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14. UDOM amino acid hydrolysis was conducted at 150°C for 70 min, generally with the method of Cowie and Hedges (*29*). Individual D– and L–amino acids were quantified as pentafluoropropyl isopropyl esters by gas chromatography with flame ionization detection (*41*), and peak identities were verified by GC-MS. Analytical variability in D/L ratios of UDOM samples was less than 15%. Racemization blanks were determined by multiple hydrolyses of pure L–amino acid mixtures, as well as protein standards. Enantiomeric ratios in commercially available D–amino acid–containing peptides could be repeatably determined to within 5%.
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The CO_2 Balance of Unproductive Aquatic Ecosystems

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Community respiration (*R*) rates are scaled as the two-thirds power of the gross primary production (*P*) rates of aquatic ecosystems, indicating that the role of aquatic biota as carbon dioxide sources or sinks depends on its productivity. Unproductive aquatic ecosystems support a disproportionately higher respiration rate than that of productive aquatic ecosystems, tend to be heterotrophic ($R > P$), and act as carbon dioxide sources. The average *P* required for aquatic ecosystems to become autotrophic ($P > R$) is over an order of magnitude greater for marshes than for the open sea. Although four-fifths of the upper ocean is expected to be net heterotrophic, this carbon demand can be balanced by the excess production over the remaining one-fifth of the ocean.

Aquatic ecosystems cover 70% of Earth's surface (*1*) and contribute 45% of the global primary production (*2*). Yet, the role of their biota in the global CO_2 budget remains a subject of debate (*3–5*). Many freshwater ecosystems act as CO_2 sources (*6*); in contrast, oceanic ecosystems are assumed to act as CO_2 sinks (*7, 8*). This assumption has been challenged by calculations suggesting that the coastal ocean may be net heterotrophic (*9*) and by the finding that bacterial metabolism exceeds phytoplankton production in unproductive waters (*10*), which make up >30% of the ocean. These conclusions are based on indirect calculations and controversial assumptions (*3*). Here, we compare the gross primary production (*P*) and respiration (*R*) rates of aquatic communities to elucidate whether the biota of aquatic ecosystems acts as net CO_2 sources ($R > P$) or sinks ($R < P$). We compiled data obtained over the past five decades from studies in which oxygen evolution was used as a surrogate for carbon fluxes (*11*).

Community metabolism varied by over four orders of magnitude across aquatic ecosystems (Table 1). Marshes tended to be more productive than other aquatic ecosystems, whereas open sea communities showed the lowest production and respiration rates (Table 1). The

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Table 1. Median and range of the gross primary production, community respiration, and production to respiration ratio (*P*/*R*); the percentage of the observations where communities were net heterotrophic ($R > P$); the parameters (*a*, *b*, and the coefficient of determination, R^2) of the power equation $R = a\,P^b$, describing the scaling between primary production (*P*) and respiration rate (*R*), both in grams of O_2 per cubic meter per day; and the gross primary production required to balance production and respiration (*P* at $P = R$) for the planktonic (Pl) and combined planktonic and benthic (Pl + B) communities of aquatic ecosystems. The slope *b* for marshes, uncorrected for net sulfate reduction, was recalculated to be 0.63 when this effect was accounted for (*14*).

System	Type	Gross production (g of O_2 m^{-3} day^{-1})	Respiration (g of O_2 m^{-3} day^{-1})	*P*/*R*	$R > P$ (%)	$R = a\,P^b$			*P* at $P = R$ (g of O_2 m^{-3} day^{-1})	*N*
						a	*b*	R^2		
Freshwater										
Lakes	Pl	1.38 (0.028–36.3)	0.82 (0.027–37.3)	1.14 (0.08–5.9)	38.3	1.0	0.65 ± 0.04	0.81	1.0	82
Rivers	Pl + B	3.94 (0.016–36.6)	3.36 (0.12–42.0)	1.08 (0.006–11.5)	35.0	1.1	0.85 ± 0.07	0.68	2.65	89
Marine										
Coastal	Pl + B	3.78 (0.0004–69.5)	3.03 (0.001–20.7)	1.17 (0.03–34.3)	34.6	1.1	0.72 ± 0.03	0.60	1.62	397
Marshes	Pl + B	6.9 (3.7–16.3)	2.7 (2.0–12.6)	0.98 (0.09–2.9)	50	3.2	0.49 ± 0.1	0.63	3.2	26
Open sea	Pl	0.14 (0.0008–12.7)	0.084 (0.0012–2.29)	1.71 (0.05–45.7)	26	0.2	0.50 ± 0.04	0.42	0.035	280
Overall	Pl + B	3.94 (0.0004–69.5)	3.0 (0.001–42.0)	1.25 (0.006–45.7)	34.4	1.0	0.78 ± 0.02	0.66	1.17	874

central tendency was for gross production and community respiration rates to be similar, leading to median *P*/*R* ratios close to or slightly greater than 1 (Table 1). Yet, the *P*/*R* ratio ranged by over three orders of magnitude across systems (Fig. 1); 34% of the communities [26 to 50%, depending on the systems (Table 1)] were heterotrophic ($R > P$). Communities with high respiration rates tended to be associated with ecosystems with high rates of gross primary production (Fig. 2 and Table 1). The slope of the power equation describing the overall relation was <1.0 [*t* test, probability (*p*) < 0.0001], but this slope was lowest for marshes and the open sea and was highest for rivers and coastal ecosystems (Table 1). Moreover, the community respiration supported for a given gross primary production was, on average, 2.5-fold higher [analysis of covariance (ANCOVA), *t* test, $p < 0.0001$] when the benthic compartment of shallow systems (rivers, marshes, and coastal ecosystems) was considered (*12*). The slope of the power relationship between *R* and *P* was consistently <1.0, implying that community respiration declined more slowly toward unproductive ecosystems than did gross primary production. Hence, the *P*/*R* ratio decreases as the gross primary production of the ecosystems decreases ($p < 0.0001$; Fig. 3). Community respiration rates tend, therefore, to exceed gross primary production in unproductive aquatic ecosystems, whereas highly productive ecosystems tend to be autotrophic (Fig. 3). The gross primary production required for aquatic ecosystems to become net autotrophic averaged 1.17 g of O_2 m^{-3} day^{-1} and was almost two orders of magnitude lower for open sea communities than for other aquatic ecosystems (*t* test, $p < 0.00001$; Table 1).

Our results confirm the generality of earlier reports that the relation between community respiration rate and gross production is not linear (*13*). Community respiration is scaled as the approximate two-thirds power of gross production, implying that unproductive aquatic ecosystems support a disproportionately higher respiration rate than do productive ecosystems. The imbalance between respiration and production rates in unproductive ecosystems was greater when the planktonic and benthic compartments were considered together, indicating that the benthic compartment of shallow systems is, in general, net heterotrophic. Although the conversion of these results, based on oxy-

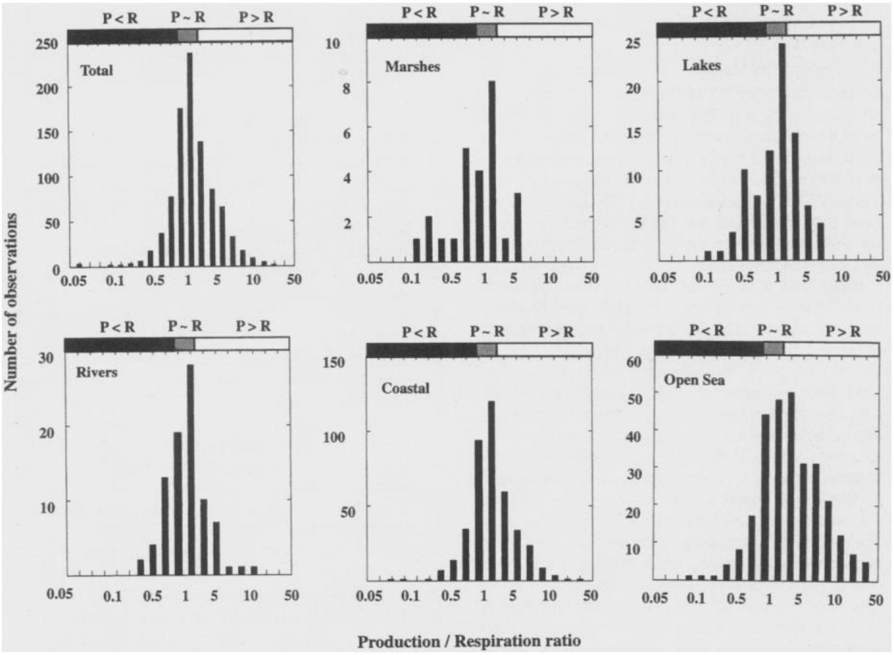

Fig. 1. Frequency distribution of the ratio of gross primary production to community respiration in aquatic ecosystems. Open and black bars encompass the range of *P*/*R* ratios of autotrophic ($P > R$) and heterotrophic ($P < R$) communities, respectively, and the gray bar encompasses the 95% confidence limits for *P*/*R* values with balanced production and respiration [that is, $P = R$; compare (*14*)].

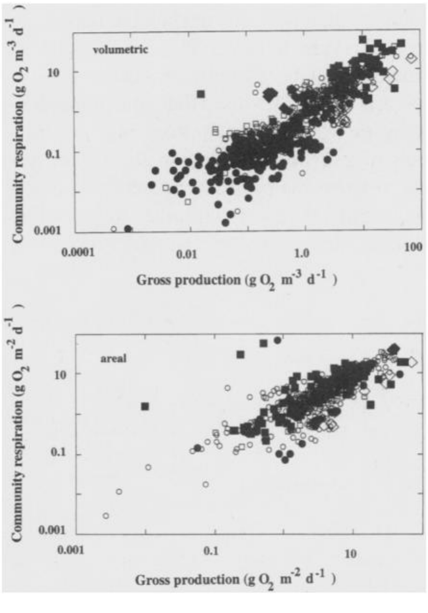

Fig. 2. The relation between volumetric and areal rates of community respiration rate and gross primary production in aquatic ecosystems (□, lakes; ■, rivers; ◇, marshes; ○, coastal systems; ●, open sea).

gen exchange, to carbon exchange involved some uncertainties, error analysis showed that the results were robust against them (*14*) and that the scaling between community respiration and gross production in marshes should be closer to the two-thirds power once net sulfate reduction is considered (*15*) (compare Table 1).

The observation that unproductive aquatic ecosystems tend to be heterotrophic implies that they must partially rely on allocthonous carbon subsidies. The primary production needed to drive aquatic ecosystems toward net autotrophic metabolism was highest for rivers and marshes (Table 1), which must, therefore, rely more heavily on imported organic carbon. Coastal ecosystems also receive substantial inputs of organic carbon from land (*9*) but require a somewhat lower gross primary production to become autotrophic. The gross primary production needed to render open sea ecosystems autotrophic (0.035 g of O_2 m^{-3} day^{-1}) is only about 2% of that required in coastal ecosystems.

Although it is obvious that freshwater and coastal ecosystems receive high inputs of allocthonous carbon (*9, 15*), the source of the allocthonous carbon subsidies supporting excess respiration in the open, oligotrophic sea is not clear (*16*). Lateral inputs to the ocean of organic carbon derived from land or coastal ecosystems are now believed to be important (*17*). In addition, organic carbon supplied vertically, upwelled to surface waters, or deposited from the atmosphere may also be important. For instance, the atmosphere receives a high loading of volatile organic carbon compounds of natural and anthropogenic sources (*15, 18*), which result in substantial wet and dry depositions of organic carbon (*19, 20*).

Our results show that the biota of unproductive ecosystems tends to be net CO_2 sources, whereas the biota of highly productive ecosystems acts as a CO_2 sink. High aquatic production is thought to derive from high external inputs of inorganic nutrients to aquatic ecosystems, whereas the primary production of oligotrophic ecosystems is controlled by recycling processes driven by heterotrophic organisms (*21*). Relatively small allocthonous carbon inputs should, therefore, suffice to drive the biota of oligotrophic aquatic ecosystems toward net heterotrophy, acting as CO_2 sources. We calculated (*22*) that the planktonic communities in 25 of 56 biogeochemical provinces in the ocean, which make up 80% of the ocean's surface, are expected to be heterotrophic (mean area-weighted $P/R = 0.74$). Yet, the average areal excess CO_2 incorporation by the autotrophic communities over the remaining one-fifth of the ocean was estimated to be fivefold greater, on average, than the small net CO_2 release by the heterotrophic communities of unproductive provinces, leading to an overall balance between production and consumption in the global upper ocean. Hence, although many aquatic ecosystems are likely to be heterotrophic, aquatic biota can act as CO_2 sinks at the global scale because the areal excess CO_2 incorporation by the productive autotrophic communities is greater than the small net areal CO_2 release by the heterotrophic communities occupying unproductive aquatic ecosystems.

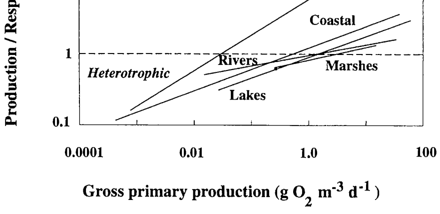

Fig. 3. Regression lines describing the relation between the ratio of gross primary production to respiration rate and the gross primary production of different aquatic ecosystems.

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11. We searched the literature for reports of community metabolism comprising estimates of community respiration and gross primary production in aquatic ecosystems. The resulting data set comprised 874 estimates, derived from 452 natural systems, including estimates of system metabolism for rivers (89), lake plankton (82), marshes (26), coastal ecosystems (397), and the biogenic zone of the open sea (280). Many of the reports for shallow-water ecosystems included both benthic and planktonic metabolism (77% for rivers, 54% for marshes, and 63% for coastal ecosystems), whereas those for lakes and the open sea referred to the planktonic compartments alone. The observational time scale of the individual estimates ranged from daily (690) to annual (70). Most (95.6%) of the estimates were derived from estimates of oxygen evolution and consumption, and the rest, based on examination of carbon incorporation and consumption rates, were converted to oxygen-based values with the assumption of a molar stoichiometry of 1.25 between O_2 and C. Ecosystem metabolism is reported here as daily rates per unit volume (that is, grams of O_2 per cubic meter per day). The estimates originally reported as integrated (that is, per square meter) values, which were, in most cases, derived from volumetric changes in oxygen (or carbon) concentration, were transformed to volumetric (that is, per cubic meter) estimates by dividing them by the integration depth. The data set is available by anonymous FTP at atlantis.ceab.csic.es/pub/duarte/metabolism.rtf.
12. ANCOVA was used to test the importance of considering the combined planktonic and benthic compartments for the scaling between community respiration and gross primary production in shallow systems. This analysis showed that the consideration of the benthic compartment affected the intercept a ($p < 0.0001$) but not the slope b ($p = 0.32$) of the allometric equation scaling community respiration to gross primary production (compare Table 1).
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14. Oxygen exchange rates are not direct estimates of carbon evolution and are converted to carbon exchange rates with the stoichiometric ratios between these elements in respiration and photosynthesis. The respiratory quotient (RQ) and photosynthetic quotient (PQ) range by about 10 to 20% around the mean value of 1.25 used here. This variation is small in comparison with the ranges of variation of P, R, and P/R in the data set and has, therefore, a negligible effect in our analysis. This effect was confirmed by sensitivity analysis, with the addition of a random 10 to 20% error to the PQs and RQs, which showed this source of error, involving a 3% uncertainty about the slopes and intercepts (Table 1), to be below the resolution of our analysis. However, this variation added uncertainty to the P/R values (95% confidence limits ± 16%), so that only ecosystems with P/R ratios <83% and >1.16% could be statistically considered to be heterotrophic and autotrophic, respectively. In addition, anoxic metabolism may result in an underestimation of respiration rates in shallow marine ecosystems, where sulfate reduction may be important (*15, 23*), by oxygen-evolution techniques (*23*). Because most of the sulfate reduced in shallow coastal sediments is reoxidized (*15, 23–25*), the underestimation of benthic remineralization by the use of oxygen-based methods has been estimated to be, at most, 25% in productive ecosystems (*23*). The covariation of the relative importance of net sulfate reduction with primary production (*23*) may result in an underestimation of the power slope between community respiration and aquatic gross production (Table 1). The importance of this underestimation was simulated by assuming that the underestimation of community respiration by net sulfate reduction ranged from 1 to 25% of the oxygen-based values from the least productive to the most productive shallow marine systems. The slope obtained was within the error of our estimate for coastal ecosystems (0.737 compared with our estimate of 0.72 ± 0.03) but increased substantially for marshes (0.63 compared with 0.49 ± 0.1), thereby approaching the two-thirds scaling between community respiration and aquatic gross production once net sulfate reduction is considered (Table 1).
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