

## **Organic carbon supply to a large lowland river and implications for aquatic ecosystems**

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**Abstract** The supply of organic carbon to large river systems is generally poorly understood. At issue are the relative contributions of in-channel, headwater catchment and flood plain primary production and how these contributions vary with flow conditions. Recent work has indicated that fine suspended particulate organic matter (FSPOM) is the most important form of carbon for riverine aquatic food webs. C/N and  $\delta^{13}\text{C}$  ratios in samples of FSPOM collected from along a large lowland river system show that during a 1 in 10 year flood catchment soil sources dominate. During non-flood periods the contribution from soil organic matter and C3-riparian vegetation decreases systematically with distance downstream while carbon derived from in-channel primary production increases, dominating (>75%) in the lower reaches. The  $\delta^{13}\text{C}$  ratios and radiocarbon dating indicates that the in-channel primary producers are using carbon derived from the breakdown of terrestrial organic matter photosynthesized from the atmosphere 40–50 years ago. These results show that organic matter derived from catchment soils is a major carbon source for large rivers, and reveals the importance of in-channel carbon cycling and primary production.

**Key words** carbon; cycling; rivers; Murrumbidgee River; Australia

### **INTRODUCTION**

The three best known conceptual models of organic carbon supply to large rivers are the river continuum concept (Vannote *et al.*, 1980), the flood pulse concept (Junk *et al.*, 1989), and the river productivity model (Thorp & Delong, 1994). The river continuum concept emphasizes the downstream transport and processing of organic matter derived from headwater riparian vegetation. In this model upper catchment sources are considered to dominate the supply of organic matter to the lowland reaches and lateral supply from the flood plain or riparian zone is considered to be unimportant. In contrast, the flood pulse concept, proposed for systems with regular floods, emphasizes the lateral links and suggests the bulk of riverine organic carbon is derived from the flood plains. The river productivity model proposes that the major source of organic matter is either local in-channel primary production or direct input from the local riparian zone.

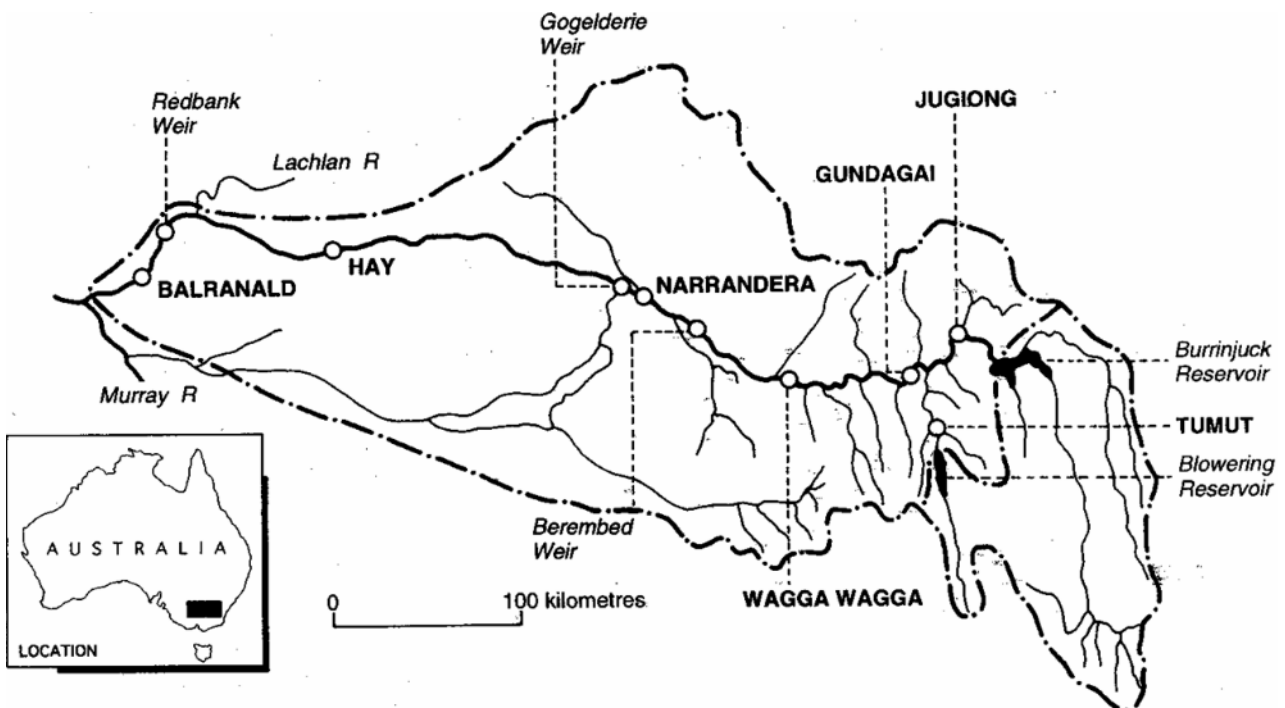
The applicability of these conceptual models to Australian lowland rivers which have irregular floods, are highly regulated and have extended periods of little or no flow, is not clear (Robertson *et al.*, 1999). It is likely that each of the models applies depending on flow conditions, a fact recognized by Walker *et al.* (1995). Further development of these models is hampered by a lack of data (Walker *et al.*, 1995; Thorp

*et al.*, 1998). Recent work has indicated that fine suspended particulate organic matter (FSPOM) is the most important form of carbon for riverine aquatic food webs (Thorp *et al.*, 1998). In this paper stable carbon isotope and C/N ratios are used to examine the sources of carbon to the FSPOM in the Murrumbidgee River, a large inland river in Australia.

Stable carbon isotope ratios and C/N ratios have been widely used to determine the sources of organic matter in aquatic environments (Hedges & Stern, 1984; Pocklington & Tan, 1987; Bird *et al.*, 1992; Thornton & McManus, 1994; Onstrad *et al.*, 2000), though in-channel production is often ignored (Bird *et al.*, 1992; Hedges *et al.*, 1986). Here they are used to distinguish between organic matter derived from catchment soils, catchment vegetation and in-channel primary production. Radiocarbon dating is used to determine the age of the organic matter in the FSPOM. The implications for carbon supply to lowland rivers are discussed.

## CATCHMENT DESCRIPTION

The Murrumbidgee River drains approximately 84 000 km<sup>2</sup> of the Murray–Darling basin. Its catchment can be divided into three distinct geomorphic regions: the upper, mid, and lower Murrumbidgee (Page, 1994). The upper region is mountainous and hilly and is separated from the mid-region by two large storage reservoirs, Burrinjuck and Blowering (Fig. 1). These dams trap most of the sediment delivered from the upper basin (Wasson *et al.*, 1987). The mid-basin area, from below the reservoirs to the township of Wagga Wagga, is characterized by undulating terrain dissected by numerous



**Fig. 1** Map of the Murrumbidgee catchment, New South Wales, Australia, showing key locations.

gully networks. These erosion gullies, formed shortly after European settlement (Wasson *et al.*, 1998) 180 years ago, are the primary source of suspended particulate matter (SPM) in the lower river (Olive *et al.*, 1996; Wallbrink *et al.*, 1998) with ~80% of the SPM derived from subsoil sources (Wallbrink *et al.*, 1998). These gullies have also been assumed to be the dominant source of particulate organic matter (Robertson *et al.*, 1999). Most of the major tributaries of the mid to lower Murrumbidgee join the river in this mid-region, their average catchment size is ~1000 km<sup>2</sup>.

Downstream of Wagga Wagga the river enters the lower region (50 000 km<sup>2</sup>) where it becomes highly sinuous as it crosses the riverine plains to its confluence with the Murray River, approximately 1500 km from the Murrumbidgee's headwaters. The gradient in the lower region is low (<0.1%), and the climate is semiarid. Much of the river channel below Wagga Wagga is fringed with River Red Gum.

## SAMPLING

Samples of FSPOM were collected from along 1000 km of the main channel from below Burrinjuck Dam to Balranald, during a 1 in 10 year flood event and on five occasions during non-flood flows. Samples of surface and subsurface soil were collected from sites selected to cover the full range of rock types and land uses in the mid-region (the primary source area for sediment to the lower river). To ensure that soil samples were representative, numerous (~25) subsamples were taken at each site; these were then combined to give one subsoil and one topsoil sample from each site.

Samples of leaf litter and grasses were collected from the soil sampling sites and combined to provide a single sample of leaf litter and a single combined sample of grass. Leaves were also collected from River Red Gums (*Eucalyptus camaldulensis*) which are the dominant riparian tree species along the studied reach.

Freshwater algal samples were not collected during this study and literature values are used. The C/N weight ratios of freshwater algae are usually close to the Redfield ratio ~ 6. The  $\delta^{13}\text{C}$  isotopic ratios can range from -12 to -47‰ (Rau, 1978; Forsberg *et al.*, 1993; Fry *et al.*, 1977) depending on the source of the carbon. The more negative values <-30‰ are associated with algae which are accessing carbon derived from the breakdown of terrestrial organic matter (Rau, 1978; Fry *et al.*, 1977; Herczeg *et al.*, 2001).

## ANALYTICAL METHODS

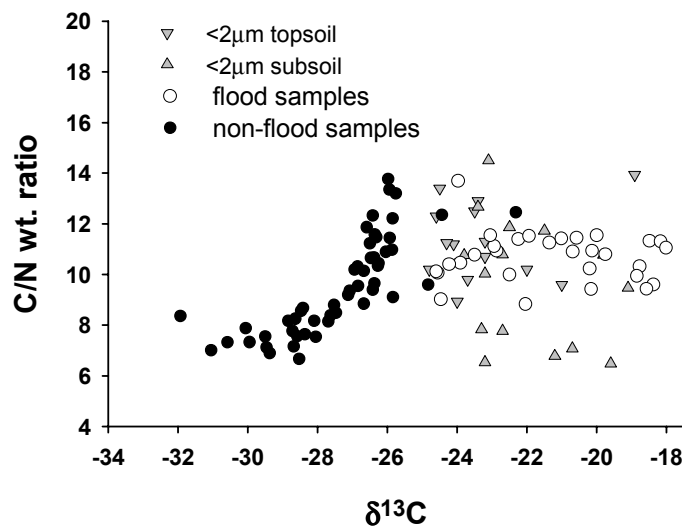
All of the samples were air dried at 45°C prior to analysis. The <2 µm fraction from the soil samples was separated by settling. Carbon and nitrogen concentrations and stable isotope values ( $\delta^{13}\text{C}$ ) were determined using a Europa 20-20 isotope ratio mass spectrometer with an ANCA preparation system. Reference samples were run after every eight samples. The carbon isotope ratios are expressed as parts per mille (‰) deviation from world recognized standards (PDB), and analytical uncertainties are ±0.3‰. Radiocarbon dating was performed by Beta Analytic Incorporated, USA.

## RESULTS AND DISCUSSION

Grassland areas in the catchment, particularly in the upper and mid regions, are dominated by plants which use the C3 photosynthetic pathway (Hattersley, 1983). Organic matter derived from C3 trees and shrubs and temperate grasses typically has  $\delta^{13}\text{C}$  ratios of between  $-25$  and  $-28\text{‰}$ ; grasses which use the C4 pathway have ratios which range from  $-10$  to  $-14\text{‰}$  (Smith & Epstein, 1971). The  $\delta^{13}\text{C}$  ratio of the combined grass sample ( $-23.4 \pm 0.3\text{‰}$ ) shows that C3 grasses dominate the sample. The  $\delta^{13}\text{C}$  ratio of the leaf litter and Red Gum leaf samples also fall in the range expected for C3 plants ( $-25.4 \pm 0.3\text{‰}$  and  $-28.2 \pm 0.3\text{‰}$  respectively). Given that the C/N weight ratio of the Red Gum leaves (60), mixed grass sample (40) and the leaf litter (25) are all  $>20$ , it is reasonable to expect that vegetative organic matter delivered to the river by either direct litterfall, or surface wash during storm events, will have a C/N weight ratio  $>20$ , and from the isotope data a  $\delta^{13}\text{C}$  ratio close to that expected for C3 plants.

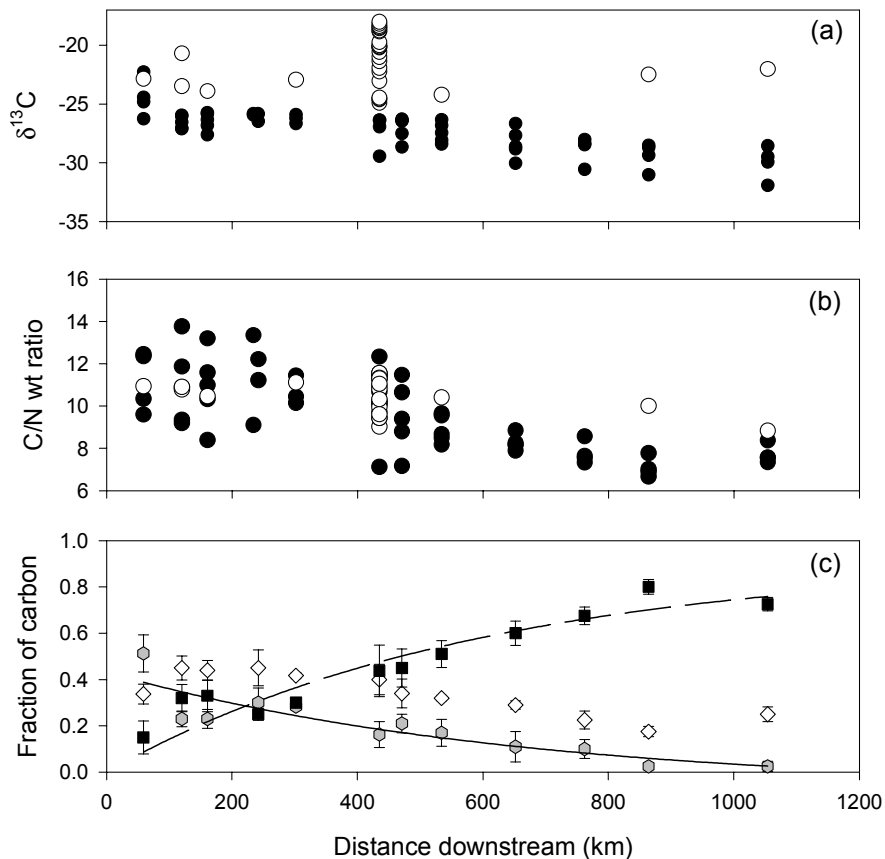
The  $\delta^{13}\text{C}$  ratio of surface soil organic matter usually corresponds to that of the covering vegetation (Hedges *et al.*, 1986; Bird & Pousai, 1997). It is expected that the smaller particle size fractions in the soil will have higher isotopic ratios due to the preferential loss of  $^{12}\text{C}$  during the breakdown of vegetative organic matter (Bird & Pousai, 1997). The SPM in the river is generally  $<2 \mu\text{m}$ . The  $\delta^{13}\text{C}$  ratios (range from  $-24$  to  $-19\text{‰}$ ) measured on the  $<2 \mu\text{m}$  fractions from the soil samples are plotted with C/N ratios (range from 15 to 7) in Fig. 2.

All of the data from the FSPOM samples collected during a 1 in 10 year flood event fall within the bivariate space of the soils data (Fig. 2). Samples at the site 435 km down river (Narrandera) were collected through the full flood hydrograph. These data indicate that, during the flood, soil organic matter dominates the carbon in the FSPOM along the river, even during flow recession.



**Fig. 2** The  $\delta^{13}\text{C}$  and C/N ratio in the  $< 2 \mu\text{m}$  fraction of soil samples and fine suspended particulate organic matter (FSPOM) samples collected from a large lowland river, the Murrumbidgee River, New South Wales, Australia. The samples of FSPOM were collected from along 1000 km of the main channel during a 1 in 10 year flood event and on five occasions during non-flood flows.

In contrast the  $\delta^{13}\text{C}$  and C/N ratio data from the FSPOM samples collected during non-flood flows are clearly separated from the soil data, indicating that the organic component in these samples is not the same as that in the  $<2\ \mu\text{m}$  fraction from the soils (Fig. 2). It is also distinct from that of the terrestrial vegetation (C/N weight ratio  $>20$  and  $\delta^{13}\text{C}$  ratio  $-23.4$  to  $-28.2\text{‰}$ ). The  $\delta^{13}\text{C}$  ratio in the non-flood flow samples varies systematically with the C/N ratio, becoming more negative as the C/N ratios decrease towards 7. The  $\delta^{13}\text{C}$  and C/N ratios both show strong systematic patterns with distance downstream (Fig. 3(a) and (b)). The C/N ratio is more variable in the first  $\sim 450$  km (range 8.4–13.6). From 450 km to 800 km the mean ratio and the variability decreases (range 6.7–8.6). Along the river  $\delta^{13}\text{C}$  ratios also decrease becoming more negative in the lower reaches. These data indicate a change in the primary source of carbon in the FSPOM along the river during non-flood flows. Isotopically light carbon is being incorporated into the FSPOM presumably by in-channel primary production. As the concentration of carbon in the FSPOM does not vary significantly along the river the isotopically heavier organic components are either being metabolized in the river and lost to solution and then to the atmosphere, or are being deposited.



**Fig. 3** The  $\delta^{13}\text{C}$  (a) and C/N (b) ratios in samples of fine suspended particulate organic matter (FSPOM) collected from along 1000 km of the main channel during a 1 in 10 year flood event (open circles) and on five occasions during non-flood flows (closed circles). (c) The contributions, during non-flood flows, of carbon derived from in-channel production (closed squares), soil organic matter (grey hexagons), and C3-vegetation (open diamonds) to the FSPOM as a function of distance downstream calculated using a three component mixing model. End member values were chosen such that the estimated in-channel derived component is a minimum.

The contributions of carbon derived from in-channel production, soil organic matter and C3-vegetation to each of the low flow FSPOM samples have been estimated from the carbon and nitrogen concentrations and the C/N and  $\delta^{13}\text{C}$  ratios using a three-component mixing model. End member values were chosen such that the estimated in-channel derived component would be a minimum. The results (Fig. 3(c)) indicate that the in-channel derived component increases with distance downstream while the carbon derived from the soils and C3 vegetation decreases.

The age of the carbon in the FSPOM was determined by radiocarbon dating. Two samples collected during non-flood flows, one from the upper reach ( $\delta^{13}\text{C} = -26.1\text{‰}$ , C/N = 10.5), the other from the lower river ( $\delta^{13}\text{C} = -30.1\text{‰}$ , C/N = 7.1), were analysed with and without acid/alkali/acid (AAA) pretreatment. This treatment is used to remove the less refractory carbon components. The  $\delta^{14}\text{C}$  (corrected for fractionation during initial uptake) on the untreated samples was  $66 \pm 4\text{‰}$  (upper) and  $44 \pm 4\text{‰}$  (lower), and for the AAA treated material  $112 \pm 4\text{‰}$  and  $84 \pm 4\text{‰}$  respectively indicating that they post-date atmospheric nuclear weapons testing. In the Southern Hemisphere the  $\delta^{14}\text{C}$  ratio of the atmosphere at the time of sample collection was  $\sim 120\text{‰}$ . The values in the untreated and treated fractions are too low for recently photosynthesized material, and are consistent with material photosynthesized from the atmosphere in the period 1955–1960 (Fig. 8 in Hua *et al.*, 1999).

## IMPLICATION FOR CARBON SUPPLY TO AQUATIC ECOSYSTEMS

The data presented support a model of carbon supply to the FSPOM in the Murrumbidgee River in which catchment soil sources dominate during flood events, even during flow recession when waters return from the flood plain. During non-flood periods riparian vegetation and catchment soil sources in the tributary catchments are important carbon sources to the FSPOM in the upper reaches of the main channel. During transport downstream much of this carbon is metabolized and enters the dissolved phase. Carbon derived from the breakdown of soil organic matter deposited along the river during the flood periods also enters the dissolved phase. In-channel primary producers then preferentially incorporate the isotopically light fraction from the dissolved phase back into the FSPOM. As the concentration of carbon in the FSPOM does not vary significantly along the river the isotopically heavy carbon is lost to the atmosphere. The isotopic ratios and radiocarbon dating indicates that in-channel primary producers are on average using terrestrial material photosynthesized from the atmosphere 40–50 years ago, indicating that there are significant stores and delays in the system.

This work demonstrates that organic matter derived from catchment soils is a major carbon source to these large inland rivers. It reveals the importance of in-channel carbon cycling of terrestrial organic matter and in-channel primary production as a source of carbon to the FSPOM, and hence aquatic food webs. It also suggests that the lowland flood plain is not a significant source of carbon to these rivers and illustrates the importance of longitudinal processing of carbon.

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