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Variable sources of organic matter in Australian estuaries: Can isotopes alone solve the problem?

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Australia's rivers and estuaries have been significantly altered since European settlement (e.g. through agriculture, urban expansion and water resource development), leading to changes in aquatic biota, nutrient and sediment loads as well as flow regimes. Such modifications to the flow and land management systems have greatly affected the sources of organic matter and nutrients that are delivered from the river to the estuary. Stable isotopic data of organic matter from estuarine sediments coupled with C/N ratios have been used in the past to define the origin (terrestrial versus aquatic) of estuarine organic matter.

Our study was conducted on two Australian estuaries: the tropical Fitzroy estuary (Queensland) characterised by a highly dynamic, macrotidal environment and the semi-arid mediterranean Coorong (South Australia), a restricted system of saline to hypersaline lagoons. We sought to test our hypotheses that organic matter in the a) Fitzroy estuary was a mixture of eroded terrestrial (soil and mangrove debris) and aquatic material and in the b) Coorong was largely algal and macrophyte-derived with little or no contributions from soil or land plant material. Usually, terrestrial-derived materials are expected to be more ^{13}C-depleted and have greater C/N ratios than aquatic-derived material.

The δ^{13}C data of both estuaries show distinct spatial variations and, in the case of the Coorong, temporal variations as defined by results obtained from sediment depth profiles. In the Fitzroy, more ^{13}C-depleted values occur in the mid-section of the estuary. In the Coorong, a trend towards more ^{13}C-depleted values was evident in core

sections consistent with early-European settlement ($\sim$100 years ago) to modern sediments. To test whether these ^{13}C-depletions correspond to increased contributions from terrestrial-derived material, we assessed the composition of the organic matter by ^{13}C-NMR spectroscopy. These analyses showed that in the Fitzroy estuary up to 42% of its organic matter was derived from terrestrial sources. Most of this terrestrial carbon was not derived from soil or living plant materials but was composed of comparably inert charcoal. The areas of greatest ^{13}C-depletion were characterised by increased amounts of lignin, most likely eroded from the nearby mangroves. In contrast, the ^{13}C-depleted sediments in the Coorong, associated with recent changes in flow regime and land management induced by European settlement, suggested a shift towards a more algal-dominated system. Conversely, the more ^{13}C-enriched sediments, deposited at the time prior to or during early European settlement showed greater input from allochthonous material (plant or soil-derived lignin).

Estuaries are highly dynamic and complex systems. The use of elemental composition and isotopic data alone was not sufficient to provide accurate interpretation of the origin of sediment carbon found in sediments of the two Australian estuaries studied. Without the additional information on the chemical structure and molecular composition derived from ^{13}C NMR, misleading interpretations are possible. Combining isotopic with an assessment of chemical and molecular composition provides an important set of tools to elucidate organic matter sources in highly dynamic and complex systems.