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ORIGINAL ARTICLE

Daily and seasonal variability of CO_2 saturation and evasion in a free flowing and in a dammed river reach

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ABSTRACT

The daily and seasonal evolution of O_2 and CO_2 saturation, water-atmosphere fluxes and budgets were measured in two fluvial reaches of the Mincio River (Italy). The northern reach is free flowing and is dominated by macrophytes while the southern reach is dammed, hypertrophic and phytoplankton dominated. We hypothesized short term regulation of gas saturation and fluxes by primary producers and the reversal of CO_2 off-gassing in the southern reach. Results indicated that both reaches were always CO_2 supersaturated. Higher CO_2 evasion rates in the northern compared to the southern reach depended on reaeration coefficient, in turn depending on water velocity. In the northern reach dissolved inorganic carbon (DIC) production was one order of magnitude higher than oxygen consumption, likely due to a combination of anoxic heterotrophic activity in the hyporheic zone and carbonate dissolution. The activity of macrophytes influenced CO_2 saturation on short time scales. A net summer abatement of DIC occurred in the southern reach, probably due to fixation by phytoplankton, which attenuated supersaturation but not reversed CO_2 efflux. This study demonstrates how in small rivers CO_2 evasion can undergo rapid and significant changes due to eutrophication, altered hydrology and shift in primary producer communities.

Key words: Carbon dioxide, fluxes, river metabolism, mass balances, macrophytes, phytoplankton.

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INTRODUCTION

Greenhouse gas (GHG) emissions from natural and human impacted inland waters are probably much larger than previously expected (Wang *et al.*, 2007; Battin *et al.*, 2008, 2009; Butman and Raymond, 2011; Rasera *et al.*, 2013). Their quantification is recognized as a priority as recent estimates (from 0.8 to 3.3 Pg C y^{-1}) are largely ignored by current models of carbon cycle (Cole *et al.*, 2007; Solomon *et al.*, 2007; Battin *et al.*, 2008, 2009; Tranvik *et al.*, 2009; Aufdenkampe *et al.*, 2011; Butman and Raymond, 2011). In particular, the regulation and the amount of C fluxes from headwater regions, drainage networks and small rivers are largely understudied, leading to strong potential bias of global C budgets (Bensted and Leigh, 2012). Most inland waters, and in particular large turbid rivers, are net heterotrophic and sources of CO_2 to the atmosphere (Raymond *et al.*, 1997; Frankignoulle *et al.*, 1998; Duarte and Prairie, 2005; Guerin *et al.*, 2007; Battin *et al.*, 2008; Butman and Raymond, 2011; Rasera *et al.*, 2013). Excess respiration of organic carbon from terrestrial inputs maintains elevated CO_2 supersaturation values, with moderate seasonal variations and very limited control by primary producers (Duarte and Prairie, 2005; Butman and Raymond, 2011). Intermediate and large rivers display limited spatial and temporal variations of CO_2 saturation values when compared to streams and small rivers likely due to higher buffer capacity, different hydrology and more constant organic input from watersheds (Dawson *et al.,* 2001; Waldron *et al.*, 2007, Teodoru *et al.*, 2009).

The saturation degree and the direction of CO_2 fluxes across the water-atmosphere interface could be altered in rivers impacted by human activities due to limited river-watershed connectivity, modified river hydrology and river eutrophication (Wang *et al.*, 2007). In those geographical areas where artificial barriers as levees impair river-watershed connectivity, minor import of allochtonous organic matter into the aquatic environment is expected, together with a major role of within river autotrophic and heterotrophic processes as regulators of CO_2 dynamics (Sobek *et al.*, 2005; Gu *et al.*, 2011). All over industrialised countries (Bergstrom *et al.*, 2004; Poff *et al.*, 2011) and more recently in tropical areas (Fearnside, 2002; Guérin *et al.*, 2006; Hamilton, 2010; Roland *et al.*, 2010; Kemenes *et al.*, 2011) and developing countries (Wang *et al.*, 2007, 2011), an increasing number of rivers are dammed with a relatively longer water retention time compared to pristine natural environments. Heavy alteration of natural hydrology, along with nutrient enrichment, can affect aquatic vegetation in terms of community composition and activity, with implications for the whole river metabolism (Nilsson and Swedmark, 2002; Dodds, 2006). The absence of lateral interactions, hydromorpho-

logical discontinuities and primary producers community shifts can ultimately modulate CO_2 concentrations, determining fluxes variable in terms of direction and entity at different temporal and spatial scales.

We hypothesize short term (hourly) rather than long term (seasonal) variability of CO_2 saturation and fluxes and strong regulation of river metabolism in upstream reaches colonized by meadows of submerged vegetation. We hypothesize also net autotrophy, undersaturation and the reversal of CO_2 fluxes (influx of CO_2 from the atmosphere into the water) in lowland eutrophic reaches dominated by phytoplankton. To test these hypotheses we studied oxygen and inorganic carbon concentrations and their daily and seasonal budgets in two reaches of a small, regulated river (Mincio River, Northern Italy). The northern reach is shallow, free flowing and dominated by benthic phanerogams and biofilms while the southern one is leeved, dammed, phytoplankton dominated and hypertrophic.

The aims of this study were i) to analyse changes of CO_2 concentrations and fluxes at different spatial scales, from hours to seasons; and ii) to identify factors that control inorganic carbon fluxes and downstream transport, with emphasis on ecosystem metabolism. This study adds valuable information to the large body of literature dealing with oxygen and carbon budgets in aquatic environments for two main reasons. The first deals with the dimension of the analyzed system (intermediate, with a catchment area of 780 km^2), which is representative of the larger fraction of inland lotic ecosystems, contributes for this reason with a relevant fraction of GHG and is at present understudied (Bensted and Leigh, 2012; Battin *et al.*, 2008, 2009). The second aspect is more specific: as in the Mincio River the dam construction dates back to the XII century the southern reach allows to analyze the long-term effects of river damming, a practice which is intensifying worldwide, on gas budgets.

METHODS

Study site

We compared two reaches of the Mincio River (Northern Italy, Fig. 1) which extends over a 780 km^2 basin. The Mincio River is the emissary of Lake Garda and flows into the Po River after a 75 km course. The Mincio watershed is characterized by Cambisols and Calcisols (EU Commision, Soil Atlas of Europe, 2012). In particular, the high-medium plain is mainly characterized by calcareous gravel deposits, while the low plain presents calcareous silty-clay sediments. The hydraulic scheme and the hydrologic regime of the Mincio River reflect the result of ancient and recent engineering infrastructures. The Vasarone dam was realized in 1190 A.D. to create different water levels between adjacent river segments, feed a number of mills and protect the city of Mantua by invasions. Along the centuries this and other downstream dams determined the formation of fluvial lakes (the Mantua Lakes, Fig. 1). At present the lakes are hypertrophic and export downstream large amounts of phytoplankton (Pinardi *et al.*, 2011). In the last century a series of artificial diversions and canals were constructed along the Mincio River for irrigation and industrial purposes and, in the case of floods or high water levels, to bypass the natural river course and discharge directly in the Adriatic Sea (Fig. 1). This explains the very limited seasonal variations of flows and water velocity in the natural rivercourse. The two reaches identified for the present study do not have significant tributaries or withdrawals along their path. The northern reach (N), from Pozzolo to Goito (length 8.1 km, average depth ≤1 m, average stream velocity ~1.0 m s^{-1}), is characterized by natural banks, meanders, gravel bottom, occurrence of vegetated islands, low turbidity. Primary producers are represented by submerged macrophytes (*e.g. Vallisneria spiralis*; Pinardi *et al.*, 2009), epiphytes and benthic biofilms of algae. The southern reach (S), from Formigosa to Governolo (length 8.3 km, average depth ~4.5 m, average stream velocity ≤0.1 m s^{-1}), is channelized, has organic slimy-sandy sediments and turbid stratified waters. Primary production is entirely sustained by phytoplankton, as very limited light penetration (<3 m in winter and <1 m in summer) does not allow for benthic photosynthesis. We sampled four stations, located at the extremes of the two reaches (N1-Pozzolo, N2-Goito, S1-Formigosa and S2-Governolo) (Fig. 1).

Water sampling and analyses

Field activities were based on repeated samplings over 24 h and were carried out seasonally (6-7 August and 6-7 November 2006, 6-7 February, 16-17 April and 11-12 June 2007). On each campaign a total of 56 samples (4 stations x 7 periods within the 24 h from the surface and integrated over the water column) were collected and analyzed. A water sample was collected just below the water-atmosphere interface by means of a 100 mL glass syringe to analyze dissolved gas saturation and water-atmosphere gradients. Another water sample was collected by means of hollow PVC poles (i.d. 3 cm, length 1-5 m) integrating the whole water column and then transferred into 1 L glass bottles. Temperature, dissolved oxygen, pH and irradiance at the water interface were measured on site with an YSI multiple probe (mod. 556 MPS), a Radiometer mV meter (ABU91, DK) connected to a combined electrode (Radiometer, GK2401C) and a Delta OHM spectroquantophotometer (mod. HD 9021). Water flow data were obtained by AIPO (Interregional Agency for the Po River) and Mincio Consortium, water velocity was measured with a current meter (Scubla mod. 2030). Once collected, water samples from both the surface and the whole water column were transferred into two 12 mL exetainers (Labco, UK) flushing at least 3 times the vial

volume. Winkler reagents for iodometric oxygen titration were then added to an exetainer (APHA, 1981) while 100 µL of $HgCl_2$ were added to the second, later analysed for total dissolved inorganic carbon ($DIC=\Sigma H_2CO_3+CO_2+HCO_3^-+CO_3^{2-}$) determination with Gran titration (0.1 N HCl) within 24 h from sampling. The analytical precision of both oxygen and inorganic carbon titration was ±1%. The concentration and saturation level of dissolved CO_2 in the upper water layer was calculated by CO_2-System from pH and DIC measurements, with appropriate corrections for temperature (Stumm and Morgan, 1981; Lewis and Wallace, 1998). Other aliquots of the integrated water column sample were filtered (GF/F glass fiber filters) and transferred to plastic and glass vials for inorganic nitrogen ($N\_NO_3^-$), ammonium ($N\_NH_4^+$) and soluble reactive phosphorus (SRP) determination (Valderrama, 1977; Rodier, 1978; APHA, 1981). One filter for each water sample was frozen for later spectrophotometric determination of Chlorophyll *a* (Chl-*a*) according to Lorenzen (1967).

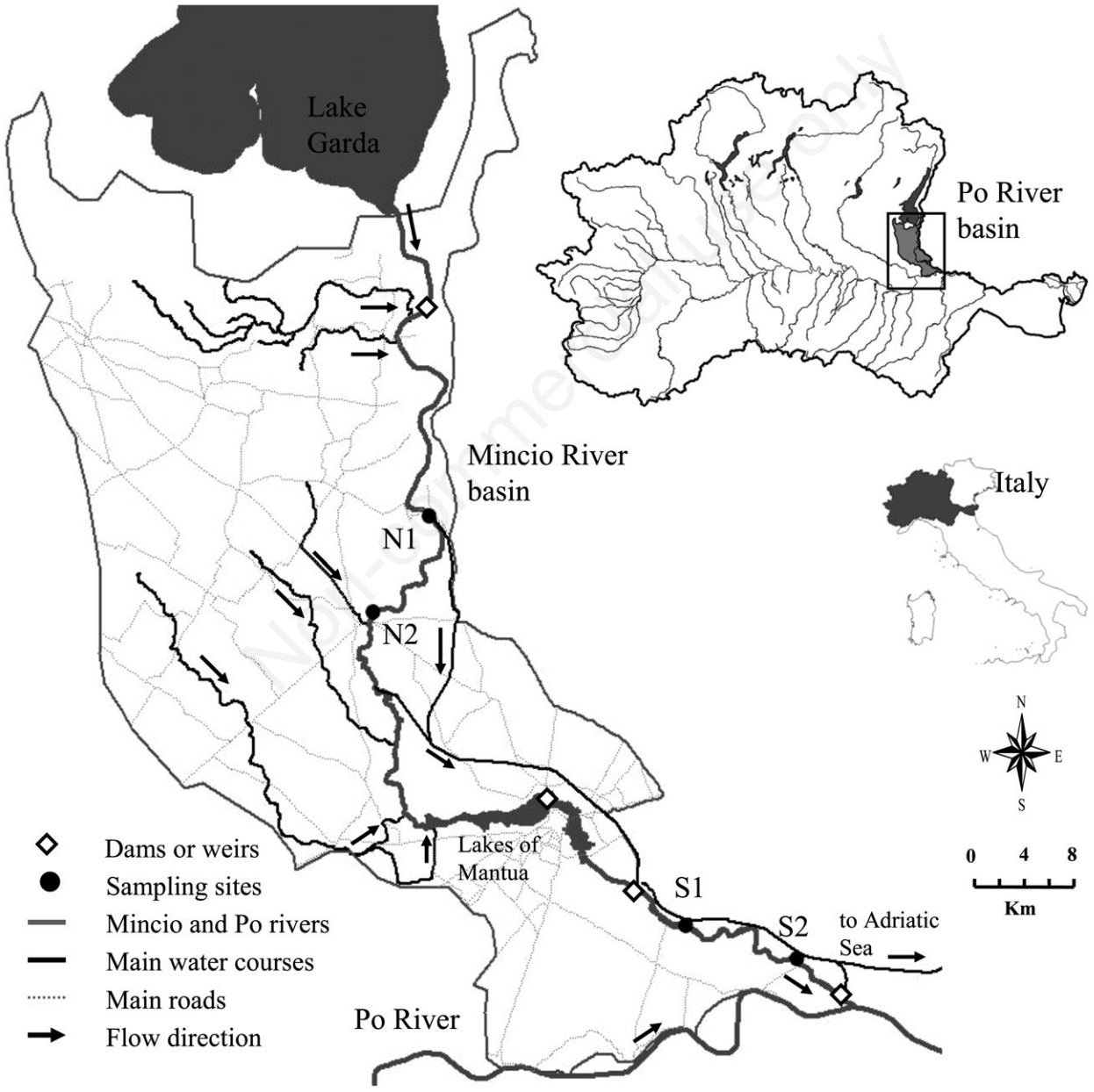

Fig. 1. Location of the two investigated fluvial reaches of the Mincio River (Northern Italy): N1-Pozzolo (46 m asl), N2-Goito (30 m asl), S1 Formigosa (22 m asl), S2-Governolo (20 m asl).

O_2 and CO_2 fluxes across the water-atmosphere interface

The atmospheric flux (*AF*) of O_2 and CO_2 (mmol m^{-2} d^{-1}) was calculated as:

$$AF = \sum [k \times (C_t - C_S) \times \Delta t] \quad \text{(eq. 1)}$$

where k is the gas transfer coefficient (m h^{-1}), C_t is the gas concentration in the water at time t (mmol m^{-3}) and C_S is the gas concentration at equilibrium (mmol m^{-3}), calculated from the gas partial pressure in the atmosphere and the Henry constant k_H corrected for temperature and salinity (Weiss, 1974), and Δt is the time interval between samplings (h).

In order to calculate the gas transfer coefficient for the two fluvial reaches we used two different approaches. At high water velocities and in shallow systems, in fact, benthic turbulence is generally considered the primary driver of gas exchange (Baulch *et al.*, 2010). At low water velocities and in deep water systems (in particular, where the ratio of stream velocity to stream depth is less than 0.03 s^{-1}, Schwarzenbach *et al.*, 1993), instead, benthic turbulence can be considered negligible and wind-based turbulence dominates gas exchange processes (Raymond and Cole, 2001; Baulch *et al.*, 2010). Accordingly, for stations N1 and N2, characterised by moderate to high current velocity and shallow waters, we calculated the reaeration coefficient for oxygen at 20°C, $K_{O2,20°C}$ (h^{-1}) from current velocities u (m s^{-1}) and water depths d (m) using the following equation (Genereux and Hemond, 1992):

$$K_{O_2,20^\circ C} = a \cdot \frac{u^b}{d^c} \quad \text{(eq. 2)}$$

In the present study, we used the parameterizations (*i.e.* values of *a*, *b* and *c*) proposed by O'Connor and Dobbins (1958), Churchill *et al.* (1962), Owens *et al.* (1964), Langbein and Durum (1967), Isaacs and Gaudy (1968) and Bennett and Rathbun (1972), which provided the following values for $K_{O2,20°C}$: 0.21±0.03 h^{-1} for N1 and 0.27±0.04 h^{-1} for N2 (mean±standard deviation obtained from the application of the above equations). By multiplying these reaeration coefficients by water depth (Hornberger and Kelly, 1975; Devol *et al.*, 1987; Jahne and Haussecker, 1998; Mulholland *et al.*, 2001), the following transfer coefficients for oxygen $k_{O2,20°C}$ were obtained: 0.21±0.03 m h^{-1} for N1 and 0.23±0.03 m h^{-1} for N2. The equations of Genereux and Hemond (1992) cannot be applied in the southern reach due to low current velocities. Empirical relationships from several authors (Cole and Caraco, 1998; Crusius and Wanninkhof, 2003; Guerin *et al.*, 2007) show that $k_{CO2,20°C}$ falls in the range 0-0.023 m h^{-1} for stagnant water subjected to low wind speed (0-1 m s^{-1}, as in the Po valley). Thus, we considered reasonable to assume a k value of 0.017±0.002 m h^{-1} (average±standard deviation obtained from the above mentioned empirical equations), corresponding to a boundary layer of ~350 μm for the southern reach (sites S1 and S2).

For both reaches, in order to calculate the value of $k_{CO2,20°C}$ from $k_{O2,20°C}$ (m h^{-1}) or *viceversa*, we used the following equation (Jähne *et al.*, 1987):

$$\frac{k_{CO_2}}{k_{O_2}} = \left(\frac{Sc_{CO_2}}{Sc_{O_2}}\right)^n \quad \text{(eq. 3)}$$

where k_{CO2} and k_{O2} are gas coefficients, Sc_{CO2} and Sc_{O2} are the Schmidt numbers for carbon dioxide and oxygen, respectively, and the exponent n was assumed to be equal to -2/3, a common assumption for wind speed <3.7 m s^{-1} (Liss and Merlivat, 1986; Jähne *et al.*, 1987). Tab. 1 reports the calculated gas transfer coefficients for the two reaches.

We then used the relationship from Elmore and West (1961) to correct the k values for temperature:

$$k_T = k_{20^\circ C} \times 1.0241^{(T-20^\circ C)} \quad \text{(eq. 4)}$$

Inorganic carbon and oxygen mass balances

To calculate the net daily oxygen and inorganic carbon mass balances (*MB*) (mmol d^{-1}) in the two reaches, we used the following equation:

$$MB_t = \sum [C_t \times \Delta t \times Q]_D - \sum [C_t \times \Delta t \times Q]_U + \sum [WS \times k \times (\overline{C}_t - C_S) \times \Delta t] \quad \text{(eq. 5)}$$

where: C_t, downstream (D), upstream (U) or daily average ($\overline{C}$) concentration of O_2 or DIC at time t (mmol m^{-3}); Δt, time interval between samplings (h); Q, water flow (m^3 h^{-1}); *WS*, water surface (m^2) of each reach, measured by GIS ArcView 3.2; k, gas transfer coefficient of O_2 or CO_2 (m h^{-1}).

Calculation of production and respiration rates from O_2 data

All the processes affecting dissolved oxygen concentrations in a lotic system are expressed quantitatively by the following equation:

Tab. 1. Calculated gas transfer coefficients at 20°C (± standard deviation) for dissolved carbon dioxide and oxygen. See the text for more details.

Sampling station	k_{CO2} (m h^{-1})	k_{O2} (m h^{-1})
N1	0.17±0.02	0.21±0.03
N2	0.19±0.03	0.23±0.03
S1, S2	0.017±0.002	0.020±0.002

$$GPP(dt) = \frac{C_t - C_0}{\Delta t} - K(C_s - C_t) + ER + A \quad \text{(eq. 6)}$$

where *GPP* is the Gross Primary Production (mmol O_2 m^{-3} d^{-1}), $(C_t - C_0)/\Delta t$ is the rate of variation of oxygen concentration, *K* is the reaeration coefficient (d^{-1}), C_s is the concentration of oxygen at saturation, C_t is the concentration of oxygen at time *t*, *ER* is the Ecosystem Respiration and *A* is the gas exchange associated to the accrual, that is the groundwater infiltration. The eq. 6 could be solved by two methods: *single station* (Eulerian solution) or *two stations* (Lagrangian solution). If the curves of diel variation of two stations a few kilometers away are the same, this means that the longitudinal gradient of oxygen concentration is negligible compared to the temporal gradient. Therefore it is possible to apply an Eulerian approach, where a measure at one station could be used to predict the future concentration in the same point (Hornberger and Kelly, 1975).

In order to estimate river metabolism we used the open-channel method firstly introduced by Odum (1956). We applied this approach only to the northern stations N1 and N2 because in the southern reach the water column is deep and stratified, and no water stratification is an assumption of the method. We also assumed that groundwater inflow is negligible and therefore the term *A* is equal to 0. In particular we used the single station method, so that the mass balance equation for oxygen can be solved using an Euler approximation. Areal fluxes were obtained by multiplying all terms of equation (6) by the water depth (Hall and Tank, 2005):

$$NEP = GPP - ER = z\left(\frac{Ct - C_0}{\Delta t} - K(C_s - C_t)\right) \quad \text{(eq. 7)}$$

where *NEP* is Net Ecosystem Production (mmol O_2 m^{-2} d^{-1}) and *z* is the water depth (m).

Repeated samplings during night hours, when NEP is zero, allowed to calculate mean and standard deviations of ER while repeated samplings during the light hours allowed to calculate NEP (mean±standard deviation); gross ecosystem primary production was then calculated combining NEP and ER.

Calculation of errors and statistical analyses

We associated standard deviation to measurements made in replicates. The error associated to the values obtained from mathematical elaboration was calculated with the error propagation equation:

$$\varepsilon_{f(x1,x2,\ldots xn)} = \sqrt{\sum\left(\frac{\partial f}{\partial x}\varepsilon_x\right)^2} \quad \text{(eq. 8)}$$

where *f* is function of x_1, x_2, … x_n variables; if errors associated to x_n variables are known, it is possible to calculate the error associated to the function *f*. Specifically, errors associated to the estimated O_2 and CO_2 fluxes (eq. 1) and to O_2 and DIC mass balances (eq. 5) were computed assuming as source of error the standard deviation of gas transfer coefficients *k* and the analytical error of the gas concentration in the water. All relationships between physico-chemical variables were tested with the Pearson correlation test. A *t*-test was used to determine if two sets of data (*i.e.,* north-south or within reach gas saturation values) were significantly different from each other. The Analysis of Variance (ANOVA) was performed to test whether the factors site, season and hour of the day affect gas saturation values and CO_2 fluxes (three way ANOVA with interaction). A logarithmic transformation was applied to data before ANOVA analysis. The tests were accepted as significant at $P<0.05$. The R version 2.13.0 software package (R Development Core Team, 2011) was used to perform all statistical tests.

RESULTS

Chemical and physical features at sampling stations

Water velocity and flow averaged 1.0±0.3 m s^{-1} and 10±2 m^3 s^{-1} in the upstream reach and 0.1±0.1 m s^{-1} and 17±4 m^3 s^{-1} downstream (average ±standard deviation of the whole dataset 2006-2007, n=140). The water discharge measured during the experimental activities fell within the (limited) annual range of flow variation at the two reaches. Water temperature was not significantly different upstream and downstream (*t*-test, $P>0.05$, n=136), and averaged 21.7±2.7°C in summer and 10.6±2.6°C in winter (whole dataset). Within sampling periods daily differences between maximum and minimum water temperatures peaked in August 2006 (6.1°C, S1, Fig. 2). Water pH was alkaline, varied between 7.77 and 8.86 (whole dataset) and was not significantly different at the two reaches (*t*-test, $P>0.05$, n=136).The concentrations of Ca^{2+} and Mg^{+} were significantly higher at N2 (44.1±6.9 mg Ca^{2+} L^{-1} and 11.0±1.3 mg Mg^{+} L^{-1}) than at N1 (34.8±3.5 mg Ca^{2+} L^{-1} and 9.5±1.0 mg Mg^{+} L^{-1}) (for both: *t*-test, $P<0.0001$, n=39) (ARPA Lombardy database, 1994-1999; http://ita.arpalombardia.it/ita/servizi/servizi2.asp). However, in the southern reach the concentrations of the two ions were similar at S1 and S2 (nearly 51 mg Ca^{2+} L^{-1} and 13 mg Mg^{+} L^{-1}).

Daily average inorganic phosphorus (SRP), nitrogen ($N\_NH_4^+$ and $N\_NO_3^-$) and chlorophyll *a* (Chl-*a*) concentrations are reported in Tab. 2. Hourly evolution of these parameters within each sampling day was erratic and not significantly correlated with irradiance at both upstream and downstream sites (Pearson correlation, $P>0.05$, n=136). However, nitrate (in February 2007) and ammonium (in April and June 2007) were higher at the downstream reach (Tab. 2). SRP concentration peaked in the northern reach (3.60±1.24 µM) in June 2007 and it was 9 fold higher than the concentration in the southern reach

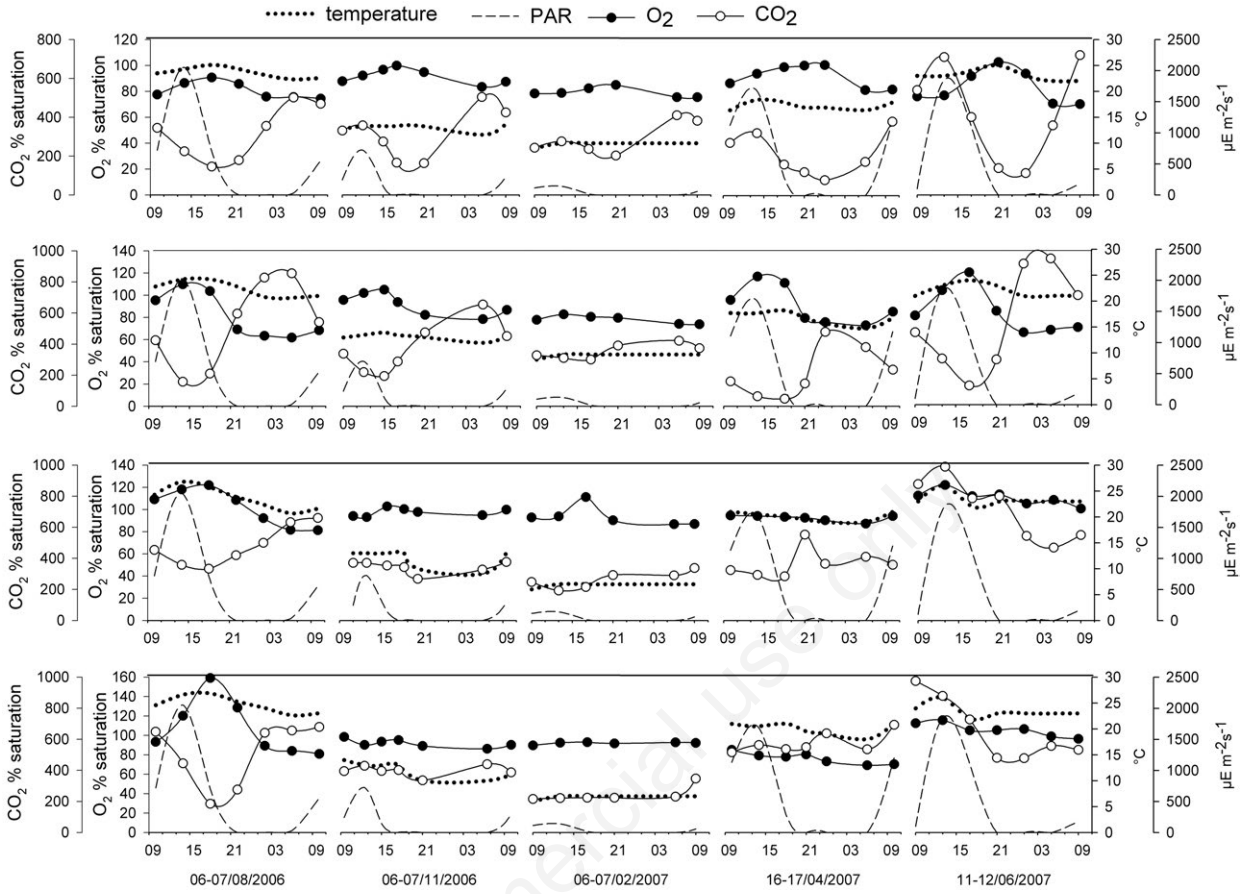

Fig. 2. Daily evolution of dissolved oxygen and carbon dioxide saturation during the 5 sampling periods (from August 2006 to June 2007); water temperature and irradiance (PAR) are also reported.

Tab. 2. Daily average concentration (±standard deviation, n=7) of soluble reactive phosphorous (SRP), ammonia ($N\_NH_4^+$), nitrate ($N\_NO_3^-$) and chlorophyll *a* (Chl-*a*) in the northern and southern reaches of the Mincio River in all sampling dates.

	Date	Northern reach		Southern reach	
		Average	SD	Average	SD
SRP (µM)	06/08/2006	1.46	0.23	1.09	0.46
	06/11/2006	0.70	0.32	0.85	0.49
	06/02/2007	0.70	0.20	1.80	0.20
	16/04/2007	1.07	0.31	1.00	0.23
	11/06/2007	3.60	1.24	0.40	0.25
$N\_NH_4^+$ (µM)	06/08/2006	5.33	3.82	3.93	2.48
	06/11/2006	0.94	0.47	2.18	1.02
	06/02/2007	3.26	1.81	2.19	3.07
	16/04/2007	1.78	1.54	11.17	2.89
	11/06/2007	2.27	0.95	6.37	2.27
$N\_NO_3^-$ (µM)	06/08/2006	82.74	45.61	81.83	19.42
	06/11/2006	72.27	35.19	84.67	12.88
	06/02/2007	76.99	23.21	112.13	20.67
	16/04/2007	45.74	17.81	42.85	8.73
	11/06/2007	163.41	58.50	156.84	42.59
Chl-*a* (µg L^{-1})	06/08/2006	1.61	0.87	32.63	21.58
	06/11/2006	0.67	0.67	13.05	12.72
	06/02/2007	5.27	6.52	30.96	39.84
	16/04/2007	1.65	1.17	52.56	33.69
	11/06/2007	1.16	0.21	101.33	54.76

SD, standard deviation.

(Tab. 2). Conversely, Chl-*a* concentrations were significantly different at the two river reaches (*t*-test, P<0.001, n=136). In the southern reach we measured Chl-*a* concentrations one or two orders of magnitude higher than in the northern one (Tab. 2), and were typical of a hypertrophic system (>100 μg L^{-1}).

Daily and seasonal gas saturation and calculated CO_2 fluxes

Dissolved oxygen saturation values displayed small variations across seasons and sampling sites, in particular when compared to CO_2 saturation (Fig. 2). They were significantly different between sites and seasons, but such differences depended on the factor *hour*, which is the sampling moment within the day (Tab. 3). Average values calculated for the two reaches (whole dataset) were slightly below the equilibrium value and tended to increase from the northern (86±13%) to the southern reach (97±15%). This suggests net heterotrophy of the two reaches, decreasing downstream and approaching an equilibrium between oxygen consuming and oxygen producing processes. Looking data at a finer scale it is to remark that in the southern reach dissolved O_2 was supersaturated at S2 in the light hours of summer 2006 and 2007.

Carbon dioxide was generally above saturation and extremely variable on a diel basis; variations within the 24 hours period peaked in summer (from nearly 200% to 1000%, station N2, Fig. 2). CO_2 excess was assumed to be a result of the net heterotrophy of the two reaches, already evidenced by oxygen data. Saturation values were significantly higher downstream compared to upstream (*t*-test, P<0.01, n=136) and at the extremes of the two reaches they averaged 314±160% and 483±190% at N1 and S2, respectively. Within each reach, CO_2 saturations were significantly different between sites, but such differences depended on the factors *date* and *hour* (Tab. 3). The upstream and downstream reaches were always CO_2 sources to the atmosphere. In August 2006 and June 2007 the northern reach was characterized by large hourly variations in CO_2 release, from 3 up to 16 mmol CO_2 m^{-2} h^{-1}, reflecting large variations in saturation values (Fig. 2). In the southern reach, CO_2 fluxes were nearly one order of magnitude lower compared to those at the northern reach (between 0.3 and 1.5 mmol CO_2 m^{-2} h^{-1}). Despite higher

Tab. 3. Results and significance of the three-way ANOVA performed on O_2 and CO_2 saturation values and CO_2 fluxes; we tested the effects of the factors *sampling site*, *date* and *hour* and their interactions.

	Df	Sum Sq.	O_2 Mean Sq.	F value	Pr(>F)
Site	3	0.5964	0.1988	17.59	3.53E-09 ***
Date	4	0.1883	0.0471	4.17	3.73E-03 **
Hour	1	0.4985	0.4985	44.11	1.86E-09 ***
Site × date	12	0.7249	0.0604	5.35	7.46E-07 ***
Site × hour	3	0.1460	0.0487	4.31	6.79E-03 **
Date × hour	4	0.1632	0.0408	3.61	8.73E-03 **
Site × date × hour	12	0.0596	0.0050	0.44	9.43E-01
Residuals	96	1.0849	0.0113		
	Df	Sum Sq.	CO_2 Mean Sq.	F value	Pr(>F)
Site	3	4.7666	1.5889	9.06	2.42E-05 ***
Date	4	7.0481	1.7620	10.05	7.73E-07 ***
Hour	1	1.5934	1.5934	9.09	3.29E-03 **
Site × date	12	6.5098	0.5425	3.09	9.79E-04 ***
Site × hour	3	2.5639	0.8547	4.88	3.37E-03 **
Date × hour	4	1.3381	0.3345	1.91	1.15E-01
Site × date × hour	12	1.2953	0.1079	0.62	8.24E-01
Residuals	96	16.8277	0.1753		
	Df	Sum Sq.	Flux CO_2 Mean Sq.	F value	Pr(>F)
Site	3	116.2650	38.7550	80.37	<2.20E-16***
Date	4	7.2590	1.8150	3.76	6.98E-03 **
Hour	1	2.6050	2.6050	5.40	2.23E-02 *
Site × date	12	9.8550	0.8210	1.70	7.84E-02 .
Site × hour	3	3.9450	1.3150	2.73	4.85E-02 *
Date × hour	4	2.6140	0.6530	1.36	2.56E-01
Site × date × hour	12	2.1500	0.1790	0.37	9.70E-01
Residuals	93	44.8450	0.4820		

saturation rates, the calculated CO_2 effluxes were attenuated and significantly lower in the southern compared to the northern reach (*t*-test, P<0.001, n=20). Daily rates of CO_2 evasion (mmol m^{-2} d^{-1}) at each station and sampling period are reported in Figure 3. A positively correlation was found between daily CO_2 emissions and water temperature, but only for the downstream reach (r=0.75, P<0.05 for S1; r=0.85, P<0.05 for S2).

River metabolism, inorganic carbon and oxygen mass balances

Repeated O_2 measurements in the light and in the dark at stations N1 and N2 allowed to estimate at both sites gross primary production (GPP) and ecosystem respiration (ER) (Fig. 4). GPP ranged between 35.8±6.0 mmol O_2 m^{-2} d^{-1} at N1 in February and 388.9±12.9 mmol O_2 m^{-2} d^{-1} at N2 in June 2007 (Fig. 4). GPP was positively related with a logarithmic function to daily irradiance (y=48.5 ln(x) – 1.07, R^2=0.62, P<0.05 for N1; y=104.4 ln(x) – 63.4, R^2=0.88, P<0.05 for N2). Daily ER was significantly higher than daily GPP (*t*-test, P<0.001, n=10) during all sampling periods resulting in negative net primary production and confirming the results of O_2 (and CO_2) saturation data, suggesting net heterotrophy of this river reach. The photosynthetic activity by the macrophyte meadows, despite elevated, did not counterbalance the whole ecosystem respiration. At N1 and N2 ER values were minimum in November 2006 (287.9±39.4 and 397.8±57.6 mmol O_2 m^{-2} d^{-1}, respectively) while maximum rates were calculated in the summer (500.5±39.6 mmol O_2 m^{-2} d^{-1}, June 2007, N1 and 739.9±42.5 mmol O_2 m^{-2} d^{-1}, August 2006, N2) (Fig. 4). Net ecosystem production (NEP) ranged from -230.7±76.8 mmol O_2 m^{-2} d^{-1} (N1) to -290.1±84.1 mmol O_2 m^{-2} d^{-1} (N2).

The mass balance (MB) of O_2 showed that the northern reach was a net sink of O_2 in all seasons, in particular in the winter, when the highest consumption was measured. Oxygen undersaturation always resulted in oxygen uptake from the atmosphere. Negative oxygen balances were calculated also in the southern reach during all sampling periods, with August 2006 as only exception; in that sampling date the reach was net oxygen producing. In the summer of the two sampling years the surface water of the southern reach were supersaturated and net released oxygen to the atmosphere (Tab. 4). The MB of dissolved inorganic carbon in the upstream reach was always largely positive and showed a seasonal trend with highest inorganic carbon accumulation measured in the summer (Tab. 4). Interestingly, and in agreement with oxygen results, in the southern reach DIC mass balance was negative in the summer of the two sampling years while in all the other samplings the balance was positive (Tab. 4). The summer net consumption of inorganic carbon from S1 to S2 was coupled to a decrease of the CO_2 saturation level but not below 100%, meaning that the flux of this gas remained directed from the water to the atmosphere.

Our calculations suggest that on average the amount of CO_2 evaded to the atmosphere differed by a factor ~6 between reaches; in the upstream segment it represented nearly 2% of the incoming DIC load while downstream the percentage was much lower (0.1%) (Tab. 4).

DISCUSSION

Daily and seasonal gas saturation and calculated CO_2 fluxes

Average CO_2 saturation values in the Mincio River were within ranges reported in the literature for large and small lotic environments and for world estuaries, which

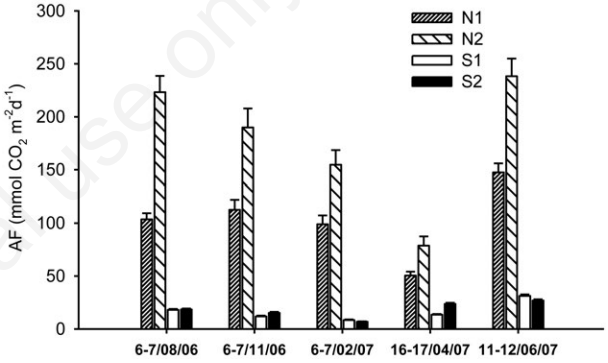

Fig. 3. Atmospheric fluxes (AF) of carbon dioxide across the water-atmosphere interface calculated for the 5 sampling periods at the 4 studied sites (mmol CO_2 m^{-2} d^{-1}). Daily values±standard deviations are reported; please refer to the material and methods section for the calculation of uncertainties.

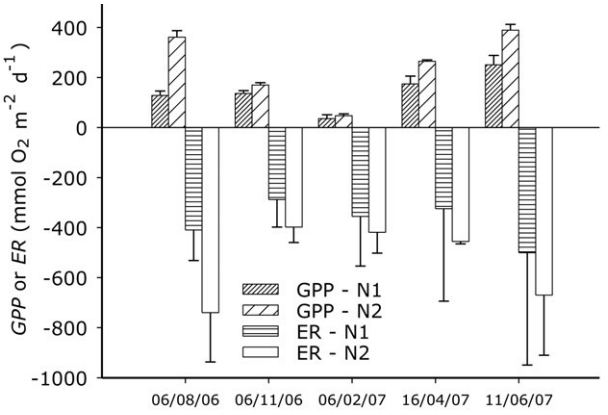

Fig. 4. Rates of GPP (gross primary production) and ER (ecosystem respiration) (mmol O_2 m^{-2} d^{-1}) at stations N1 and N2 in the 5 sampling periods. Daily values±standard deviations are reported; please refer to the material and methods section for the calculation of uncertainties.

all exhibit a different degree of supersaturation (Supplementary Tab. 1). With this respect very high and rather constant supersaturation generally characterizes large turbid rivers, that are net heterotrophic and whose water mass buffers process-related CO_2 variations (Devol *et al.*, 1987; Raymond *et al.*, 1997). In large rivers variations of CO_2 levels may occur, but over a seasonal time scale or over large spatial scales, of the order of hundreds km (Raymond *et al.*, 1997). On the contrary, processes within the water mass or occurring in the hyporheic zone have the potential to alter CO_2 levels in small rivers, at much shorter or smaller temporal and spatial scales (Neal *et al.*, 2002; Teodoru *et al.*, 2009). This is likely due to frequent (*i.e.*, daily) variations of the equilibrium between heterotrophic and autotrophic processes within the river, in particular in those segments that are macrophyte or phytoplankton dominated as the two reaches considered in this study (Neal *et al.*, 2002). In the northern reach of the Mincio River we demonstrated that CO_2 diel changes (difference between minimum and maximum values of CO_2 saturation during the day) were higher than those occurring on a seasonal basis (difference between average CO_2 saturation measured in winter and summer months). Such result is in contrast to most published analogous works, where seasonal trends generally dominate over short term, daily variations. Lynch *et al.* (2010) suggested for the Clark Fork River (Montana, USA) a primary diel control of CO_2 by net ecosystem production, to which seasonal variations of temperature and discharge are superimposed. A similar regulation of CO_2 probably occurs in the northern reach of the Mincio River as a consequence of the activity of submerged phanerogams, that are widespread and exhibit biomass peak in summer (Pinardi *et al.*, 2009; Ribaudo *et al.*, 2011).

Despite elevated chlorophyll *a* concentrations in the southern reach (annual average ~45 μg L^{-1}, Tab. 2) our results suggest that inorganic carbon limitation was not established and our hypothesis of CO_2 undersaturation in a hypertrophic reach was not verified. Minimum or below equilibrium values of CO_2 saturation were measured during summer months in highly eutrophied rivers with intense phytoplankton blooms (*e.g.* Loire estuary in Bozec *et al.*, 2012; River Spree in Gelbrecht *et al.*, 1998), and in other ecosystems as the Kaneohe Bay, Oahu, Hawaii, where CO_2 efflux was reversed and directed from the atmosphere to the water (Drupp *et al.*, 2011; Massaro *et al.*, 2012). On the contrary, likely due to increasing water temperatures, lower solubility and higher microbial respiration, CO_2 peaks in the southern reach of the Mincio River were measured in the summer, as reported in other temperate rivers (Raymond *et al.*, 1997; Koné *et al.*, 2009). Similar results are reported by Raymond *et al.* (1997) that evidenced in the Hudson River a constant CO_2 supersaturation that was independent from chlorophyll *a* concentration in the water, but was positively correlated with water temperature. However, we remark that our CO_2 supersaturation data suggest, in particular for the summer samplings, a marked decrease of values from S1 to S2 in the daylight hours, suggesting the active role of phytoplankton as carbon sink in this river reach. Such evidence is confirmed by summer mass balances of inorganic carbon, revealing a net decrease of loads from S1 to S2 (see later). CO_2 evasion rates calculated for the northern reach of the Mincio River were close to those reported for streams (Teodoru *et al.*, 2009) or unregulated rivers (Koné *et al.* 2009) (Supplementary Tab. 1). CO_2 release calculated for the southern reach were comparable to those reported for large and intermediate rivers (Raymond *et al.*, 1997; Teodoru *et al.*, 2009) or for dammed rivers (Koné *et al.*, 2009) (Supplementary Tab. 1).

In the present study gas fluxes were calculated on the basis of extensively used empirical equations that are based on concentration gradients and gas exchange coefficients. As water-atmosphere gradients in the two reaches were comparable (or slightly higher in the southern one) the difference between calculated evasion rates are due to the chosen coefficients, which in turn depends upon river features. Lower CO_2 evasion calculated in the southern reach compared to the northern one is mainly due to a 90% decrease of water velocity, affecting the factor k on which calculations are based (Fig. 3). The k values calculated for the Mincio are slightly higher and lower for northern and southern reach, respectively, compared to the range (0.04-0.15 m h^{-1}) reported by Wang *et al.* (2007) for worldwide large rivers. With respect to the small scale temporal variability of saturation (and fluxes) we believe that accurate calculations of CO_2 evasion in small productive rivers can be performed only with the sampling strategy we adopted, with repeated analyses during a daily cycle of investigation. Bozec and Merlivat (2011) calculated that monthly CO_2 fluxes can be under or overestimated by 8-36% if samplings are performed only during daytime or night-time; our data suggest that in productive rivers as the Mincio such error can be one order of magnitude higher. Our data also confirm the relevance of monitoring headwater ecosystems where the combination of allochtonous carbon input from the watershed, limited primary production and fast water velocity can determine elevated CO_2 degassing to the atmosphere (Bensted and Leigh, 2012). Rasera *et al.* (2013) demonstrated that relatively small streams (<100 m in width) may contribute for ~55% of the entire C efflux from the Amazon central quadrant. In the specific case of the small river examined in this study, one of the many tributaries of the Po River, we calculated that the CO_2 degassing is nearly one order of magnitude higher in the upstream compared to the downstream reach. Monitoring activities limited to large, slowly flowing systems as the Po River can therefore re-

sult in a large underestimate of watershed inland water true CO_2 emissions (Bensted and Leigh, 2012).

River metabolism, inorganic carbon and oxygen mass balances

Cole and Caraco (2001) stated that respiration exceeds autochthonous GPP resulting in net CO_2 evasion for the majority of aquatic ecosystems. This was always true for the northern reach but not downstream, in the eutrophic plankton-dominated reach, where seasonal exceptions occurred, as we hypothesized (Tab. 4).

In the northern reach benthic primary production displayed high rates of GPP, comparable to those reported in the literature (Tab. 5). Simultaneously, our results suggest for this reach an intense mineralization of carbon, probably fuelled by particulate or dissolved organic matter generated upstream station N1. As oxygen uptake and inorganic carbon production were not coupled, with inorganic carbon production one order of magnitude higher than oxygen consumption, we suggest two possible explanations. The first deals with anaerobic processes as dominant pathways of carbon mineralization in the permeable riverbed. The second deals with carbonate dissolution, as suggested by the significant increase of Ca^{2+} and Mg^{+} concentrations from N1 to N2. The occurrence of these processes can impair the budgets of inorganic carbon and dissolved oxygen, even if with the available data we cannot address their relative importance. In favor of the first explanation is what found by Pinardi *et al.* (2009, 2011), during monthly or seasonal measurements of benthic oxygen and inorganic carbon exchange at both river segments. In the northern reach, incubations of intact cores including bottom water, benthic vegetation and the upper sediment layer resulted in O_2 and DIC fluxes that represent a small fraction of those calculated either via

Tab. 4 Inflowing and outflowing loads and their difference, atmospheric fluxes, mass balances, and sedimentary fluxes of dissolved oxygen and total inorganic carbon measured at the two study reaches and in the 5 sampling periods. Average seasonal values are also reported.

		06/08/2006		06/11/2006		06/02/2007	
		Northern reach ($\times 10^3$ mol d^{-1})	Southern reach ($\times 10^3$ mol d^{-1})	Northern reach ($\times 10^3$ mol d^{-1})	Southern reach ($\times 10^3$ mol d^{-1})	Northern reach ($\times 10^3$ mol d^{-1})	Southern reach ($\times 10^3$ mol d^{-1})
O_2	IN	269.5±6.3	575.0±13.6	292.0±7.3	499.9±12.8	219.4±6.0	432.3±11.6
	OUT	271.5±6.4	606.0±14.8	281.9±6.9	462.9±12.2	215.1±5.8	426.0±11.5
	DELTA	1.9±9.0	31.0±20.1	-10.1±10.1	-37.0±17.7	-4.3±8.3	-6.3±16.2
	AF	-49.8±4.2	2.2±0.3	-32.6±3.4	-2.8±0.2	-71.9±5.3	-3.5±0.2
	MB	-47.9±5.0	33.2±10.1	-42.7±5.3	-39.8±8.8	-76.2±4.9	-9.8±8.1
	SF	-1.6±4.5	-24.0±2.9	-7.1±1.6	-9.8±2.2	-0.7±0.9	-7.1±1.7
DIC	IN	2590.0±60.7	7360.8±172.6	2176.6±54.6	5230.3±133.0	1841.0±50.2	4048.7±109.3
	OUT	3485.8±82.8	6984.0±163.2	2566.4±64.9	5309.1±140.2	2212.2±60.4	4090.5±110.6
	DELTA	895.8±102.6	-376.8±237.6	389.8±84.8	78.8±193.3	371.2±77.9	41.8±154.2
	AF	47.6±2.4	7.6±0.2	44.1±3.0	5.7±0.2	37.0±2.3	3.2±0.1
	MB	943.4±51.3	-369.2±118.8	433.9±42.4	84.4±96.7	408.2±39.0	44.9±77.1
	SF	-8.1±8.7	34.7±13.9	1.7±2.0	7.9±7.1	2.8±3.0	32.3±12.5
		16/04/2007		11/06/2007		Seasonal average	
		Northern reach ($\times 10^3$ mol d^{-1})	Southern reach ($\times 10^3$ mol d^{-1})	Northern reach ($\times 10^3$ mol d^{-1})	Southern reach ($\times 10^3$ mol d^{-1})	Northern reach ($\times 10^3$ mol d^{-1})	Southern reach ($\times 10^3$ mol d^{-1})
O_2	IN	248.2±6.3	314.5±7.5	182.2±4.4	433.2±10.2	242.3±2.7	451.0±5.1
	OUT	239.9±6.0	259.9±6.2	189.1±4.6	411.4±9.7	239.5±2.7	433.2±5.0
	DELTA	-8.3±8.8	-54.6±9.7	6.9±6.4	-21.7±14.1	-2.8±3.8	-17.7±7.1
	AF	-26.7±3.5	-6.1±0.3	-40.3±3.8	3.0±0.2	-44.2±1.8	-1.4±0.1
	MB	-35.0±4.7	-60.7±4.8	-33.4±3.7	-18.7±7.0	-47.0±2.1	-19.2±3.6
	SF	5.7±3.6	-27.1±8.8	6.7±3.7	-23.2±8.5	0.6±1.4	-18.2±2.6
DIC	IN	1888.2±48.2	3351.2±79.8	2106.0±49.6	4824.1±113.2	2120.4±23.6	4963.0±56.1
	OUT	2037.7±52.2	3439.4±81.8	2618.7±61.6	4789.4±112.1	2584.2±29.1	4922.5±55.8
	DELTA	149.5±71.1	88.3±114.3	512.8±79.1	-34.6±159.4	463.8±37.5	-40.5±79.0
	AF	18.8±1.4	7.7±0.2	56.2±2.7	12.1±0.3	40.7±1.1	7.3±0.1
	MB	168.3±35.6	96.0±57.1	569.0±39.6	-22.5±79.7	504.5±18.7	-33.3±39.5
	SF	-7.1±3.3	24.8±18.2	-17.0±6.8	-13.5±16.0	-5.6±2.4	17.2±6.3

IN, inflowing; OUT, outflowing; DELTA, difference between inflowing and outflowing (=OUT-IN); AF, atmospheric fluxes (calculated from saturation gradients and empirical equations); MB, mass balances (=DELTA+AF; from eq. 5); SF, sedimentary fluxes (from intact sediment incubations; Pinardi et al., *2009, 2011); DIC, dissolved inorganic carbon.*

open channel or mass balance approaches (SF *vs* MB, Tab. 4). As cores allow to explore a limited sediment horizon, we speculate that discrepancies between incubation and open or whole system approaches are due to the thick hyporheic horizon where microbial processes can occur. Similar large discrepancies, with rates differing by up to 1-2 orders of magnitude, can be found for N_2 production estimated from core incubation or via open channel methods (Laursen and Seitzinger, 2005).

In the southern reach, the mass balances of dissolved oxygen and inorganic carbon were comparatively much more coupled (Tab. 4). In two out of five samplings (August 2006 and June 2007) the mass balances of DIC were negative, suggesting net C fixation by the phytoplankton community. These results demonstrate that primary producers may turn the ratio between production and respiration above unity also in a fluvial system. During summer, phytoplankton attenuates at the southern reach the large DIC load generated upstream; however CO_2 supersaturation (and degassing) persists in this net autotrophic river segment (Tab. 4). Sediments at S1 and S2 are permanently in the dark; here, intact core incubations revealed that the riverbed was an O_2 sink and a DIC source (Tab. 4; Pinardi *et al.*, 2011). The comparison of these fluxes with the O_2 and DIC average seasonal budgets (SF *vs* MB; Tab. 4) suggests that the sediment oxygen demand is comparable to the whole reach oxygen consumption and that regenerated CO_2 is not exported downstream and is buffered by phytoplankton fixation. A major difference between the two investigated reaches deals with the relevance of internal processes with respect to the pool of inorganic carbon transferred downstream. In the northern reach, hyporheic zone-associated processes (either microbial metabolism of carbonate dissolution) were probably responsible for as much as a 24% increase of the DIC load measured at N1 and about 8% of such inorganic carbon input evaded to the atmosphere. In this reach we demonstrated that photosynthetic activity by macrophytes modulated dissolved CO_2 saturation values, resulting in large daily and seasonal variations of fluxes. However, despite the GPP was elevated, macrophyte activity fixed a minor amount of the DIC load, and the fraction of C retained was negligible if compared to the C produced within the system and transferred downstream.

The southern reach transported twice as much inorganic carbon compared to the northern one due to higher DIC concentrations and water flow, and lower off-gassing rates. Contrarily to what measured upstream, the differences between loads at S1 and S2 were smaller (generally ~1-3%) with August 2006 as exception (Tab. 4). In fact, in that summer sampling the budget was negative and represented nearly 5% of the load. The net decrease of DIC loads in the summer is a partial validation of our hypothesis on the relevant role of primary production in eutrophic and regulated river reaches. However, we already explained that the elevated CO_2 supersaturation levels were only attenuated by the primary production occurring in the water column and evasion from the water to the air was never reversed, not even in the summer. In August 2006, CO_2 effluxes represented a minor fraction (less than 0.1%) of the load generated upstream and were nearly 50 times smaller than the amount of C fixed by phytoplank-

Tab. 5. Published rates of gross primary production and ecosystem respiration for different river typologies; values reported in the present study are included.

GPP (mmol m^{-2} d^{-1})	ER (mmol m^{-2} d^{-1})	References
300	265	Ivel River, England. Edwards and Owens, 1962.
171	317	Itchen River. Odum, 1956 (data of Butcher, Pentelow, Woodley, 1930).
582	548	Silver springs, Florida. Odum, 1957.
9-306	20-672	Seeley, 1969.
10-110	135-252	Small streams. Marzolf *et al*., 1994.
3-468	7-343	Streams in U.S.A. Mulholland *et al*., 2001.
4-32	21-415	Streams in Grand Tetonal National Park, Wyoming. Hall and Tank, 2003.
75-375	191-513	Blue River reach 5-6 (R>P), Oklahoma. Duffer and Dorris, 1966.
316-1500	281-622	Blue River reach 6-7 (P>R), Oklahoma. Duffer and Dorris, 1966.
47-159	191-344	Blue River reach 12-13 (R>P), Oklahoma. Duffer and Dorris, 1966.
36-250	288-500	Mincio River, N1. This study.
47-389	398-740	Mincio River, N2. This study.

GPP, gross primary production; ER, ecosystem respiration.

ton (Tab. 4). These numbers stress the quantitative potential relevance of C fixation by phytoplankton in river reaches with altered hydrology and nutrient content. This outcome should be carefully considered as a vast majority of the world small and large rivers are under the risk of damming, alteration of hydrology and eutrophication (Nilsson and Swedmark, 2002; Dodds, 2006; McGill University, 2011; Poff *et al.*, 2011).

CONCLUSIONS

Results of the present study demonstrated that both the free flowing, low chlorophyll and the dammed, hypertrophic reaches were always CO_2 supersaturated, with higher CO_2 evasion in the northern compared to the southern reach mainly due to higher water velocity affecting the reaeration coefficients. As we hypothesized, at both reaches primary producers were strong regulators of dissolved gas saturation. Contrarily to what we expected, the photosynthetic activity of phytoplankton in the southern reach was not strong enough to reverse the CO_2 evasion to the atmosphere. In hypereutrophic sites water column primary production is strongly regulated by light penetration and at the southern reach the high density of microalgae confined the photosynthetic horizon to a thin surficial zone while most of the water column and surface sediments were strictly oxygen consuming and CO_2 producing.

We remark the need of including headwater and small river ecosystems in C budgets due to different reasons. The main is that they represent a large majority of lotic environments worldwide and are not included in global C budget, despite their quantitative relevance. Another important reason follows the outcome of the present study, as it demonstrates that CO_2 evasion rates undergo pronounced variations at small spatial and temporal scales, due to the combined effects of eutrophication, altered hydrology and primary producers activity. Increasing conflicts for multiple water use, in particular in undeveloped countries, are expected to alter the chemical quality of river water, its flow and as a consequence the communities of primary producers. Ultimately these changes should be monitored and accounted for as they will produce cascade effects on C budgets.

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