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Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism

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Abstract. For a majority of aquatic ecosystems, respiration (*R*) exceeds autochthonous gross primary production (GPP). These systems have negative net ecosystem production ([NEP] = [GPP] – *R*) and ratios of [GPP]/*R* of <1. This net heterotrophy can be sustained only if aquatic respiration is subsidized by organic inputs from the catchment. Such subsidies imply that organic materials that escaped decomposition in the terrestrial environment must become susceptible to decomposition in the linked aquatic environment.

Using a moderate-sized catchment in North America, the Hudson River (catchment area 33 500 km^2), evidence is presented for the magnitude of net heterotrophy. All approaches (CO_2 gas flux; O_2 gas flux; budget and gradient of dissolved organic C; and the summed components of primary production and respiration within the ecosystem) indicate that system respiration exceeds gross primary production by ~200 g C m^{-2} $year^{-1}$. Highly ^{14}C-depleted C of ancient terrestrial origin (1000–5000 years old) may be an important source of labile organic matter to this riverine system and support this excess respiration. The mechanisms by which organic matter is preserved for centuries to millennia in terrestrial soils and decomposed in a matter of weeks in a river connect modern riverine metabolism to historical terrestrial conditions.

Extra keywords: river, watershed, pCO_2

Introduction

In most terrestrial ecosystems the amount of organic C produced by photosynthesis (Gross Primary Production; GPP) is largely consumed by the combined respiration (*R*) of the plants themselves and heterotrophic consumer organisms. The difference between GPP and *R*, or net ecosystem production ([NEP] = [GPP] – R) is small compared with either GPP or *R*. There are only three fates for this terrestrial NEP: long term storage, burning in fires, and export.

The export of organic C from terrestrial ecosystems is an import of organic C to aquatic ecosystems. This export can be a substantial fate for terrestrial NEP compared with burial. For example, in the small (15–20 ha) catchments at the Hubbard Brook Experimental Forest (Likens *et al.* 1977), hydrologic export of organic C and burial in forest soils are co-equal (Fig. 1). These catchments are relatively young, ~12 000 years old, and are still storing some organic C in soils (Likens *et al.* 1977). It is conceivable that older catchments are closer to steady state with respect to organic C storage; in these cases, export would be the dominant fate of NEP.

Since export is a large term for terrestrial NEP, it is reasonable to ask what is the fate of the exported terrestrial organic matter. The amount of organic C that is buried on the continental shelves, one of the largest depositional environments on the planet, is about equal to the amount of terrestrial particulate organic C (POC) transported by rivers (Mulholland and Watts 1982; Berner and Berner 1987; Hedges *et al.* 1997). The amount of dissolved organic carbon (DOC) transported by rivers is large enough to support turnover of the marine DOC pool (Williams and Druffel 1987). It is tempting to equate riverine delivery with sedimentary burial or DOC accumulation in the ocean but, intriguingly, new chemical and isotopic evidence suggests that very little of this terrestrial C actually accumulates in

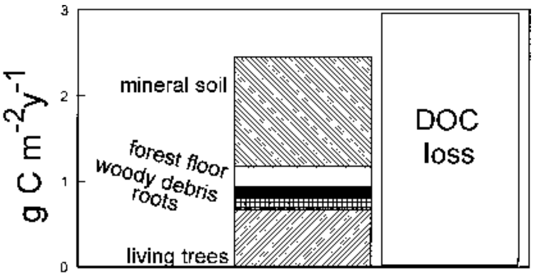

Fig. 1. Loss and net accumulation of organic C for an undisturbed watershed at the Hubbard Brook Experimental Forest in New Hampshire, USA. Data from Gosz *et al.* (1978), Likens *et al.* (1977), Bormann and Likens (1979) and McDowell and Likens (1988). DOC is not the only form of organic matter lost from the forest; thus, the loss term is an underestimate of true loss.

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the ocean (Prahl *et al.* 1994; Hedges *et al.* 1997; Opsahl and Benner 1997; Druffel *et al.* 1998). The inference is that it must decompose on the continental margins, in river deltas or perhaps in the lower reaches of rivers themselves. The decomposition of terrestrial organic C in rivers is the subject of this review.

The hydrologic export of organic C from terrestrial systems represents an import into the receiving aquatic system. This input of allochthonous organic C can be quite large in comparison to autochthonous primary production within the aquatic system itself. The import can be visualized as the product of water load and the concentration of organic C in the water. Water load is the volume of water (m^3) per unit area of the receiving aquatic system (m^2) per year. Since the terrestrial catchment is generally much larger than the aquatic receiving system, the water load (m $year^{-1}$) often greatly exceeds the precipitation input of water, especially for rivers, and especially in non-arid regions. For example, consider conditions representative of the north-eastern USA and Canada. At representative riverine DOC concentrations of 830 μM (10 mg C L^{-1}) and a water load of 100 m year $^{-1}$ (precipitation – evapotranspiration = 0.5 m $year^{-1}$; catchment area 200 times larger than the area of the river), the input of terrestrial DOC is 1000 g C m^{-2} $year^{-1}$, which is considerably larger than primary production in all but the most productive riverine environments. The input of terrestrial POC would make this import term larger still.

Clearly, terrestrial POC and DOC enter riverine systems, and this input is large in comparison to autochthonous primary production, and this allochthonous organic matter may simply flow through the system without being metabolized. If some of it were metabolized we would expect to see an effect on the fluxes of CO_2 or O_2 into or out of the river. Obviously, the net effect would depend on the magnitudes of autochthonous GPP, the fraction of GPP that was respired *v.* exported, and the amount of terrestrial organic matter that was oxidized. For example, suppose that the allochthonous load was 1000 g C $m^{-2}year^{-1}$ (83 mol C $m^{-2}year^{-1}$) and 25% of this were respired in the river. This riverine respiration of terrestrial organic C generates a CO_2 source, or O_2 sink, of ~57 mmol m^{-2} day^{-1}. At zero autochthonous GPP this source would be seen as a net source of CO_2 of this magnitude. As riverine GPP increases, this net heterotrophy decreases. Similarly, when the fraction of autochthonous GPP that is respired approaches 100%, net heterotrophy approaches the full 57 mmol m^{-2} day^{-1} (Fig. 2). The net flux could be manifested either as gas exchange with the atmosphere or as the export of water which was elevated (compared with water inputs) in dissolved inorganic C (DIC) or depleted in oxygen. The net gas exchange of CO_2 or O_2 between the river and the atmosphere is, thus, a minimal estimate of net heterotrophy

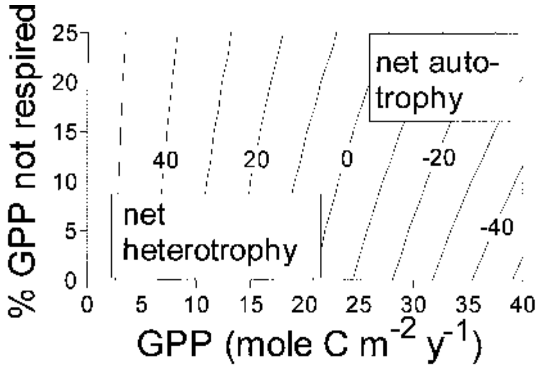

Fig. 2. Simple model of the effect of the metabolism of terrestrial organic matter in a riverine system. Calculation based on a load of terrestrial material of 83 mol m^{-2} (of river) $year^{-1}$ (1000 g C m^{-2} $year^{-1}$ of which 25% is respired within the river). *X*-axis, range of riverine GPP expected among rivers; *Y*-axis, the fraction of this riverine GPP that is exported or buried but not respired within the river. The iso-lines denote CO_2 (or O_2) net gas flux (mmol $m^{-2}day^{-1}$). At this hypothetical level of allochthonous loading as metabolism of allochthonous organic matter, only the most productive systems (GPP >20 mol m^{-2} $year^{-1}$ or 240 g C m^{-2} $year^{-1}$) are likely to be net autotrophic.

and an underestimate of the amount of terrestrial organic matter respired in the river.

This paper demonstrates that a majority of large rivers for which we can obtain data are net sources of CO_2 to the atmosphere, consistent with the idea that they are net heterotrophic. It considers in detail the C budget of one river, the Hudson River, (USA) and suggests that terrestrial organic matter that was produced 1000–5000 years ago fuels a substantial portion of metabolism in the Hudson.

The Hudson River

The 33 500 km^2 Hudson River basin includes eastern New York, parts of Vermont, Massachusetts, Connecticut and New Jersey. The river is divided into the upper, non-tidal section and the tidal river. The tidal portion extends 240 km south from Albany to New York City, NY, where it empties into the sea. The upper 200 km of this stretch consists of fresh water and is not influenced by NY City's sewage or possible ^{14}C inputs from nuclear power plants in the lower, oligohaline, section of the river. This section of the Hudson averages 0.8 km in width and is an 8th-order river with average annual flow of near 400 m^3 s^{-1} at Albany; this flow increases by only 15% over the 115-km stretch. The river is relatively deep (mean 8 m) but is mixed from top to bottom in terms of temperature, CO_2, dissolved oxygen and chlorophyll (Cole *et al.* 1992; Raymond *et al.* 1997). For this paper, we identify stations km north from the southern tip of Manhattan (km 0) and the reach we discuss extends from km 125 to km 240.

The Hudson watershed (catchment) includes parts of the Adirondack and Catskill Mountains where much of the land is almost completely forested. The watershed also includes agricultural areas (25% of watershed). Approximately 80 tonnes year^{-1} of organic C (or 700 g C m^{-2} year^{-1} of river area) leave the watershed and enter the study reach. Direct measurements (Phillips and Hanchar 1996; Findlay *et al.* 1998) and models (Howarth *et al.* 1992) indicate that much of the organic C comes from the agricultural sub-watersheds. Sewage loads to the study area are far less than non-point loads, and enter primarily at Albany, the top of the stretch examined in this study (Fruci and Howarth 1989). Marshlands along the main stem of the lower Hudson contribute only a few percent of the total organic C load (Findlay *et al.* 1998). Thus, the major allochthonous inputs are delivered upstream of the study area; within the stretch (river km 240 to km 125) there are few new allochthonous C inputs.

Autochthonous C inputs within this 115-km stretch come from phytoplankton production, submerged aquatic vegetation (dominantly *Vallisneria*) and floating-leaved vegetation (dominantly *Trapa*). Phytoplankton net production is limited by a combination of low light intensity, rapid flow, and benthic grazing by the zebra mussel *Dreissena polymorpha* (since 1992; Caraco *et al.* 1997; Strayer *et al.* 1999). At present, these factors combine to restrict most of the phytoplankton biomass and production to between June and October in a narrow reach of ~10 km (near km 210). In this reach, net phytoplankton production may be >100 g C m^{-2} year^{-1}, but over the entire 115-km study stretch it appears to average ~30 g C m^{-2} year^{-1} (Cole *et al.* 1992; Caraco *et al.* 1997, 2000). Submerged aquatic vegetation is present in greatest abundance in a 50-km stretch south of the phytoplankton peak at km 210. Considering biomass, photosynthetic parameters and light (Harley and Findlay 1994; Caraco *et al.* 1997), production in this zone is presently ~70 g C m^{-2} year^{-1} over the entire study stretch. *Trapa* is in highest abundance in the southern stretch and production is probably <30 g C m^{-2} year^{-1} in the river (Findlay *et al.* 1998). Thus, combined, the net production of phytoplankton, submerged aquatic vegetation and *Trapa* is ~100 g C m^{-2} year^{-1} or 20% of the allochthonous load.

The within-river respiration of organic C by microbes and grazers appears to be substantially larger than the net production within the system. On the basis of measurements of microbial production and growth efficiency, planktonic microbes alone respire ~200 g C m^{-2} year^{-1} (Findlay *et al.* 1991; Roland and Cole 1999). Sediment core studies in the Hudson suggest that respiration by benthic microbes is relatively low, as was that of all benthic grazers before 1992 (S. E. G. Findlay, personal communication; Strayer *et al.* 1999). The invasion of the system by an exotic bivalve (the zebra mussel) resulted in dramatic increases in benthic biomass, and at present zebra mussel respiration alone in the study reach is near 100 g C m^{-2} year^{-1} (Strayer *et al.* 1999). Taken together, therefore, the production and respiration estimates for the Hudson indicate respiration in excess of primary production of 100 g C m^{-2} year^{-1} prior to the zebra mussel invasion, and ~200 g C m^{-2} year^{-1} after the invasion (Caraco *et al.* 2000).

Methods

Direct measurement of pCO$_2$

For the Hudson River, we have direct measurements of pCO$_2$ at approximately weekly intervals from 1992 through 1999. Water was collected just below the surface (0.05-m depth) and CO$_2$ was obtained by headspace equilibration with ambient air (1200 mL water and 50 mL air; Cole *et al.* 1994; Raymond *et al.* 1997). The extracted headspace gas was returned to the laboratory and analysed on a Shimadzu AIT gas chromatograph with a thermal conductivity detector against NBS CO$_2$ standards. Samples of ambient air were taken at the same time as the extractions and treated the same way. For the extractions, corrections were made for barometric pressure and for the small amount of CO$_2$ introduced during the headspace equilibration. Temperature-dependent Henry's constants (K_h) were calculated according to Butler (1992). At the same time and on the same schedule dissolved oxygen in the surface water was measured either by Winkler titration or by use of polarographic electrodes (YSI-model 1000).

Calculated values of pCO$_2$

Direct measurements of pCO$_2$ are rare in the literature, but data are widely available from which pCO$_2$ can be calculated. For the literature data set (Table 1) we obtained measurements of pH, temperature and conductivity, and coupled these with measures of DIC or alkalinity depending on which was available. The calculations include dependence on temperature and ionic strength for both dissociation constants (k_1 and k_2) and corrections for the effects of ionic strength on ion activity from the chemical equilibrium model MINEQL (Schecher and McAvoy 1991; see Cole *et al.* 1994)

For the Hudson, on the same schedule as the direct CO$_2$ measurements we also measured pH (with a Fisher accumet meter and a gel-filled ATC electrode) and DIC (with a Shimadzu model 5050 TOC/TIC analyser) in order to calculate values of pCO$_2$ as well. We did this to evaluate how well calculated values reproduced actual measured values in river water (Herczeg and Hesslein 1984; Herczeg *et al.* 1985).

Literature data

Data for 46 different large river systems with a nearly worldwide distribution were obtained from a range of literature sources (Table 1). We included only those systems for which we could find monthly data for at least three years. In total, the data set contains 7638 individual records (rivers by dates, excluding the Hudson). The largest sources of information were from the United States Geological Survey (Alt 1993 and http://usgs.gov) and from the work of Kempe (1982). The data set is geographically biased, in that North America is over represented and for one continent (Australia), we did not find appropriate published data. We have included only freshwater rivers and refer the reader to a recent review by Frankignoulle *et al.* (1998) for estuaries.

Estimation of gas flux

The flux of a gas is governed by the concentration gradient between the water and the air and by turbulent energy exchange across the air–water interface. Thus

$$\text{Flux (mmol m}^{-2}\text{day}^{-1}) = k\alpha(\mathrm{CO_{2water}} - \mathrm{CO_{2sat}}).$$

Table 1. pCO_2 in large rivers

River	pCO_2 µatm Mean	pCO_2 µatm s.d.	Stations × Dates N	Reference
Alabama, USA	3028	256	140	Alt 1993
Allegheny, USA	3212	649	120	Alt 1993
Amazon,Brazil	3420	842	28	Kempe 1982, Devol *et al*. 1987
Appalochicola, USA	4132	638	42	Alt 1993
Arkansas, USA	3320	121	749	Alt 1993
Brazos, USA	3115	180	299	Alt 1993
Caroni, Venezuela	2957	2280	11	Paolini *et al*. 1987
Changjiang, China	1383	372	14	Wei and Jie 1987
Colorado, USA	4295	195	486	Alt 1993
Columbia, Canada	1123	1175	140	Kempe 1982
Cumberland, USA	6171	599	106	Alt 1993
Delaware, USA	2172	144	229	Alt 1993
Elbe, Germany	4095	1758	116	Kempe 1982
Gambia, Gambia	2072	669	12	Lesack *et al.* 1984
Garonne, France	1675	741	47	Kempe 1982
Huanghe, China	1137	189	28	Gan *et al.* 1983
Hudson, USA	1062	417	327	This study
Illinois, USA	4419	240	339	Alt 1993
Indus, India/Pakistan	1748	2288	18	Arain 1985
Kansas, USA	1849	1213	132	Alt 1993
Loir, France	1240	926	60	Kempe 1982
MacKenzie, Canada	4663	3893	10	Telang 1985
Mississippi, USA[A]	4593	183	628	Alt 1993
Mississippi, USA[A]	4752	3566	155	Kempe 1982
Missouri, USA	1113	62	318	Alt 1993
Niger, Nigeria	35617	46757	21	Camail *et al.* 1987
North Platte, USA	3166	136	544	Alt 1993
Ohio, USA	6238	493	160	Alt 1993
Parana, Brazil	3139	3240	37	Depetris and Kempe 1993
Platte, USA	3903	207	356	Alt 1993
Red, USA	2342	180	169	Alt 1993
Rhone, France	2015	944	47	Kempe 1982
Rio Grande, USA	1205	72	283	Alt 1993
Sacramento, USA	1955	161	148	Alt 1993
Seine, France	1982	780	59	Kempe 1982
Snake, USA	1648	82	406	Alt 1993
South Platte, USA	2121	862	89	Alt 1993
St. Lawrence, USA[A]	2322	214	118	Alt 1993
St. Lawrence, Canada[A]	2240	3841	91	Kempe 1982
Tennessee, USA	9475	993	91	Alt 1993
Upper Jordan, Jordan	2461	608	89	Salinger *et al.* 1983
Wabash, USA	1849	1243	51	Alt 1993
Weser, Germany	4395	2966	9	Kempe 1982
White, USA	679	543	120	Alt 1993
Willamette, USA	3234	268	146	Alt 1993
Yangtze, China	1222	264	25	CCRU 1982; Gan *et al.* 1983
Yellowstone, USA	3306	207	254	Alt 1993
Yukon, USA[A]	5205	1021	26	Alt 1993
Yukon, USA[A]	2767	4123	72	Kempe 1982

[A]These rivers are listed twice because data came from diverse sources and covered different times and locations.

CO_{2water} is the concentration of CO_2 in the water that is the product of K_h and the measured value of pCO_2. CO_{2sat} is the concentration the water would have if it were in equilibrium with the air, and it is the product of K_h and the measured pCO_2 in the air. k is piston velocity of gas exchange (m day^{-1}). This piston velocity has rarely been measured for large rivers. In the case of the Hudson River, we have two independent estimates of k. Marino and Howarth (1993) used a floating-dome approach, and Clark *et al.* (1994) conducted a purposeful tracer experiment *in situ* using ^4He and SF_6. Both found that k varied with wind speed (see Raymond *et al.* 1997), and we use the Clark *et al.* (1994) data here as the basis of the flux calculations, assuming that the whole-river tracer addition gives a result under more realistic conditions than does the dome approach. α is the coefficient of chemical enhancement for CO_2, a term that becomes important only at relatively high pH. It is needed because at high pH and low values of k, CO_2 can react with aqueous carbonate more quickly than normal diffusion can occur. We used Wanninkhof and Knox's (1996) formulation of Hoover and Berkshire's (1969) to compute α.

^{14}C and ^{13}C information for the Hudson River

There is very little information for rivers in general on the ambient ^{14}C content of the various C pools. Raymond (1999) reports values of ^{14}C and ^{13}C for Hudson River DIC and for POC and DOC from a longitudinal transect taken in early summer of 1998. The methods are detailed in Raymond (1999).

Results

pCO_2 and gas flux in the Hudson

The 8-year record of direct measurement of pCO_2 showed that the water was consistently supersaturated in CO_2 with respect to the atmosphere, indicating that the Hudson is nearly always a net source of CO_2 to the atmosphere (Fig. 3*upper*). Calculated values of pCO_2 produced a relatively unbiased estimate of directly measured values. Thus, a plot of measured (X) versus calculated (Y) pCO_2 had a slope just under 1.0 (0.93 ± 0.011 s.e.) and an r^2 value of 0.94. This means that calculated values are slightly lower than directly measured ones. Average water pCO_2 (1014 μatm) was 2.5 times greater than the average pCO_2 in the air (406 μatm). While there was little variation in the air value (coefficient of variation, cv 11.8%), there was considerable seasonal variation in the water value (cv 33%) and a distinct seasonal cycle. Lowest values, near atmospheric equilibrium, generally occur in late fall and early winter. Highest values occur in early July through early September. There is some obvious inter-annual variation as well, especially in the magnitude of peak water pCO_2 and its precise timing.

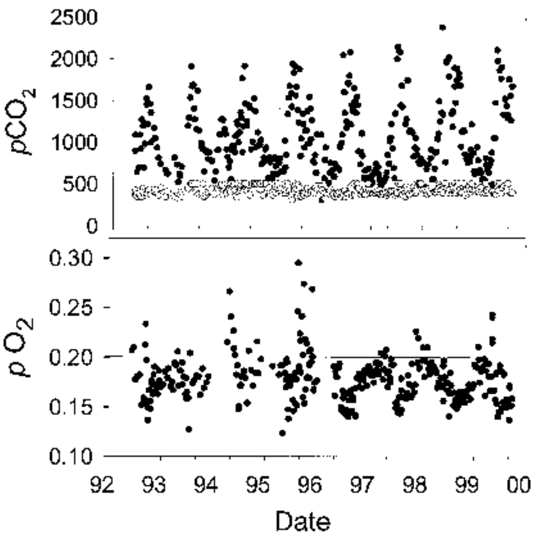

Fig. 3. Direct measurements in the Hudson River at weekly intervals, 1992 – 1999. *(upper)* partial pressure of CO_2 (pCO_2): ● in the surface water; ○ in the overlying atmosphere *(lower)* partial pressure of O_2 (pO_2): ● in the surface water; solid line, in the atmosphere.

Coupling these data to an analysis of hourly wind data at the meteorological station of the Institute of Ecosystem Studies, ~10 km from the river, Raymond *et al.* (1997) calculated the annual net flux of CO_2 to the atmosphere of 16–36 mmol m^{-2} day^{-1}. The range reflects different assumptions used in modelling k as a function of wind speed. The seasonal cycle of the gas flux is dominated by the seasonal cycle of pCO_2; the seasonal variation in wind speed is minor in comparison.

The Hudson is persistently undersaturated in O_2 with an average pO_2 of 0.181 ± 0.02 μatm (saturation of 90.5%) over the same time period as the CO_2 data (Fig 3*lower*). The average concentration difference between the O_{2water} and O_{2sat} is 30 μM, which is very close to the difference in CO_2 concentration. Thus, the Hudson is undersaturated in O_2 by about the same magnitude that it is supersaturated in CO_2. Since oxygen at saturation is a much larger pool (~240 μM at 20°C) than is CO_2 (13 μM at 20°C), it is more difficult to resolve small changes in O_2. Further, the methods for O_2 are less precise. Nevertheless, although the relationship is not highly correlated (r^2 = 0.3), pCO_2 and pO_2 are significantly (P <0.001) and negatively correlated. The net oxygen flux has been estimated at –20 mmol m^{-2} day^{-1} (Caraco *et al.* 2000), which is approximately the inverse of the CO_2 gas flux and works out to an annual value of ~230 g C m^{-2} $year^{-1}$.

The Hudson exports water that is supersaturated in CO_2 and this represents an additional term in the budget of ~7 mmol m^{-2} day^{-1}. Because the total DIC pool in the Hudson is relatively large (~1100 μM), we cannot easily measure an increase in the loss of HCO_3. If some alkalinity is generated within the river, this loss could be significant.

Taken together, the data for CO_2 and O_2 gas flux give comparable, minimum estimates of the amount of allochthonous organic C that is metabolized in the Hudson of 20–40 mmol m^{-2} day^{-1} or ~100–200 g C m^{-2} $year^{-1}$. The net gas flux is a measure of the net difference between all respiration and all primary production in the river (NEP). Another approach is to compare the upstream and downstream transport of organic C in the river (Fig. 4). This provides a more direct measurement of the loss of allochthonous organic C. In the Hudson, DOC, the major pool of organic C, declines slightly with distance. Thus,

$$\text{DOC loss} = (Q[\text{DOC}]_{\text{input}} - Q[\text{DOC}]_{\text{output}}) \,/\, \text{river area}.$$

This approach provides estimates of allochthonous C metabolism ranging from 85 to 185 g C m^{-2} $year^{-1}$. POC does not decline monotonically with distance downstream and does not lend itself to this analysis. Presumably, including a POC loss term would increase the metabolism of DOC.

Howarth *et al.* (1996) calculated total system *R* for the Hudson by measuring night-time declines in O_2, corrected for diffusion; they then subtracted an estimate of net primary production and obtained an NEP estimate, slightly larger, of 293 g C m^{-2} $year^{-1}$. The various estimates of NEP in the Hudson River are summarized in Table 2.

pCO$_2$ in other rivers

The Hudson River is supersaturated in CO_2, and the net gas flux of CO_2 from the river is comparable to other estimates of NEP for the Hudson. How does the Hudson compare with other rivers in terms of CO_2 supersaturation? For the database we have compiled (Table 1), mean pCO$_2$ among the 47 rivers averaged 3230 µatm (Fig. 5). No river had average pCO$_2$ values that were undersaturated, although some individual samples (3.6% of total) from some rivers were undersaturated. The average pCO$_2$ of the Hudson is

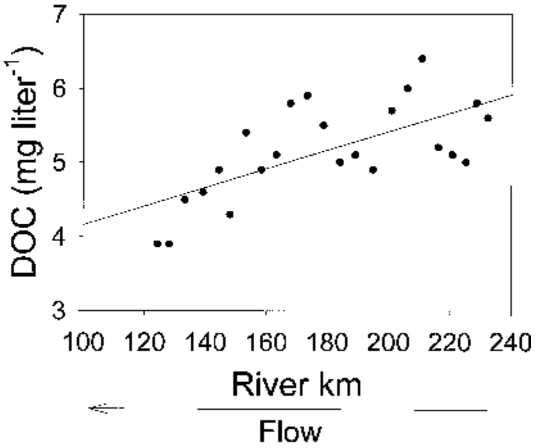

Fig. 4. DOC concentrations along a longitudinal transect in the Hudson River. River km (X-axis) is distance along the river that flows from the north (Albany, NY; river km 245) towards New York City (river km 0). Slope of regression line, 0.012 mg C L^{-1} km^{-1} — consistent with a loss term of ~100 g C m^{-2} $year^{-1}$ of allochthonous organic C. The line is significant (P <0.01) but the r^2 low 0.44, so the data generate a range of loss terms from 85 to 185 g C m^{-2} $year^{-1}$.

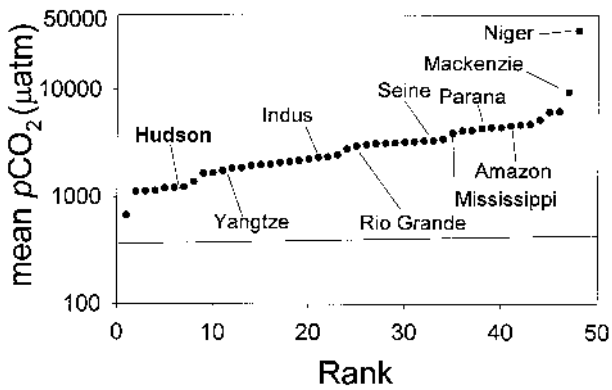

Fig. 5. Average partial pressure of CO_2 (pCO$_2$) in a series of 47 rivers with a near-global distribution (see text). Each point represents the mean pCO$_2$ in a different river, calculated from pH, temperature and alkalinity (Table 1); data for the Hudson are direct measurements (see text). Some of the individuals are labelled for reference. The rivers are ordered along the X-axis from the least to the most supersaturated in CO_2. The solid line denotes approximate equilibrium with air. Note log scale.

Table 2. Estimates of net heterotrophy in the Hudson River (for a 115 km tidal freshwater reach from Albany to Newburg) obtained by various approaches

Allochthonous input based on 650 g C $m^{-2}year^{-1}$ (Howarth *et al.* 1996). '% input respired' is the minimum estimate of the allochthonous input respired in the river

Method	Notes	Reference	g C m^{-2} $year^{-1}$	% input respired
Annual CO_2 balance	(include gas flux and advection) 1992–99	Raymond *et al.* 1997 This study	100–190	15–29
Annual O_2 influx	1992–99	Caraco *et al.* 2000 This study	~230	35
DOC decline	Upstream–downstream DOC flux	This study DOC from Cole unpubl.	85–185	13–29
Night time O_2 declines	System R-Npp	Howarth *et al.* 1996	293	45
Internal component of C budget	all GPP – all *R* (see text) 1992–99	Caraco *et al.* 2000 Strayer *et al.* 1999 Findlay *et al.* 1991 Roland and Cole 1999	~200	31
Mean of estimates			183	28

~2.5 standard deviations lower than the mean for the global data set. The range for the entire data set is quite large (647–38 000 μatm). Even if we exclude the suspiciously high value for the Niger, the range is still 14 fold from lowest to second highest. Calculated values of pCO_2 in softwaters are frequently too high compared with measured values as a result of common bias in pH measurements (Herczeg and Hesslein 1984; Herczeg *et al.* 1985). In the relatively hard waters of the Hudson (DIC ~1 mM) the bias was small and in the opposite direction. Thus, we expect that the calculated values from the other rivers, for which we do not have direct measurements, should not be too far from reality.

We do not have direct *in situ* estimates for the piston velocity of gas exchange in these other rivers so we cannot estimate a global river gas flux with confidence. However, since the Hudson is relatively deep and slow moving, it is likely that k for most rivers in the data set is as large as or larger than measured in the Hudson. If we use a k of 0.8 m day^{-1} for the entire data set, the average CO_2 flux from these 45 major rivers would be 93 mmol m^{-2} day^{-1} or ~407 g C m^{-2} year^{-1}. If these rivers are representative of flowing waters in general, which cover ~0.5% of land surface area, this flux adds ~0.3 Pg C year^{-1} as CO_2 to the atmosphere. Intriguingly, the loss of CO_2 from rivers is about as large as the transport of organic C in rivers to the sea (0.4 Pg C year^{-1}; Holland 1995). Thus, if these estimates are correct, to deliver 0.4 Pg C to the sea, 0.7 Pg would be delivered from land into rivers and 0.3 Pg (43%) respired in the rivers themselves.

^{14}C in the Hudson

Values of ^{13}C and ^{14}C in the various C pools for which we have data are shown in Table 3 as a function of river km. The POC entering the Hudson (and to a lesser degree DOC) is greatly depleted in ^{14}C. This depletion suggests that the particulate material entering the north end of the tidal Hudson was originally formed on average ~5000 years ago. The $\delta^{13}C$ suggests that it is of terrestrial rather than marine origin (Table 3). Thus, it is unlikely that very ancient marine sedimentary rocks are the source of this old organic matter. Sediment cores from depositional areas further down river confirm our finding. Olsen *et al.* (1978) found that carbonate shells contained modern (bomb) carbon, whereas the humic and residual organic fractions even in the surface sediments were near 3000 years old and of terrestrial origin. It is likely that the old C was produced in the watershed since the last glaciations and is <14 000 years old. If we assume that the 'average' organic matter entering the Hudson comprises two pools (modern and old) and that the 'old' pool is 14 000 years old, the 5000-year age of the average C implies that most of it (73%) is in the 'old' pool. Even if the old pool is 50 000 years old, the same calculation shows that 45% is in the 'old' pool. These considerations imply that the source of old C is large compared with the source of modern C at the input to the stretch. The DOC is old but less so. For both DOC and POC, the ^{14}C becomes less depleted ('younger') in the downstream direction. We can rule out the possibility that riverine photosynthesis using ^{14}C-depleted inorganic C (DIC) is the source of this old organic matter. Although the DIC in the Hudson is depleted in ^{14}C, it is not depleted enough to generate organic C with apparent ages of 1000 to 5000 years BP.

Discussion

The various approaches suggest that the NEP in the Hudson is negative and ~200 g C m^{-2} year^{-1} (Table 2). This net metabolism is ~20–30% of the total allochthonous loading to this 115 km stretch of river, and NEP represents a minimum estimate of the total amount of allochthonous material that is respired. Thus, a large fraction of allochthonous loading is required to support net respiration

Table 3. ^{14}C and ^{13}C content of particulate organic C (POC), dissolved organic C (DOC) and dissolved inorganic C (DIC) in the Hudson River during June 1998

Data of Raymond (1999), and Raymond and Bauer (in press). Samples taken at three stations indicated by river km. The 'input' is at the fall line at the head of tide north of Albany, New York. The lower river km are farther down stream. ^{14}C values are given as both Δ and as age in years BP

Carbon pool	River km 240 (input)		River km 200		River km 145	
	^{14}C Δ‰	Age Years	^{14}C Δ‰	Age Years	^{14}C Δ‰	Age Years
POC	–451.6	4780	–383.8	3840	–101.8	820
DOC	–155.4	1310	–128.2	060	–38.9	270
DIC	–62.9	475	ND		–35.7	250
	^{13}C δ‰		^{13}C δ‰		^{13}C δ‰	
POC	–27.2		–27.1		–28.1	
DOC	–25.5		–26.8		–27.1	
DIC	–5.6		–7.0		–7.6	

in the Hudson River. On the other hand, the allochthonous loading is dominated by very old (>1000 years BP) organic C. One might expect this old carbon to be well worked over by soil microbes and be quite recalcitrant to further decomposition. If, of the allochthonous loading, the younger material were selectively metabolized, the residual, transported organic C would get increasingly depleted (older) in ^{14}C as it moved downstream. Although we have only a few data points, the initial ^{14}C pattern suggests the opposite. That is, the organic pools become increasingly ^{14}C enriched (younger) during transport (Table 3).

If the Hudson were strongly net autotrophic, this longitudinal change in apparent ^{14}C age could have occurred by the dilution of old organic C with newly photosynthesized C. The degree of net autotrophy required for this dilution is, however, very large (~1320 g C m^{-2} $year^{-1}$). This degree of net ecosystem production is an order of magnitude greater than measurements suggest for even gross primary production (Cole *et al.* 1992; Harley and Findlay 1994; Findlay *et al.* 1996; Howarth *et al.* 1996; Caraco *et al.* 1997). Additionally, net autotrophy of this magnitude would lead to undersaturated CO_2 and supersaturated O_2 conditions that do not occur (Fig. 3). On the basis of an atmospheric gas exchange value actually measured in the Hudson of 0.7 m day^{-1} (Marino and Howarth 1993; Clark *et al.* 1994), dissolved O_2 values would have to be 950 μM (4.3 fold higher than actually measured) while CO_2 would be depleted to near <1 μM (30 fold lower than we measure) under these conditions. In reality, O_2 is undersaturated, averaging near 220 μM, and CO_2 values are correspondingly supersaturated, averaging near 750–1000 matm (or 26–35 μM). Lastly, as burial of C appears to be relatively small in the Hudson (Howarth *et al.* 1996) this implied amount of input from autochthonous GPP would suggest TOC should increase along the length the river from near 6 mg L^{-1} to 25 mg L^{-1}. In contrast, measurements show decreases of TOC along this stretch (Findlay *et al.* 1996, 1998; Fig. 4). Thus, it does not appear that net autotrophy and dilution of old organic C by new autochthonous C will explain the observed ^{14}C pattern.

Inputs of allochthonous material along the length of the river between km 240 and km 140 could also explain the ^{14}C dilution, analogously to the situation described for the Amazon (Richey *et al.* 1990). This could occur while the system maintained net heterotrophy. Detailed studies of C loads derived from tributaries and marshes of the Hudson suggest, however, that the vast majority of the C inputs are delivered at the confluence of the Mohawk and Upper Hudson, upstream from the present study area. (Findlay *et al.* 1998). Further, the dilution of old organic C with new allochthonous inputs (like autochthonous inputs) implies large TOC increases between Albany and Kingston, increases that we do not observe.

A third alternative is preferential sedimentation and burial of old organic C, while younger allochthonous material is transported and metabolized downstream. If true, this would suggest that sediments of the Hudson, even surface sediments, should be very old (*c.* 8000 years BP). Second, it would suggest that a large fraction of the organic C load is buried. In fact, combined burial in marshes and the main stem of the Hudson appears to be <10 g C m^{-2} $year^{-1}$ (Zelenke 1997), and the few ^{14}C measurements to date on Hudson sediments close to the area suggest ages of ~2000 years BP (Olsen *et al.* 1978). Thus, although sedimentation could play a role in controlling ^{14}C changes observed in the river, on the basis of present measurements it does not appear to explain most of the observed trends in ^{14}C in the study area.

The remaining alternative is that the downstream ^{14}C enrichment of POC and DOC is due, in part, to the utilization of old organic C and, in part, to dilution by new GPP. We investigated this possibility using inverse modelling (e.g. Vézina and Pace 1994) where the constraints on the minimal utilization of old organic C are as follows: the overall O_2 and CO_2 balance of the system; the change in organic C export between Albany and Kingston; the ^{14}C and ^{13}C content of organic C; and rate measurements made on primary production within the stretch. For this initial exercise, sedimentation is ignored. The above conditions constrain decomposition to a relatively narrow range and suggest that nearly 70% of the old organic C entering Albany must be respired by the time the water reaches Kingston. This reach is a 100-km length of river with a residence time of only 1 month during summer.

Thus, a situation emerges whereby at least 30% and possibly as much 70% of the old organic C that enters the Hudson River is respired within the river during transit times of ~30 days. Just how organic C could reside in the soil for centuries to millennia without decomposing and then decompose in a few weeks in the riverine environment is an intriguing question. There is no reason to suspect that the Hudson is unusual in either respect. The use of natural ^{14}C has not been widely applied in rivers or in fresh waters in general. Where it has, old C of terrestrial origin has been found to enter aquatic systems (Hedges *et al.* 1986*a*; Schiff *et al.* 1990) and possibly be metabolized there (Schell 1983). In some cases such as the Susquehanna and Rappanoak (Spiker and Rubin 1975), like the Hudson, the riverine organic C is centuries old; in others such as the Amazon (Hedges *et al.* 1986*b*) or the York (Raymond 1999), the organic C is only a few decades old. It is not clear what causes this variation in average age, and explanations differ (Raymond 1999).

Although we lack details for other major river systems, the available data suggest that a majority, like the Hudson, are strong sources of CO_2 to the atmosphere (Fig. 5). We do not have individual organic loads for each river in the data set, but a crude global budget suggests that nearly as much terrestrial organic matter is decomposed within rivers as is delivered from rivers to the sea (Caraco and Cole 1999). Whether the organic material in many rivers is very old is not yet clear. However, it is clear that some organic matter produced in the terrestrial environment escapes that environment without decomposing. Once it is in the receiving river, a substantial fraction decomposes relatively quickly.

The high rate of decomposition of terrestrial organic matter in the lower reaches of some rivers may help to explain, in part, a large question in the global C cycle, that terrigenous material leaves land but does not accumulate in the ocean (Hedges *et al*. 1997). Further, if we are correct, organic C that was sequestered in the terrestrial environment for considerable periods of time (1000–5000 years) is presently entering, and being decomposed in, the river itself. This linkage, over long times and large spatial scales, between terrestrial primary production and aquatic C cycling may connect the modern aquatic environment with the terrestrial conditions of another era.

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