R-cholestane, a product formed during slightly later stages of diagenesis (Mackenzie et al., 1982), which showed increasing abundances with sediment age typical of a diagenetic product (Fig. 4b).The ternary diagram in Fig. 5 showed distinct changes in ster-2-ene distributions in recent sediments, with a significantly increased abundance of cholest-2-ene and other C_{27}-steroids.

3.1.3. Other biomarkers

The aliphatic fractions also contained a series of C_{10}-C_{25} 1-chloro-*n*-alkanes which can be identified in the *m/z* 91 mass chromatograms (Grossi and Raphel, 2003) illustrated in Fig. 6. This product series may extend to higher MW homologous, but co-elutions with other analytes (i.e., alkenes, hopanoids and steroids) would have compromised their detection. Nevertheless, $C_{30:1}$ and $C_{32:1}$ chloro-*n*-alkenes have been tentatively identified by relative retention times which were consistent with previous reports (Zhang et al., 2011) and by mass spectral features. The abundance profiles of the C_{16}-1-chloro-*n*-alkane (representative of other homologues) and the putative $C_{32:1}$ chloro-*n*-alkene throughout the core are displayed in Fig. 4c.

The PAH perylene (**II**) was only present in trace amounts in sediments of the uppermost 30 cm but increased significantly in concentration at greater depths (Fig. 4d).

3.2. Stable isotope analysis

3.2.1. $\delta^{13}C$ analysis

$\delta^{13}C$ profiles of bulk organic carbon and selected biomarkers throughout the analysed core are displayed in Fig. 2b. The profiles of mid to long-chain *n*-alkanes (and corresponding monoenes if present, see section 2.2.4) showed comparatively minor variations in older sediments representing several thousand years (25-115 cm; average $\delta^{13}C$: -23.5 ± 2.5‰), but a marked negative shift of ~ 5 ‰ in recent sediments (< 20 cm; average $\delta^{13}C$: -28.2 ±2.0 ‰), indicating significant changes in the ecosystem of the North Lagoon since the ~1950s. The $\delta^{13}C$ depth profiles for C_{17}-C_{20} *n*-alkanes and hopanoids largely resembled the longer chain *n*-alkanes, although the isotopic shift in the most recent sediments is somewhat less pronounced, particularly compared to the odd-chain *n*-alkanes (Fig. 2b). The bulk $\delta^{13}C_{OM}$ profile also exhibited a -5 ‰ shift coincident with this point but showed an additional sharp negative spike shortly below 20 cm reflecting depleted terrestrial OM being flushed into the system during the large flood event in 1956, consistent with the TOC-profile, however the second potential flood event indicated by the TOC-profile was not evident in $\delta^{13}C_{OM}$ values. The direct effects of the flood in 1956 were also not visible in the other depth profiles due to their lower resolution. The bulk $\delta^{13}C_{OM}$ signatures were generally slightly heavier than corresponding values obtained for *n*-alkanes, consistent with lipids in autotrophs being generally more depleted compared to total biomass (Monson and Hayes, 1982). A further difference in stable isotope ratios of *n*-alkanes between recent and older sediments were distinct sawtooth patterns with ^{13}C-depleted even-carbon-numbered *n*-alkanes in older sediments (>25 cm), whereas these features were absent in more recent samples (e.g. Fig. 3).

The $\delta^{13}C$ values of C_{17}-C_{20} *n*-alkanes (average -29.1 ±2.5 ‰), hop-17(21)-ene (average -29.7 ±3.5 ‰) and 17β, 21β-22R-homohopane (average -31.8 ±2.2 ‰) were generally lower than the values of >C_{21} *n*-alkanes (average -24.8 ±3.1 ‰). On the contrary, $\delta^{13}C$ signatures of the C_{29} *n*-alkadiene (average -23.3 ± 1.1 ‰), which was abundant only in recent sediments, were slightly more ^{13}C-enriched. The C_{20}HBI was significantly more ^{13}C-enriched compared to the other hydrocarbons with an average $\delta^{13}C$ value of -15.2. ±1.5 ‰ Its sedimentary $\delta^{13}C$ depth profile also showed strong differences (Fig. 2b).

3.2.2. δD analysis

δD depth profiles of representative *n*-alkanes are displayed alongside other potential molecular salinity indicators throughout the analysed core in Fig. 7. The measured δD values showed some variations but a general trend towards a D-enrichment in younger sediments. The most pronounced positive shift was evident in recent

sediments (< 20 cm). Similar to $\delta^{13}C$ values, only the δD values of *n*-alkanes in older sediments (> 25cm) exhibited a sawtooth pattern with D-enriched even-carbon-numbered *n*-alkanes (Fig. 3).

4. Discussion

4.1. Salinity increase in the North Lagoon due to recent human impact

The palaeosalinity markers displayed in Fig. 7 consistently indicate a recent increase in salinity following the beginning of extensive human water-management in the 1950s, which was significantly more pronounced than salinity variations over the previous thousands of years represented by the deeper sediments. In an environmental setting like the Coorong lagoons, δD signatures of *in situ* produced biolipids generally reflect the D/H abundance in the lake water (Sachse et al., 2006; Mügler et al., 2010), which is largely determined by the extend of evaporation and freshwater input. Therefore more depleted δD values of these biolipids indicate lower salinities. Since the *n*-alkanes detected here are largely produced by allochthonous sources (i.e. aquatic macrophytes, algae and bacteria; see following sections), the general trend towards enriched δD values in younger sediments, evident in all their profiles (e.g. Fig. 7), indicates an overall rising salinity, despite some variations. Nevertheless, the most pronounced D-enrichment occurred in recent sediments (< 20 cm). The *n*-alkanes deposited shortly after the flood event in 1956 showed a slight depletion in δD values, reflecting a temporary freshening of the system. Similar variations in salinity, including the pronounced increase over the past decades, have also been observed in studies of diatom assemblages in the North Lagoon (McKirdy et al., 2010). Relatively large variations of δD values in older sediments also seem consistent with variations in aridity in the Coorong region throughout the Late Holocene e.g. (Ahmad, 1996; Mee et al., 2007). Possibly these changes would have been more pronounced in δD profiles at a higher time resolution. Furthermore, the shift in δD values of *n*-alkanes in the recent sediments might also be enhanced by a change in source organisms, which will be discussed in the following sections and is also indicated by the loss of the sawtooth pattern in δD signatures of *n*-alkanes in recent sediments (Fig. 3).

Another potential parameter reflecting the rising salinity in recent sediments is the increasing abundance of the hop-(17)21-ene relative to other hopanes (Fig. 7). Hop-(17)21-enes seem to be formed during early diagenesis in hypersaline environments in preference to 17α,21β-hopanes (ten Haven et al., 1985, 1988). However, longer chain homologues (C_{31}-C_{35}), which are also indicative of high salinities (e.g. ten Haven et al., 1985), were not abundant in the North Lagoon. The R_{22}-index, displaying the abundance of the C_{22} *n*-alkane relative to the C_{21} and C_{23} *n*-alkanes, can also be a marker for hypersaline depositional environments (ten Haven et al., 1985, 1988). In the recent sediments from the North Lagoon it increases significantly, as it is expected for

316 rising salinities. However, the average recent sediment values of 0.32 are still much lower than those reported
317 by ten Haven et al. (1985) in hypersaline environments, which is to be expected since the increasing salinity in
318 the North Lagoon had not yet progressed to prevalent hypersalinity.
319 Unfortunately the parameters measured here do not reflect ecological changes of the most recent flood
320 event in 2010, since the analysed core was collected in 2005. However, the determined salinity indicators reflect
321 the high impact of the drastic reduction of freshwater inflow through the barrages, on the ecosystem of the North
322 Lagoon. The increase of salinity is generally considered the driving force for the observed ecological decline in
323 the Coorong.
324
325 **4.2. Changes of OM sources in the North Lagoon following human impact**
326 The marked shifts in the sedimentary depth profiles of $\delta^{13}C_{OM}$ and $\delta^{13}C$ of hydrocarbons (Fig. 2b),
327 which coincided with the intensification of human water management in the 1950s, reflect a major change in the
328 type of source organisms caused by the increasing salinity as well as the progressive isolation from riverine
329 inflow and seawater exchange. Although environmental factors can also influence $\delta^{13}C$ values in biomarkers
330 and sediments, this was most likely not the major cause for the isotopic shifts observed here. An elevated
331 salinity as reported in the Coorong over the past decades may influence $\delta^{13}C$ values, however it is usually
332 associated with heavier isotopic signatures in biolipids (Schidlowski et al., 1984; Grice et al., 1998; Andersen et
333 al., 2001) and the opposite (lighter isotopic signatures) is observed in the North Lagoon. Furthermore, an
334 increased abundance of dissolved CO_2 caused for example by enhanced heterotrophic activity after algal blooms
335 or by a slight decrease of the pH would lead to a ^{13}C-depletion in lipids of primary producers. With limited
336 supply of $[CO_2]_{aq}$ phytoplanktonic organisms show less discrimination against ^{13}C resulting in significantly
337 enriched biolipids whereas a high abundance of this carbon source leads to an enhanced discrimination and
338 more depleted biolipids (Takahashi et al., 1990; Freeman and Hayes, 1992). This effect may have also
339 intensified the observed $\delta^{13}C$ shifts in the North Lagoon. Although the Coorong remains an alkaline system
340 (Revill et al., 2009) temporary stratification with more acidic bottom waters (pH: 6.8) have been observed in the
341 past decades (Geddes, 2003).
342 Most shifts in the stable isotope profiles in the recent sediments described here were distinctly greater
343 in magnitude than natural variations over thousands of years, thus indicating unambiguous ecological changes in
344 recent sediments (younger than ~1950). However, it should be noted that sediments at greater depths of this core
345 had a very different time resolution (*cf.* radionuclide dates with radiocarbon age) and averaging effects were

much more significant for these compared to the recent sediments. Furthermore, bioturbation may have also contributed to averaging of the signals.

Further indications for a change in source organisms was the disappearance of the sawtooth patterns in the $\delta^{13}C$ and δD values of $>C_{21}$ *n*-alkanes (Fig. 3) in the recent sediments (< 20 cm). Similar sawtooth patterns have been reported in various higher plant waxes due to different metabolic pathways used for the synthesis of odd and even numbered homologues (Grice et al., 2008b; Zhou et al., 2010) as well as in sediments, where this pattern may also be enhanced by or be the result of input from different source organisms such as a microalgal bias to odd numbered *n*-alkanes (Logan et al., 1999; Grice et al., 2001; Dawson et al., 2004).

The isotopic differences evident throughout the studied core were also visible in a crossplot of $\delta^{13}C$ *vs.* δD values of $>C_{21}$ *n*-alkanes in representative samples from the North Lagoon well before (105-110 cm) and after (0-15 cm) human interferences had impacted the water regime (Fig. 8). Three groups (*n*-alkanes in recent sediments and odd-chain and even-chain *n*-alkanes in older sediments) were clearly separated. The distinction was however somewhat more obvious in $\delta^{13}C$ than in δD signatures since isotopic fractionations in different metabolic pathways are usually reflected more strongly by $\delta^{13}C$ values (e.g. Chikaraishi and Naraoka, 2003; Polissar and Freeman, 2010). The D-enrichment in the most recent samples is also a result of the rising salinity and decreased freshwater input (see previous section).

4.2.1. Significant input of aquatic macrophytes in older sediments

The higher $\delta^{13}C$ values of $>C_{21}$ *n*-alkanes in older sediments are consistent with a predominant origin from aquatic C3 plants such as seagrasses, which produce relatively ^{13}C-enriched hydrocarbons compared to their terrestrial counterparts. Chikaraishi and Naraoka (2003) reported an average $\delta^{13}C$ value of *n*-alkanes extracted from three marine seagrass species of -22.8 ±1.0 ‰ and slightly more depleted values for aquatic freshwater plants of -25.3 ±1.9 ‰. There may also be a minor contribution from phytoplankton and a small allochthonous input from terrestrial plants, potentially including species from halophytes (see section 4.4).

Aquatic plants mainly synthesise *n*-alkanes of mid-chain lengths typically maximising at C_{21}, C_{23} or C_{25} (Botello and Mandelli, 1978; Cranwell, 1984; Ficken et al., 2000; Jaffé et al., 2001). Therefore the determined ACLs of *n*-alkanes, which were lower than the 28 to 33 typical of terrestrial plants (Chikaraishi and Naraoka, 2003) are consistent with a major contribution from aquatic macrophytes. It is furthermore supported by the range of P_{aq} values reported in these sediments, which are consistent with a major contribution from non-emergent aquatic plants to the *n*-alkanes found in the North Lagoon. This is in accordance with the formerly high abundance of aquatic macrophytes, in particular *Ruppia megacarpa,* which used to be a significant source

of OM before its recent extinction due to the rising salinity (Krull et al., 2009). However, particularly with a microalgal contribution to sedimentary *n*-alkanes, which is likely the case here (see following section), P_{aq} values have to be interpreted with care as the produced odd-chain *n*-alkanes might be in the same range to those of aquatic plants.

A high contribution of aquatic macrophytes to the OM in older sediments in this and other cores from the North Lagoon has also been suggested by Krull et al. (2008), to explain the lignin-rich but ^{13}C-enriched OM in these samples. In recent sediments lignin was only present in trace amounts. However, relatively low corresponding C/N values (8.4-10.1) reported in Krull et al. (2008), still indicate significant algal or cyanobacterial input, although these values may be biased by a high input from inorganic nitrogen in the North Lagoon, as noted by McKirdy et al. (2010).

Another indication for a significant contribution of macrophytes in the older sediments might be the increasing concentration of perylene (Fig. 4d), which correlates with the relative lignin abundance reported by Krull et al. (2008). However, the increase in concentrations with depth also reflects its diagenetic origin. Unlike most other unsubstituted PAHs, which are mainly of a pyrogenic or thermogenic origin, perylene has been associated with quinone pigments, particularly in wood/lignin degrading fungi but also in some other organisms (Jiang et al., 2000; Grice et al., 2009; Suzuki et al., 2010), and typically shows different sedimentary abundances compared to these combustion markers (Jiang et al., 2000; Atahan et al., 2007; Grice et al., 2009; Suzuki et al., 2010). A link to fungal wood/lignin degradation is also supported by the absence of perylene in sediments and crude oils predating the evolution of vascular plants and in marine sourced oils (Grice et al. 2009). The co-occurrence of perylene and lignin in older sediments from the North Lagoon and the absence of both in recent sediments do concur with the source correlation of perylene to fungal lignin degradation.

4.2.2. Increased microalgal and bacterial input in recent sediments

Although the ^{13}C depleted long-chain *n*-alkanes in the recent sediments of the North Lagoon are in the range of terrestrial C3 plants waxes (e.g. Chikaraishi and Naraoka, 2003), a predominant origin from these organisms seems implausible since a high allochthonous contribution to sedimentary OM in the North Lagoon, especially in recent years, is unlikely. Several studies (using various analytical approaches) confirmed only a minor terrestrial input to the sediments of the North Lagoon. These included biomarker and pigment analysis in surface sediments and the water-column (Revill et al., 2009) as well as elemental (low C/N values; Krull et al., 2009; McKirdy et al., 2010) and ^{13}C-NMR analysis (Krull et al., 2009) in sediment cores. According to Revill et al. (2009) the primary source of OM in surface sediments of the North Lagoon were benthic diatoms and

406 cyanobacteria whereas OM in the water-column was mainly derived from green algae. Nevertheless, the
407 presence of pollen (e.g. *Pinus*, Krull et al., 2009) indicates a minor terrestrial input.
408 McKirdy et al. (2010) observed a similar negative shift in $\delta^{13}C$ values of *n*-alkanes in recent sediments
409 of the South Lagoon and attributed it to a primary source change from aquatic macrophytes to bacteria. Such a
410 source transition also seems plausible in the sediments analysed here. A ^{13}C-depletion would be expected from a
411 higher bacterial contribution to the long-chain *n*-alkanes, since also other bacterial-derived hydrocarbons such as
412 short-chain *n*-alkanes or hopanoids had isotopically lighter $\delta^{13}C$ signatures in these samples (Fig. 2b).
413 Long-chain *n*-alkanes with high CPIs are typically ascribed to vascular plants waxes (Eglinton and
414 Hamilton, 1967), but they do have other sources such as microalgae or bacteria, including sulfate reducers and
415 heterotrophs. Although most microalgae and bacteria predominantly produce *n*-alkanes of shorter chain lengths
416 (C_{14}-C_{20}), longer-chain *n*-alkanes or long-chain *n*-alkyl precursors such as fatty acids, *n*-alcohols or *n*-alkenes
417 have also been attributed to some species (e.g. Cranwell, 1982, 1984; Collister et al., 1994a; Lichtfouse et al.,
418 1994; Volkman et al., 1998; Logan et al., 1999; McKirdy et al., 2010). Whereas these bacteria (Oró et al., 1967;
419 Davis, 1968; Han and Calvin, 1969; Jones and Young, 1970) and some diatoms (Volkman et al., 1980 and
420 references therein; Nichols et al., 1988) generate long-chain *n*-alkane distributions without a pronounced odd-
421 over-even predominance, green algae often synthesise long-chain *n*-alkenes with odd carbon numbers, leading
422 to *n*-alkane distributions with high CPIs (Gelpi et al., 1970; Gelin et al., 1997; Allard and Templier, 2000). The
423 decreasing CPIs observed in the most recent sediments of the North Lagoon (Fig. 2a) could therefore indicate an
424 increasing abundance of bacteria, most likely sulphate reducers or heterotrophs and possibly diatoms. Low CPI
425 distributions are sometimes also associated with contamination from petroleum products (Peters et al., 2005).
426 However such a contamination in the Coorong seems unlikely since there has been no other indication for this in
427 the present project or in previous studies.
428 An increased phytoplanktonic contribution to the recent sedimentary OM is also consistent with the
429 significant increase of bacterial and microalgal biomarkers such as short chain *n*-alkanes (C_{14}-C_{20}), C_{27}-C_{29}-
430 alkadienes, the C_{20}HBI and some hopanes in the uppermost core-section (Figs 2a and 4a). C_{14}-C_{20} *n*-alkanes
431 often maximising at C_{17} are usually attributed to diatoms, green algae or bacteria, particularly cyanobacteria
432 (Han and Calvin, 1969; Gelpi et al., 1970; Cranwell, 1982). The relatively low $\delta^{13}C$ values of these *n*-alkanes in
433 the presently analysed sediments are in the same range as the $\delta^{13}C$ values of bacterial derived hopanoids (Fig.
434 2b), indicating a common source.

Long-chain *n*-alkenes with a strong odd-over-even predominance, which were abundant in sediments < 20 cm, are produced by some green microalgae and possibly cyanobacteria (Gelpi et al., 1970; Gelin et al., 1997; Allard and Templier, 2000). The C_{27}-C_{29} *n*-alkadienes were most likely derived from the A race of the green algae *Botryococcus braunii* which is known to produce odd-carbon-numbered C_{27}-C_{31} *n*-alkadienes and minor amounts of the C_{29} *n*-alkatriene (Metzger et al., 1986; Metzger and Largeau, 2005). *n*-Alkadienes of similar chain lengths have also been isolated from some chlorococcales algae (Allard and Templier, 2000). Although *Botryococcus braunii* is a freshwater species, there is reported evidence of its presence in hypersaline environments, mainly due to salinity stratification in the water-column (e.g. Grice et al., 1998) which also periodically occurs in the Coorong (Webster, 2005). Blooms of this species have previously been observed in the Coorong region (Cane, 1976) and $\delta^{13}C$ signatures of the C_{29} *n*-alkadiene (-24.6 to -22.5 ‰) would also be consistent with an origin from these algae (Grice et al., 1998). The high relative abundance of the unsaturated aliphatics in recent sediments is in accordance with the high abundance of green algae in the water-column of the present day Coorong (Revill et al., 2009). However, the difference to older sediments, in which these compounds showed very low abundances or were absent, can also be partly attributed to their relatively unstable structures resulting in an early transformation into more stable *n*-alkanes during diagenesis. A high abundance of algal-derived OM in the most recent samples < 20 cm (possibly from the A race of *Botryococcus braunii*) is also indicated by the relative ^{13}C -enrichment of *n*-alkanes/alkenes > C_{24} compared to their shorter chain homologues (average difference: 4 ‰). However, the values were still lower than the $\delta^{13}C$ signatures of the algal-derived C_{29} *n*-alkadiene, which indicates a mixed source of these *n*-alkanes in recent sediments with contributions from bacteria as well as green algae and potentially also a minor input from terrestrial higher plants. Revill et al. (2009) reported depleted values in green algal derived phytol in the water-column sometimes approaching -30 ‰ which they attributed to a slow growth rate.

The enhanced abundance of the C_{20}HBI (Fig. 2a) presumably indicates an increased input from diatoms or significant alterations in their population. The C_{20}HBI has been frequently assigned to a diatomaceous origin based on stable isotopic compositions and abundance profiles as well as structural similarities to the C_{25} and C_{30} HBIs (**III, IV**), which are established biomarkers for these microalgae (Volkman et al., 1998; Atahan et al., 2007; McKirdy et al., 2010). However, the C_{20}HBI or potential precursors have, unlike the larger analogues, never been isolated from cultured organisms. The enriched $\delta^{13}C$ values of the C_{20}HBI in sediments from the North Lagoon (-18.8 to -13.9 ‰) are typical of lipids produced by diatoms since many species are capable of assimilating enriched bicarbonate as opposed to more depleted CO_2 (Freeman and Hayes, 1992; Bieger et al.,

1997). Also the different sedimentary $\delta^{13}C$ depth profile of the C_{20}HBI compared to the other hydrocarbons, reflect this different carbon source.

4.2.3. Alterations in bacterial and microalgal populations in recent sediments

The recent environmental changes in the North Lagoon, such as the increased salinity as well as the enhanced turbidity caused by the extinction of macrophytes, also led to significant alterations in bacterial and algal populations, which were evident in relative abundances and stable isotopic compositions of molecular indicators for these organisms. The increased abundance of the C_{20}HBI (Fig. 2a) likely reflects significant changes in diatom communities, which have also been observed in palynological analyses (Gell et al., 2007; Haynes et al., 2007). In particular, the C_{20}HBI was the dominant aliphatic product in most sections of a core from the South Lagoon, where conditions such as high salinities and a higher degree of isolation have prevailed throughout the Holocene before being significantly enhanced by the recently employed interferences with the water regime (McKirdy et al., 2010). The elevated abundance of the C_{20}HBI in recent sediments of the North Lagoon indicates important changes in the environmental conditions and water regime, since a diatom population similar to that previously present in the South Lagoon became supported.

Furthermore, changes in algal populations were reflected by variations in the steroid distributions. Although C_{29}-desmethylsteroids are often assigned to a terrestrial plant origin (e.g. Huang and Meinschein, 1979) they have also been detected in significant amounts in microalgae, seagrasses and sediments without higher plant input (Attaway et al., 1971; Volkman, 1986, 1998; Grosjean et al., 2009). Revill et al. (2009) attributed all sterols they detected in water-column and surface sediments throughout the Coorong to aquatic organisms, namely different types of green microalgae, diatoms (C_{29}- and C_{28}-sterols) and zooplankton (C_{27}-sterols). The high relative abundance of cholest-2-ene in recent sediments of the North Lagoon may be an indication for an increased population of zooplankton feeding on benthic microbial mats (McKirdy et al., 2010). The primary source organisms of the C_{29}-ster-2-ene in the North Lagoon sediments are most likely microalgae and aquatic plants (the latter particularly in older sediments) possibly with a minor contribution from terrestrial plants. The relatively lower abundance of C_{29}-ster-2-enes in recent sediments might reflect the recent extinction of aquatic macrophytes due to the rising salinities (Nicol, 2005; Krull et al., 2009; Dick et al., 2011). A slight trend towards higher relative abundances of the C_{27}-ster-2-ene was already evident before the 1950s, as indicated by the three black diamonds in the middle of the diagram, which correspond to samples between 25 and 40 cm. This likely indicates that already the smaller changes to the water-regime prior to the 1950s (see section 2.1.1.) have had a noticeable impact on the algal or zooplankton communities and possibly macrophytes.

The clear shift in steroid distributions in the most recent samples also took place slightly earlier than the stable isotopic shifts.

An indication for a change in bacterial populations are the negative δ^{13}C-shifts in the profiles of the C_{17} *n*-alkane and the 17β,21β-22R-homohopane at 25 cm, although they were not as pronounced as in (odd-carbon-numbered) long-chain *n*-alkanes (Fig. 2b). A possible explanation would be an increase of bacterial growth in benthic microbial mats, often favoured in highly saline environments, which typically produce more ^{13}C-depleted lipids compared to planktonic organisms, (Collister et al., 1994b; Freeman et al., 1994; Bieger et al., 1997;Logan et al., 1999). Differences in bacterial population were also reflected by alteration in the hopanoid distributions, which were most pronounced in the upper core-section.

4.3. Significance of 1-chloro-*n*-alkanes

Although a variety of organohalogens are produced biosynthetially, in particular by marine organisms but also by some terrestrial life forms including plants and higher animals (e.g. Gschwend et al., 1985; Gribble, 1996, 2003; Winterton, 2000), reports of mid- to long-chain 1-chloro-*n*-alkanes in sediments are sparse. Zhang et al. (2011) detected $C_{30:1}$ and $C_{32:1}$ 1-chloro-*n*-alkenes, which we also tentatively identified in this study, in sediments from a freshwater crater lake in the Galápagos Islands. A series of long-chain 1-chloro *n*-alkanes (C_{19}-C_{29}) has been isolated from 3 genera (*Suaeda*, *Sarcocornia* and *Halimione*) of halophytic Chenopodidaceae (Grossi and Raphel, 2003). Some of these species (including *Sarcocornia* and *Suaeda*) are also found in the Coorong region (Boon, 2000 and references therein) and represent a potential source for the chlorinated paraffins in the North Lagoon sediments. However, the series detected in this study did not show the odd-over-even carbon number predominance that Grossi and Raphel (2003) had previously observed in halophytes and it also comprised shorter-chain homologues (C_{12}-C_{18}), which have not been detected in the Chenopodiaceae.

Other sources of these compounds in the North Lagoon may include algae, seagrasses or cyanobacteria. Although no long-chain-chloro-*n*-alkanes/ *n*-alkenes have been isolated from these organisms so far, they are known to produce a variety of other chloro-organic compounds including volatile 1-chloro-*n*-alkanes in the range from C_1 to C_5 (Mynderse and Moore, 1978; Gribble, 1996, 2003). The increased relative abundances of 1-chloro-*n*-alkanes and 1-chloro *n*-alkenes in the most recent sediments of the North Lagoon (Fig.4c) point towards an algal or cyanobacterial source since these organisms also were significantly more abundant in that part of the core. Nevertheless, Chenopodiaceae have a high tolerance to salinity and may have become more abundant in the lagoon catchment with the rising salinities in the Coorong.

Mid and long-chain chloro-paraffins (CPs; C_{10} - C_{30}) are also known anthropogenic contaminants due to many industrial applications (Tomy et al., 1998; Štejnarová et al., 2005). However, anthropogenically-sourced CPs commonly exhibit complex distributions with various stereoisomers and different degrees of chlorination as a result of the synthesis process (Tomy et al., 1998). Therefore the relative specificity of the distinct series of 1-chloro-*n*-alkanes detected here precludes such an origin.

$\delta^{13}C$ values of the mono-chlorinated paraffins in the North Lagoon ranged from -31.8 to -24.5 ‰ (Table 1) and are consistent with both, a C3 plant source (such as the chloro-paraffin containing Chenopodiceae analysed by Grossi and Raphel (2003) and most Chenopodiaceae in the Coorong region) as well as with a bacterial or microalgal origin (*cf.* $\delta^{13}C$ values of algal- and bacterial derived hydrocarbons).

5. Conclusions

The molecular and isotopic sedimentary record included evidence that human interference with the water regime of the Coorong, namely a drastic reduction of the freshwater inflow due to installation of barrages and extensive water abstractions from the River Murray, was immediately responsible for major changes in the types of primary production, sedimentary OM and salinity in the North Lagoon over the past ~50 years. The magnitude of these parameter changes has been significantly more pronounced than natural variations over thousands of years. Aliphatic and aromatic biomarker analyses (including CSIA, C and H) in a sediment core from the North Lagoon spanning more than 5000 years revealed changes in the populations of primary producers contributing to sedimentary OM from predominantly macrophytes in sediments deposited prior to the 1950s towards bacteria and microalgae in more recent sediments. Furthermore, H-CSIA enabled the reconstruction of salinity variation in the North Lagoon, showing dynamic changes with an overall rise of salinity throughout the Holocene. However, a sharp increase took place shortly after the 1950s presumably due to the restriction of freshwater inflow through the barrages. We also detected an interesting series of mid- to long-chain 1-chloro-*n*-alkanes in these sediments. Potential sources of these compounds could be halophytic Chenopodiaceae, cyanobacteria or microalgae.

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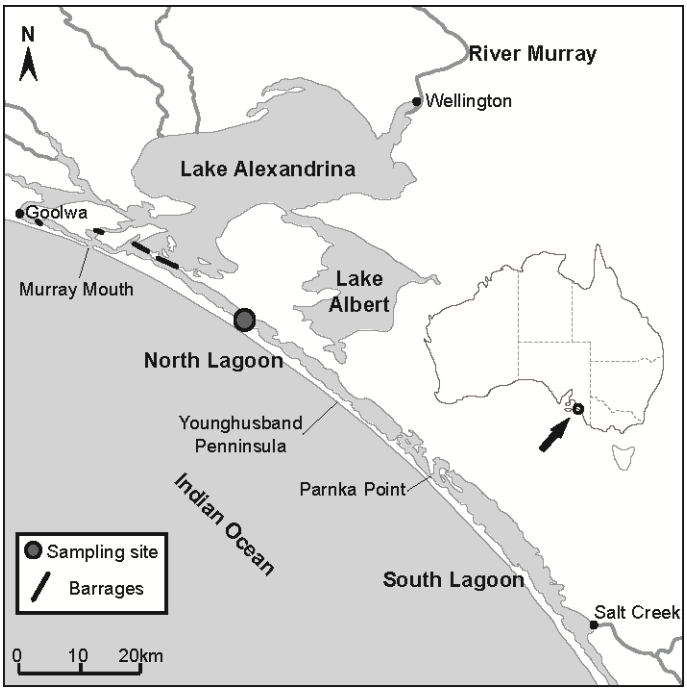
768 # Figure captions



769

770 **Fig. 1** Location of the Coorong including the sampling site

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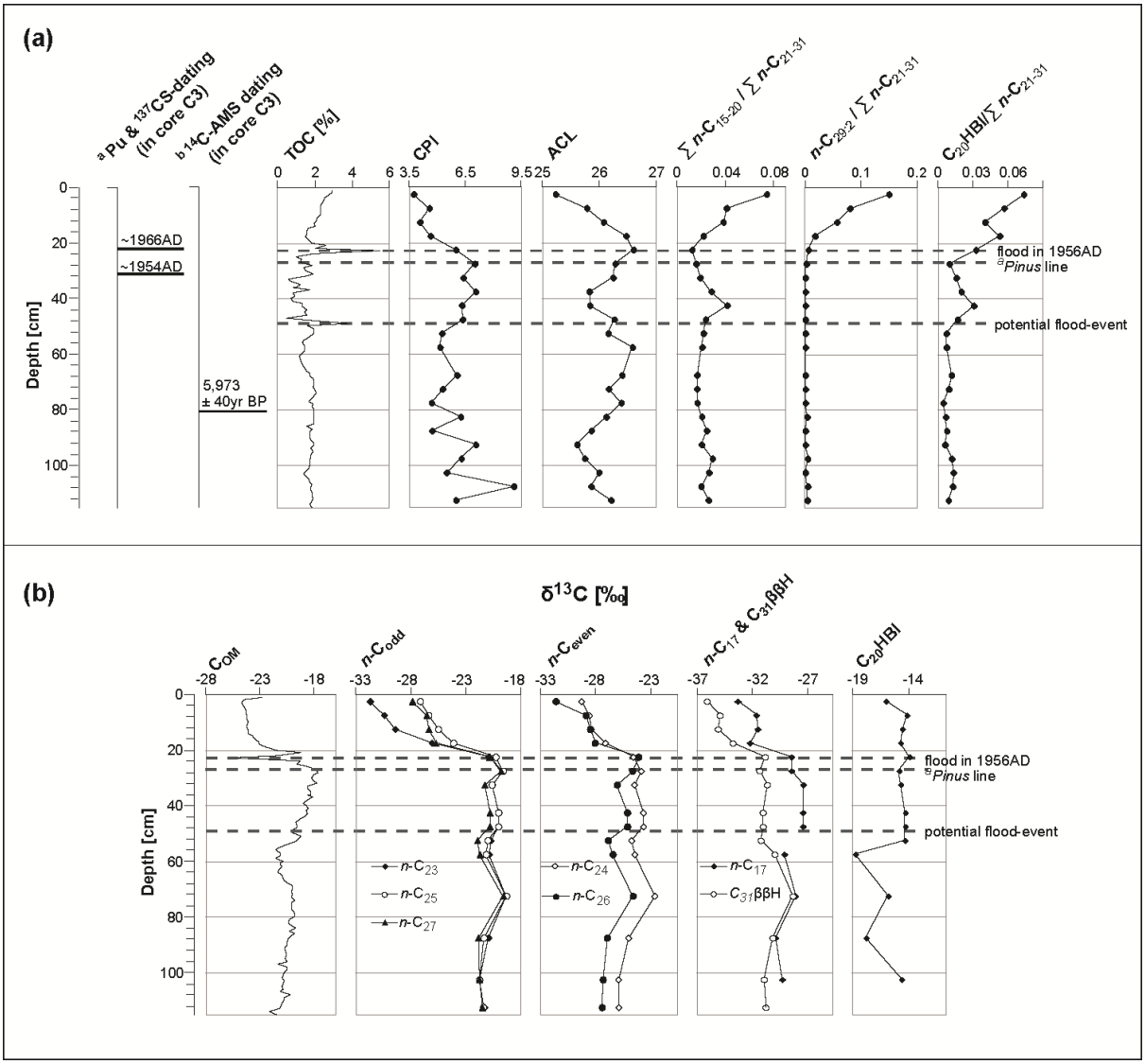

772

773 **Fig. 2** Alterations in TOC [%], *n*-alkane distributions (carbon preference index (CPI), average chain length
774 (ACL)) and abundances of selected biomarkers relative to long-chain *n*-alkanes (a) and $\delta^{13}C$- profiles in a core
775 from the northern Coorong Lagoon (b) put into perspective with events in the region and inferred sediment ages
776 from ^{137}Cs, Pu and ^{14}C-AMS dating (dating was performed on a neighbouring core). Flood events were marked
777 according to excursions in the TOC profile. The first occurrence of *Pinus* pollen (*Pinus* line) indicates the
778 beginning of European influence and roughly coincides with the 1950s (Krull et al., 2009). *n*-C_i = *n*-alkane with
779 chain length "i"; $C_{31}\beta\beta H$ = 17β,21β-22R-homohopane; CPI = $\sum C_{odd}/\sum C_{even}$ over the range from C_{21}-C_{30}, where
780 "C_{odd}" and "C_{even}" are peak areas from TIC chromatograms of *n*-alkanes with odd and even numbered chain
781 lengths, respectively; ACL = $\sum(i \times C_i)/\sum C_i$ where "C_i" is the peak area of the *n*-alkane with carbon number "i"
782 over the range from C_{21}–C_{31}; [a] from Krull et al., (2009), [b] from Fluin et al. (2007). OM = organic matter
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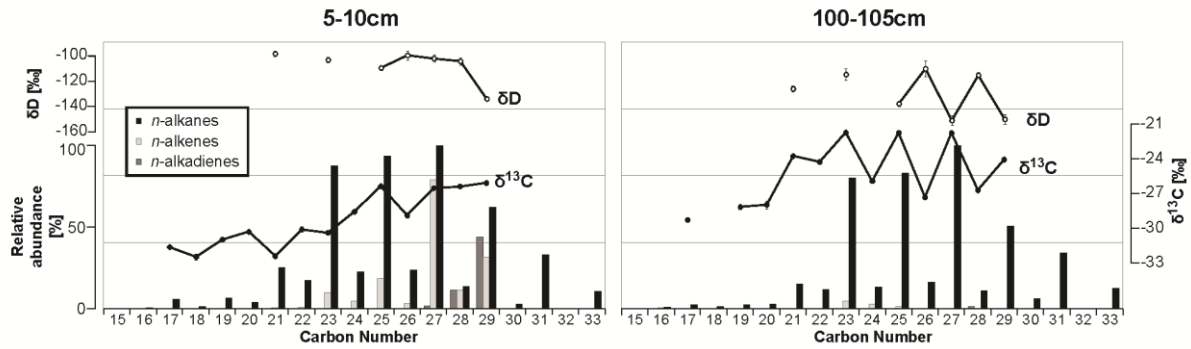

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785 **Fig. 3** Typical distributions and stable isotopic compositions ($\delta^{13}C$, δD) of *n*-alkanes, *n*-alkenes and *n*-alkadienes
786 in sediments from the northern Coorong Lagoon before (depth: 100-105cm) and after (depth: 5-10 cm) human
787 interference with the water-regime. Relative abundances were determined from peak areas in the TIC trace of
788 GC-MS chromatograms and calculated relative to the most abundant compound. Stable isotopic compositions
789 include *n*-alkanes and their corresponding monoenes. Error bars indicate standard deviations of 2 replicate
790 analyses, where error bars are not visible their size is smaller than the symbol

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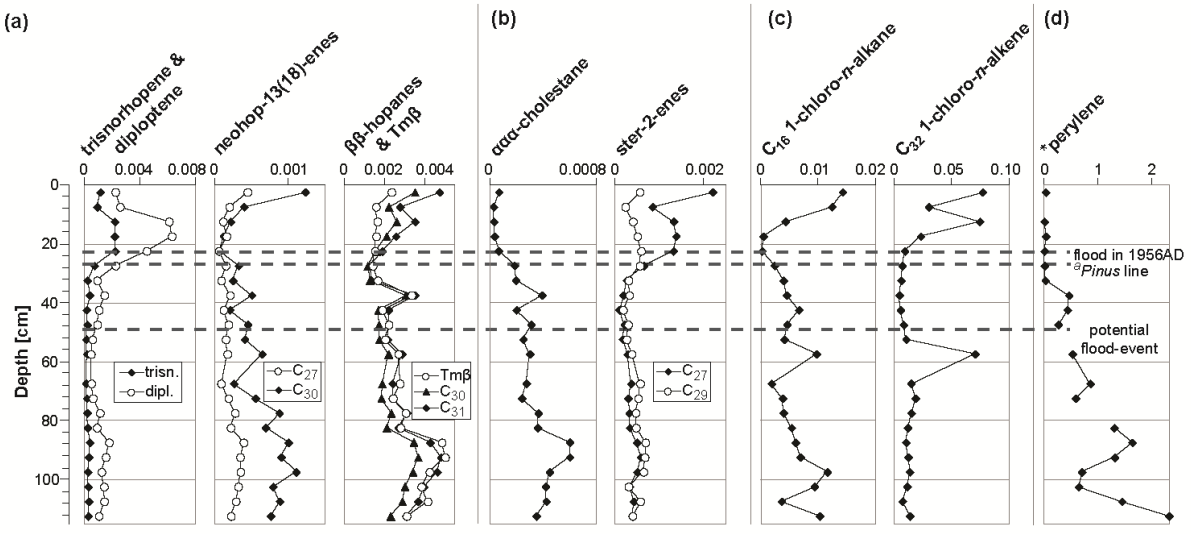

792

793 **Fig. 4** Alterations of biomarker abundances relative to $\sum C_{21}$-C_{31} *n*-alkanes in a core from the North Lagoon.
794 *Concentration in dry weight sediment [ng/g]. The first occurrence of *Pinus* pollen (*Pinus* line) indicates the
795 beginning of European influence and roughly coincides with the 1950s (Krull et al., 2009). The corresponding
796 depths of flood-events were determined from excursions in the TOC profile. [a] from Krull et al. (2009). Tm-β = .
797 17β-22,29,30-trisnorhopane

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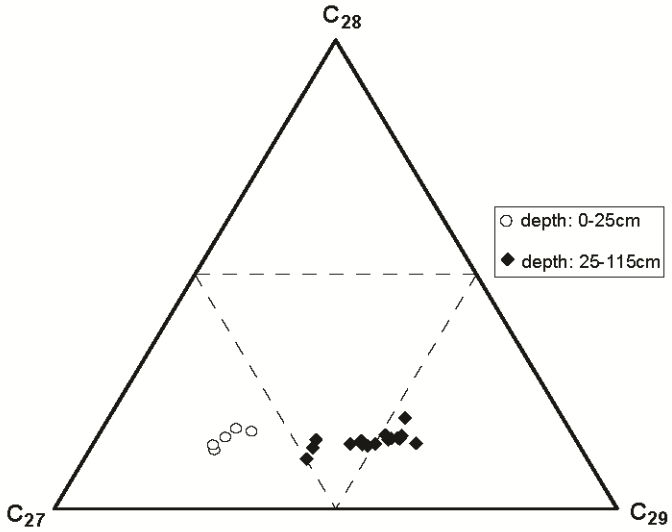

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800 **Fig. 5** Ternary diagram of ster-2-enes and cholestane (only steroids in the aliphatic fractions) in a core from the
801 northern Coorong Lagoon. Sediments between 0-25 cm were deposited after the ~1950s, a period when human
802 interference with the water regime intensified significantly. Deeper sediments were deposited over several
803 thousands of years.

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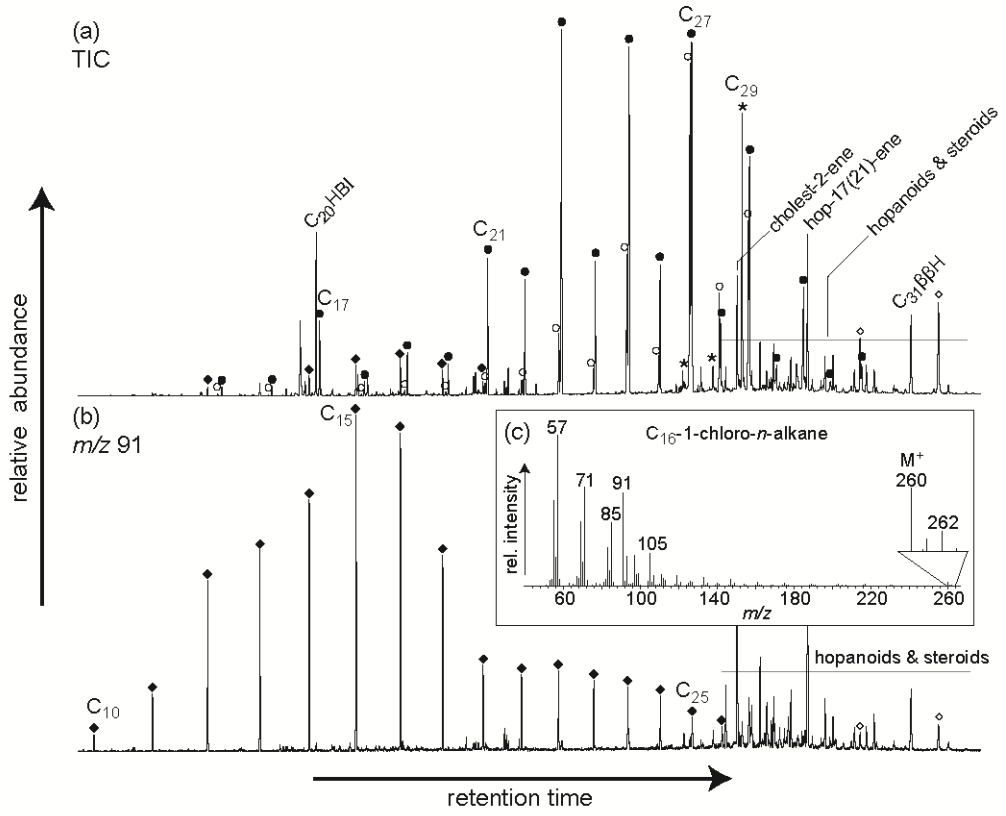

805

806 **Fig. 6** Total ion chromatogram (TIC, (a)) and m/z 91 extracted ion chromatogram (b) of the aliphatic fraction in
807 sediments from the North Lagoon between depths of 0-5 cm. (c) is the EI mass spectrum of the C_{16}-1-chloro-*n*-

alkane. C_i: carbon number of displayed compound classes; ●: *n*-alkanes; ○: *n*-alkenes; * : *n*-alkadienes; ◆: 1-chloro-n-alkanes; ◇: tentatively identified 1-chloro-*n*-alkenes; $C_{31}\beta\beta H$ = 17β,21β-22R-homohopane

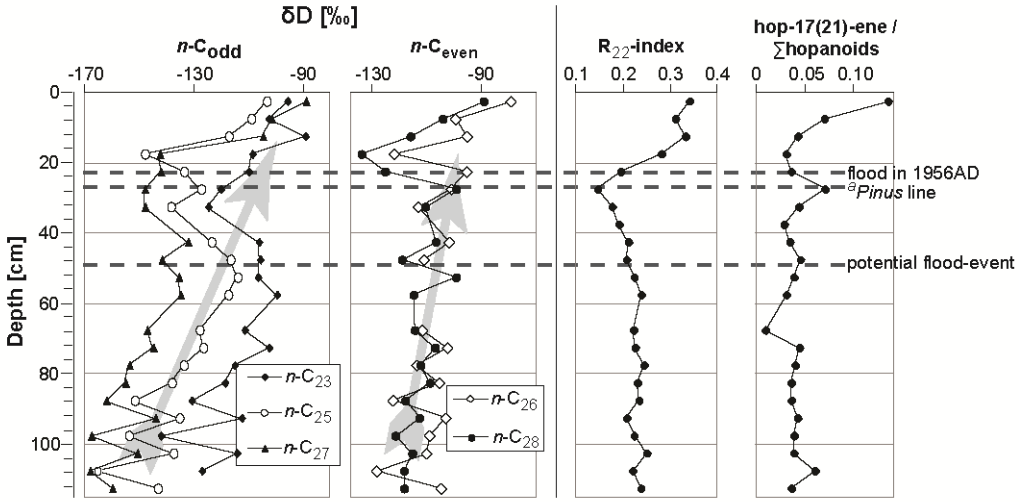

Fig. 7 δD profiles of representative *n*-alkanes with odd and even chain lengths (*n*-C_{even} and *n*-C_{odd}, respectively) and other potential salinity indicators throughout a core from the North Lagoon. R_{22}index = $2\times C_{22}/(C_{21}+C_{23})$ where "C_i" is the peak area in GC-MS chromatograms of the *n*-alkane with chain length "i" (ten Haven et al., 1988). The first occurrence of *Pinus* pollen (*Pinus* line) indicates the beginning of European influence and roughly coincides with the 1950s (Krull et al., 2009). The corresponding depths of flood-events were determined from excursions in the TOC profile. [a] from Krull et al. (2009)

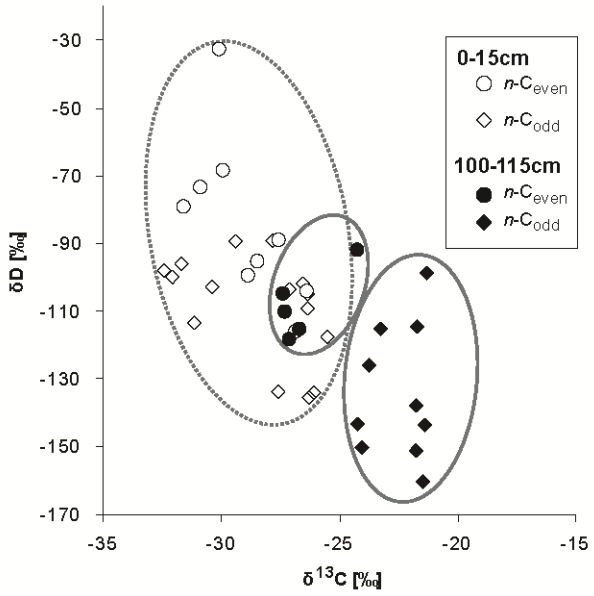

Fig. 8 Crossplot of $\delta^{13}C$ vs. δD of long-chain *n*-alkanes (C_{21}-C_{29}) in representative sediments from the northern Coorong lagoon deposited prior (100-115 cm) and significantly after (0-15 cm) the beginning of human control over the water regime in the Coorong. *n*-C_{even} and *n*-C_{odd} stands for *n*-alkanes with an even- and odd-numbered carbon chain, respectively. The large circles are for enhanced visibility of the different groups, however no cluster analysis has been performed.

Table

Table 1 $\delta^{13}C$ [‰] ± standard deviation of 2 replicates of 1-chloro-*n*-alkanes/*n*-alkenes throughout a sediment core from the North Lagoon. C_i = carbon number

Depth [cm]	1-chloro-*n*-alkanes			1-chloro-*n*-alkene
	C_{15}	C_{16}	C_{17}	$C_{32:1}$
0-5	-29.0 ±0.0	-29.2 ±0.4	-31.8 ±0.1	-29.8 ±0.1
5-10	-28.1 ±0.1	-26.5 ±0.0	-27.8 ±0.2	-26.6 ±0.3
10-15	-29.1 ±0.2	-30.4 ±0.3	n.d.	-25.4 ±0.2
15-20	n.d.	n.d.	n.d.	-26.1 ±0.4
25-30	n.d.	-26.9 ±0.1	n.d.	n.d.
30-35	n.d.	n.d.	-24.8 ±0.4	n.d.
40-45	-24.5 ±0.3	-27.4 ±0.5	n.d.	n.d.
45-50	n.d.	n.d.	n.d.	n.d.
50-55	n.d.	-26.4 ±0.0	n.d.	n.d.
55-60	-25.1 ±0.2	-25.7 ±0.1	-26.0 ±0.2	n.d.
70-75	-25.5 ±0.2	-24.8 ±0.3	-26.4 ±0.1	n.d.
85-90	n.d.	-26.0 ±0.2	-26.6 ±0.1	n.d.
100-105	-25.8 ±0.5	-26.1 ±0.2	-27.3 ±0.5	n.d.
110-115	-26.3 ±0.5	-26.3 ±0.4	-25.9 ±0.0	n.d.

n.d. = not determined

Appendix

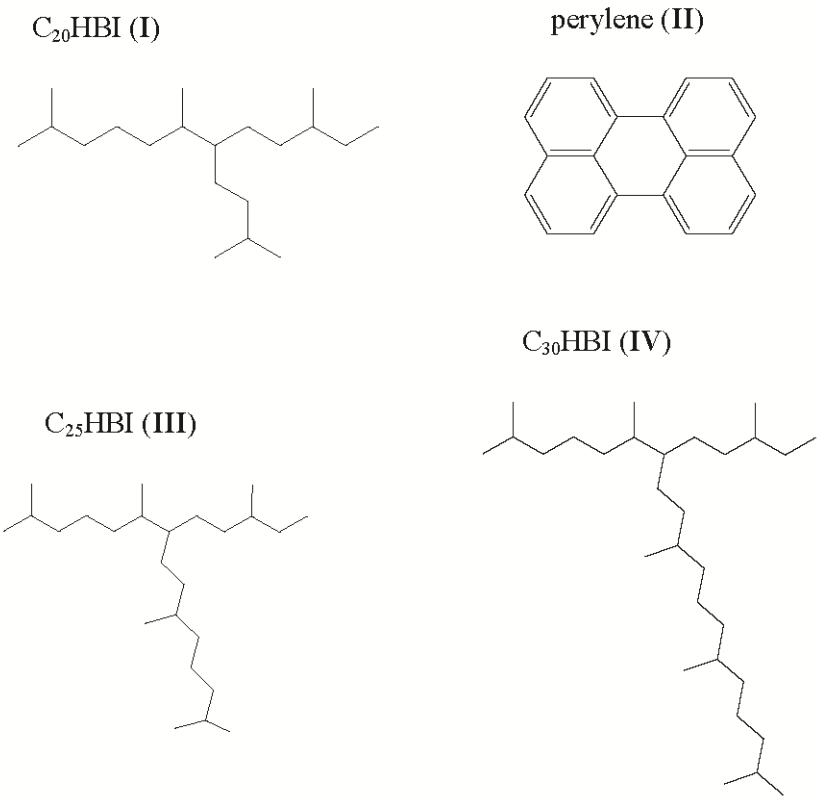

Fig. A1 Structures referred to in the text