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# Carbon source/sink function of a subtropical, eutrophic lake determined from an overall mass balance and a gas exchange and carbon burial balance

Hong Yang a,b, Yangping Xing a,c, Ping Xie a,\*, Levi Ni a, Kewen Rong a

Donghu Experimental Station of Lake Ecosystems, State Key Laboratory for Freshwater Ecology and Biotechnology of China,
 Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan 430072, PR China
 Environmental Change Research Centre, University College London, London WC1E 6BT, UK
 Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

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Due to high primary production, substantive allochthonous carbon inputs and intensive anthropogenic acitivity, subtropical, eutrophic Lake Donghu is a great carbon sink.

## Abstract

Although studies on carbon burial in lake sediments have shown that lakes are disproportionately important carbon sinks, many studies on gaseous carbon exchange across the water—air interface have demonstrated that lakes are supersaturated with  $CO_2$  and  $CH_4$  causing a net release of  $CO_2$  and  $CH_4$  to the atmosphere. In order to more accurately estimate the net carbon source/sink function of lake ecosystems, a more comprehensive carbon budget is needed, especially for gaseous carbon exchange across the water—air interface. Using two methods, overall mass balance and gas exchange and carbon burial balance, we assessed the carbon source/sink function of Lake Donghu, a subtropical, eutrophic lake, from April 2003 to March 2004. With the overall mass balance calculations, total carbon input was 14 905 t, total carbon output was 4950 t, and net carbon budget was +9955 t, suggesting that Lake Donghu was a great carbon sink. For the gas exchange and carbon burial balance, gaseous carbon ( $CO_2$  and  $CH_4$ ) emission across the water—air interface totaled 752 t while carbon burial in the lake sediment was 9477 t. The ratio of carbon emission into the atmosphere to carbon burial into the sediment was only 0.08. This low ratio indicates that Lake Donghu is a great carbon sink. Results showed good agreement between the two methods with both showing Lake Donghu to be a great carbon sink. This results from the high primary production of Lake Donghu, substantive allochthonous carbon inputs and intensive anthropogenic activity. Gaseous carbon emission accounted for about 15% of the total carbon output, indicating that the total output would be underestimated without including gaseous carbon exchange.

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Keywords: Carbon budget; Overall mass balance; Gas exchange; Carbon burial; Lake Donghu

# 1. Introduction

The increase in the concentration of greenhouse gases in the troposphere during the last 200 years has stimulated research on carbon cycling of terrestrial and aquatic environments in

the last decades of years. Studies on the carbon source/sink function have been made in various terrestrial and aquatic environments such as forests, grasslands, arable lands, peatlands and oceans. To date, relatively little attention has been paid to lake ecosystems, probably because of the small fraction of the earth's surface area which lakes occupy (less than 2%, Wetzel, 2001). However, in some area of the world where lakes occupy 10–20% of the land surface area, such as Wuhan City, China, lake carbon budget is potentially a very important component

<sup>\*</sup> Corresponding author. Tel./fax: +86 27 68780622. *E-mail address:* xieping@ihb.ac.cn (P. Xie).

of the whole area carbon budget. Studies on carbon burial in lake sediments have shown that lakes are disproportionately important carbon sinks (Dean and Gorham, 1998; Einsele et al., 2001; Mulholland and Elwood, 1982; Stallard, 1998), with the sedimentation mass of organic carbon in lakes about half that of oceans, which cover 71% of the earth's surface (Dean and Gorham, 1998). Compared to large lakes, small lakes are proportionally more important for carbon burial (Kortelainen et al., 2004). On the other hand, many studies on gaseous carbon exchange across the water-air interface have found that nearly 90% of lakes are supersaturated with CO<sub>2</sub> with a net diffusion of CO<sub>2</sub> from surface waters (Cole et al., 1994; Rantakari and Kortelainen, 2005). Some investigations have also revealed that many freshwater ecosystems are important sources of CH<sub>4</sub>, particularly eutrophic lakes (Casper et al., 2000; Xing et al., 2004; Xing et al., 2005). Based on the studies of lakes over large gradients of dissolved organic carbon (DOC) and total phosphorus (TP) in the Northern Highlands Lake District of Wisconsin, Hanson et al. (2004) suggested that the balance within lakes between gaseous carbon exchange and carbon burial in sediment, rather than only gaseous carbon exchange or carbon burial, determines whether lakes are net carbon sources or carbon sinks.

On the other hand, carbon source/sink function of lake ecosystems can alternatively be assessed by an overall mass balance approach where the net carbon budget is the difference between the total input and the total output. The overall mass balance approach is probably the most accurate method to estimate the carbon source/sink function of lake ecosystems; however, the measurements involved are both time consuming and expensive, requiring data collection for at least one year. Consequently, the number of carbon budgets from lake ecosystems using an overall mass balance is currently limited. Up until now, mass balance carbon budget studies have been heavily biased towards north temperate lakes (Charlton, 1977; Eadie and Robertson, 1976; Maier and Swain, 1978; Mcconnaughey et al., 1994; Quay et al., 1986) where gaseous carbon (CO<sub>2</sub> and CH<sub>4</sub>) fluxes, in particular CH<sub>4</sub>, were usually not taken into account. However, CO2 and CH4 fluxes across the water-air interface are relatively high (Cole et al., 1994; Xing et al., 2005) and are important parts of whole-lake carbon budgets (Quay et al., 1986; Cole and Caraco, 1998).

Although there are some studies on the carbon source/sink function of lake ecosystems from carbon burial and gas exchange balances (Hanson et al., 2004) or from overall mass balances (Charlton, 1977; Eadie and Robertson, 1976; Maier and Swain, 1978; Mcconnaughey et al., 1994; Quay et al., 1986), we have found no published lake carbon budgets made using both methods simultaneously. As such, there are currently no direct comparisons of the two methods.

In order to more accurately estimate the carbon source/sink function, we constructed a comprehensive carbon budget, including the gaseous carbon exchange across the water—air interface using the floating static chamber technology, in the subtropical, eutrophic Lake Donghu from April 2003 to March 2004. Lake Donghu is also the largest urban lake in China. The balance between gaseous carbon exchange and carbon

burial was used to estimate the carbon source/sink function of Lake Donghu, and then results from the two methods were compared. In addition, the main factors which influence the carbon source/sink function of subtropical, eutrophic lakes were also discussed.

## 2. Materials and methods

## 2.1. Site description

Lake Donghu (30°33'N, 114°23'E) is located North East of the 8450 km<sup>2</sup> Wuhan City, the alluvial plain of the middle basin of the Yangtze River. Its mean depth is 2.5 m with a maximum depth of 4.5 m. Because of the shallow depth, there is no proper stratification and the whole lake can be treated as a homogeneous mixed reactor. The lake itself is composed of several basins separated by artificial dykes with a total surface area of 32 km<sup>2</sup> (Liu, 1990). The catchment area is 187 km<sup>2</sup>. There are five main sewage inlets into the lake: Yujiahu Outlet (St. 1), Meiling Outlet (St. 2), Fengguang Outlet (St. 3), Wuda Outlet (St. 4), and Shuiguohu Outlet (St. 5) (Fig. 1). Through these outlets domestic and industrial effluents enter the lake (Tang and Xie, 2000). Lake Donghu is connected with the Yangtze River by the Qingshan Canal and the discharge is regulated by the canal to maintain a relatively constant lake level. The climate is a typical subtropical monsoon climate with a mean annual temperature of 16.7 °C, annual precipitation of 1160.3 mm and annual evaporation of 1148 mm. Wind speed is generally lower than 3 m s<sup>-1</sup>. Macrophytes began to reduce in most parts of lake from the 1970s, due to the over-stocking of grass carp, and almost completely disappeared in the 1980s (Ni, 1996). Large-sized cyanobacteria (mainly Microcystis, Anabaena and Aphanizomenon) occurred in such abundance as to cause a striking bloom from the 1970s to 1985. Since 1985, the "water bloom" suddenly disappeared and dominance of the phytoplankton switched to Bacillariophyta (mainly Cyclotella), Cryptophyta (mainly Cryptomonas) and Cyanophyta (mainly Oscillatoria and Merismopedia) (Xie and Liu, 2001). Although, the dominant fish are the filter-feeding silver carp (Hypophthalmichthys molitrix) and bighead carp (Aristichthys nobilis), some large piscivorous fish also occur at low densities. Fish grazing significantly impacts the lake's plankton (Xie and Liu, 2001). The Secchi disk depth is about 0.5 m and hence the microphytobenthos cannot receive enough photosynthetically available radiation (PAR) and the primary production is negligible (Yang et al., 2005a).

#### 2.2. Overall mass balance

A steady-state mass balance equation was used to calculate a year's carbon budget in Lake Donghu from April 2003 to March 2004:

$$S + P + L + A - F - D + G = \nabla F \tag{1}$$

where S, P, L and A are carbon inputs from sewage, precipitation, land runoff and atmospheric dustfall, respectively; F and D are carbon outputs from fish harvest and discharge into the Yangtze River, respectively; G is gaseous carbon (CO<sub>2</sub> and CH<sub>4</sub>) exchange (positive values represent influx and negative values represents efflux);  $\nabla F$  is the net carbon budget (positive values represent carbon sink and negative values represent carbon source).

Net primary production (NPP) was measured monthly at Stations I, II and III using the light—dark bottle method and Winkler oxygen analysis (APHA, 1995). In some studies primary production was considered in the carbon input (Carpenter et al., 1983; Quay et al., 1986). By taking up gaseous CO<sub>2</sub> the phytoplankton has an active role in creating concentration difference between the lake surface and the atmosphere, which is crucial for CO<sub>2</sub> influx. In fact, primary production simply changes the carbon from an inorganic to an organic form within the lake but does not affect the whole system's carbon budget (Abril et al., 2005). In our study, CO<sub>2</sub> absorption and emission by photosynthesis and respiration were included in gaseous carbon exchange (G). In this respect, therefore, G rather than primary production was considered in the carbon budget.

Sewage carbon loading was calculated from carbon concentration analyses and flow measurements. Carbon concentrations of sewage were determined

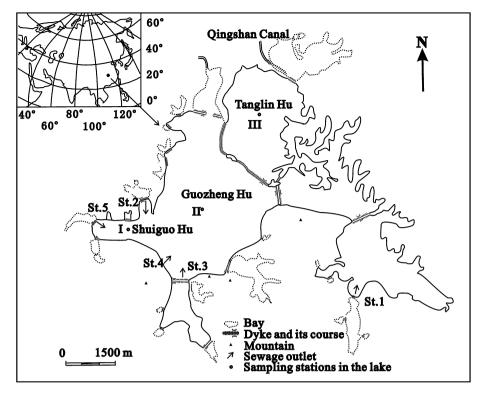


Fig. 1. Location of Lake Donghu and sampling points of gaseous carbon exchange (I Shuiguo Hu, II Guozheng Hu and III Tanglin Hu) and sewage outlets around the lake (St.1, St.2, St.3, St.4 and St.5).

(persulfate-assisted UV digestion) by infrared detection using a 1010 Wet Oxidation TOC Analyzer (O.I. Analytical Co.). Sewage flow was calculated by multiplying the area of the sewage outlets by flow rates, determined by a TAM-AYA SAN-E1 current meter every month at the five sewage outlets (Fig. 1).

Carbon in precipitation and land runoff was measured by analyzing samples of all significant rainfall ( $>10~{\rm mm~d}^{-1}$ ) which mainly occurred from April to September 2003. Carbon concentrations of precipitation and land runoff were determined by a 1010 TOC Analyzer (O.I. Analytical Co.). Precipitation was measured daily at 8 p.m. with the data provided by the Meteorology Station of Wuhan City. Land runoff from the catchment was calculated from the following equation:

$$L = \sum_{i=1}^{n} P_i A_i C_i \tag{2}$$

where L is land runoff,  $P_i$  is precipitation (mm),  $A_i$  is area (km²) of different land covers (urban area, 51.7 km²; mountain area, 69.4 km²; and farmland area, 65.9 km²; Liu, 1990),  $C_i$  is the land runoff coefficient of different land covers (0.64, 0.53 and 0.53 for urban, mountain and farmland areas, respectively; unpublished data of X.Q. Xu). In order to evaluate the errors involved in the low frequency sampling of precipitation and land runoff, we collected all the rain water and land runoff samples in the July 2003 rain season and determined the TC concentrations. The student's t-test was run using the SPSS 12.0 (SPSS Chicago, IL, USA) to assess the difference between the TC concentrations in all rains and significant rains of more than 10 mm d $^{-1}$ .

Carbon input from atmospheric dustfall was obtained by multiplying the carbon content of dustfall and the dustfall mass. The atmospheric dustfall mass data were provided by the Environment Protect Bureau of Wuhan City. For analysis of carbon content, atmospheric dustfall was collected monthly using buckets placed on the top of the barge of Donghu Experimental Station of Lake Ecosystems, Institute of Hydrobiology, which was fixed in Lake Donghu. Dustfall particles were wiped from the bottom of buckets with a brush and then washed with distilled water. Leaves, insects, and bird manure were removed from the dustfall with clean forceps prior to its washing with distilled water. The samples were filtered through GF/C filter papers

(Whatman Co.) and dried at 60  $^{\circ}$ C overnight. The carbon content of dustfall was determined as CO<sub>2</sub> on a 1010 and Solid TOC Analyzer (O.I. Analytical Co.) after combustion at 900  $^{\circ}$ C.

Carbon outflow from the discharge was calculated by multiplying the volume of lake water through the Qingshan Canal (provided by Wuhan Steel Mill) and the carbon concentration determined weekly by a 1010 TOC Analyzer (O.I. Analytical Co.).

Carbon outflow from the fish harvest was estimated through fish yields (unpublished data of G.T. Huang) and the carbon content of the fish (Liu, 1990). *Hypophthalmichthys molitrix* and *Aristichthys nobilis*, the dominated fish species accounting for over 80% of the total fish yield (Liu, 1990), were collected monthly with trawl and were dissected into four parts: muscles, organs, bones and scales. After heating and grinding, carbon concentrations of the proportionate mixture of the four parts were determined by a Carlo-Erba 1106 elemental analytical instrument (Liu, 1990).

Gaseous carbon (CH<sub>4</sub> and CO<sub>2</sub>) flux across the water-air interface was obtained by multiplying the gas exchange rate and representative areas. Gas exchange across the water-air interface was measured between 9 and 11 a.m. approximately every week at Stations I, II and III (Fig. 1) using floating static chambers, 50 cm in height and 30 cm in diameter, equipped with a dry battery driven fan and a small lateral vent stopped by silicon septum. Three replicate chambers were deployed at each measuring site (distance between replicates was 0.30 m). Four gas samples (about 50 ml) from the chamber air headspace were manually withdrawn into 100 ml syringes at 0 min, 10 min, 20 min and 30 min after deployment. At the same time air temperature inside the chamber, air temperature, water and sediment surface temperature outside the chamber were measured with a JM624 portable digital thermometer equipped with different probes which could be placed at any water depths and in the sediment surface. All samples were transported to the laboratory in a cool box and analysis of the gas composition commenced within 4 h. The samples were analyzed with a HP-4890D Gas Chromatograph (Agilent Co.) connected with a CA-5 auto-sampling (Patent Nos. ZL92100938.0 and ZL96249356.2) (Wang and Wang, 2003). After CO<sub>2</sub> was converted into CH<sub>4</sub> by Nickel catalyst at 375 °C, the concentrations of CH<sub>4</sub> and CO<sub>2</sub> in the gas samples were determined with a FID detector equipped with a column packed with SS-2mm  $\times$  2mm  $\times$  13XMS (mesh 60/80). The oven, injector and detector temperatures were 55 °C, 375 °C and 200 °C, respectively. In order to check for reproducibility of results and to evaluate the precision of measurements, standard gases were run before and after each set of samplers. Gas flux was calculated from a linear regression with gas concentration change within the chamber versus time (Wickland et al., 2001). The detection limit of the gas chromatograph is 0.1 ppm (v/v) and the minimum detectable flux is 0.1 mg m<sup>-2</sup> d<sup>-1</sup>, with analytical error on duplicate standard samples of less than 1% (for more details see Xing et al., 2005).

Because of relatively low porosity and limited hydraulic connections, the ability of the bedrock to store and conduct groundwater is negligible (Liu, 1990). So, compared to the massive input from sewage and land runoff, groundwater input is negligible (Tang and Xie, 2000).

#### 2.3. Gaseous carbon exchange and carbon burial balance

Two undisturbed sediment cores to a depth of 40 cm were collected at Stations I and II in April 2003 using a 5.7-cm diameter gravity core sampler. The cores were sectioned at 2 cm intervals and dried (105 °C) for 24 h to determine the water content. The porosity of the sediment was calculated from the wet and dry weights following the equations outlined by Crusius and Anderson (1991). Total organic carbon (TOC) and total carbon (TC) concentrations were measured as  $\rm CO_2$  on acid treated samples and untreated samples using a 1010 and Solid TOC Analyzer (O.I. Analytical Co.), after combustion at 900 °C.

Dried sediments (2.4–3.0 g) were stored in sealed containers for 3 weeks to allow radioactive equilibration and then dated radiometrically by analysing for <sup>210</sup>Pb and <sup>226</sup>Ra by direct gamma assay using a GWL-120210-S well-type, coaxial, low background, intrinsic germanium detectors fitted with NaI(Tl) escape suppression shields (Appleby et al., 1986). Sedimentation rates were calculated using a <sup>210</sup>Pb constant rate of supply (CRS) model and <sup>137</sup>Cs as a time marker. Organic matter reaching the surface sediment is easily ingested, mineralized, or resuspended and deposited elsewhere with most likely no organic matter being buried (Fitzgerald and Gardner, 1993), so the average long-term rate of carbon accumulation were calculated (Page et al., 2004). Mass accumulation rates (MAR) were averaged for the samples and were calculated with the relationship (Muller et al., 2005):

$$MAR = LAR\rho(1 - \Phi)$$

where LAR is the linear accumulation rate (cm y<sup>-1</sup>),  $\rho$  is sediment density (g cm<sup>-3</sup>), and  $\Phi$  is porosity. Sediment density ( $\rho$ ) was averaged for the samples and calculated from TOC measurements following the equation (Muller et al., 2005):

$$\rho = -0.0523 \text{TOC} + 2.65$$

Gaseous carbon samples were collected using floating static chambers and measured using a HP-4890D Gas Chromatograph (Agilent Co.).

## 3. Result

## 3.1. Overall carbon mass balance

Total carbon input was about 14 905 t. The carbon input from sewage of 13 112 t, 88% of all inputs, overshadowed all the other inputs in Lake Donghu during the study period (Table 1 and Fig. 2). Variation in the temporal pattern suggested that carbon input from sewage was higher in summer (June, July and August) (Fig. 3). Carbon inflow from land runoff was of relatively minor importance, being 1602 t, i.e. about 11% of all carbon inputs. Carbon input from precipitation was also very small, only 1% of all inputs. Carbon inflow from land runoff and precipitation varied greatly with maxima occurring in July 2003 and minima in December 2003 (Fig. 3) and there is a significant relationship between the carbon inflow from land runoff and precipitation  $(r^2 = 0.99, p \ll 0.01)$ . The student's t-test

Table 1
Annual average carbon budget for Lake Donghu from April 2003 to March 2004

	Mass (t)	Proportion (%)	
Inflow			
Sewage	13 112	88	
Land runoff	1602	11	
Precipitation	191	1	
Atmospheric dustfall	0.06	0.0004	
Total input	14 905.06		
Outflow			
Discharge	3205	65	
Fish harvest	993	20	
Emission to atmosphere	$752 \pm 407$	15	
Total outflow	4950		
Net budget	9955.06		

showed no significant difference between the TC concentrations in all rains and significant rains of more than  $10 \text{ mm d}^{-1}$  (p = 0.93), indicating that the sampling frequency does not have a significant impact on our assessment of land runoff and precipitation TC concentrations. Carbon input from atmospheric dustfall was negligible, only 0.0004% of all carbon inputs.

Total carbon output was about 4950 t, with discharge into the Yangtze River accounting for 3205 t, 65% of all carbon outputs. Carbon outflow from fish harvest peaked at 993 t, about 20% of the total outflow. Due to limits of the data used, the temporal variations of discharge and fish harvest are not available. There was an influx of CO<sub>2</sub> from the atmosphere in spring and summer (+93 t) and emission in autumn and winter (-730 t), while the net CO<sub>2</sub> flux was towards the atmosphere. The lake was slightly supersaturated with CH<sub>4</sub> with respect to the atmospheric equilibrium with whole lake CH<sub>4</sub> release estimated at -115 t (for more details see Xing et al., 2005). The average gaseous carbon (CO2 and CH4) fluxes across the water-air interface reached up to -752 t, i.e. about 15% of all carbon outputs. The standard deviation was 407 t, as such the relative standard deviation reached up to 54% in Lake Donghu during the study period (Table 1). Based on the standard deviation, the minimal gaseous carbon exchange was only 345 t, 8% of all carbon outputs; the maximum peaked at 1159 t, i.e. accounting for 22% of all outflows.

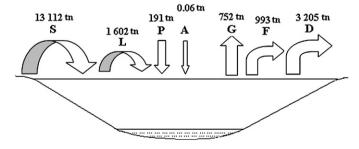


Fig. 2. Annual average carbon budget for Lake Donghu from April 2003 to March 2004. S, L, P and A refer to carbon inputs from sewage, land runoff, precipitation and atmospheric dustfall, respectively; G, F and D refer to carbon outputs from gaseous carbon (CO<sub>2</sub> and CH<sub>4</sub>) emission, fish harvest and discharge into the Yangtze River, respectively.

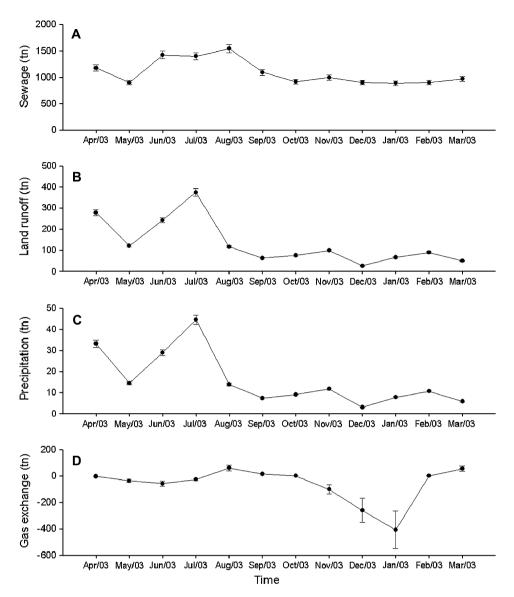


Fig. 3. Variations in monthly carbon loading from sewage (A), land runoff (B), precipitation (C) and gaseous carbon exchange (D) in Lake Donghu from April 2003 to March 2004. Positive value of gaseous carbon exchange represents consumption and negative value represents release.

The net carbon budget was about +9955 t over the study period; in other words, Lake Donghu acted as a net carbon sink and retained 9955 t carbon within the water column and sediment from April 2003 to March 2004.

# 3.2. Carbon burial

Linear accumulation rates were  $0.39~\rm cm~y^{-1}$  and  $0.46~\rm cm~y^{-1}$  at Stations I and II, respectively (Table 2) (for more details see Yang et al., 2005b). As such, 40 cm cores represent records of 103 and 87 years at Stations I and II, respectively. TC concentrations varied between 2.35% and 5.40% at Station I, with an average of 4.25%, and between 1.30% and 5.84% at Station II, average 3.90% (Fig. 4). On average TOC concentrations were 3.83% and 3.50% at Stations I and II, respectively (Fig. 4). The calculated average densities at both stations were  $2.65~\rm g~cm^{-3}$ , based on average TOC concentrations. Average

Table 2
Sediment characteristics of different lakes areas and carbon burial in Lake Donghu

	Lake areas		
	Station I	Other lake areas	
LAR (cm y <sup>-1</sup> )	$0.39 \pm 0.17$	$0.46 \pm 0.18$	
$\rho  (\mathrm{g  cm^{-3}})$	2.65	2.65	
$\Phi$	0.33	0.38	
MAR $(g cm^{-2} y^{-1})$	0.69	0.76	
TC (%)	4.25	3.90	
Area (km²)	1.14	30.86	
Carbon burial (t y <sup>-1</sup> )	334.31	9146.90	
Total carbon burial (t y <sup>-1</sup> )	9481.21		

LAR is linear accumulation rate,  $\rho$  is sediment density,  $\Phi$  is porosity, MAR is mass accumulation rate and TC is total carbon.

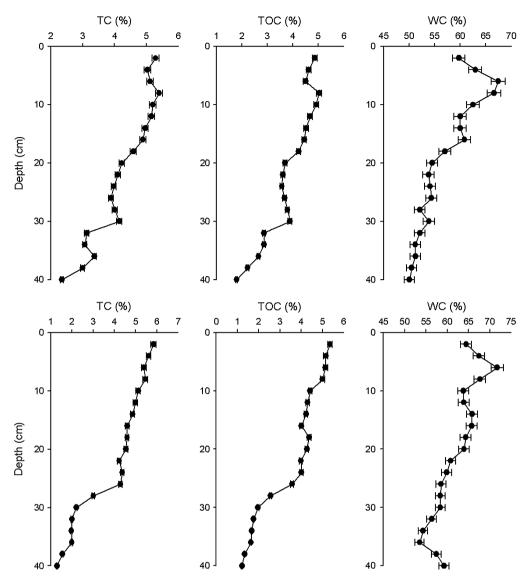


Fig. 4. Total carbon (TC), total organic carbon (TOC) and water content (WC) concentrations at Stations I (top) and II (bottom) of Lake Donghu. TC and TOC were measured from dry sediment.

porosities, respectively, were 0.33 and 0.38, calculated by average water contents (56.75% and 61.78%, Fig. 4) and average sediment density. The calculated mass accumulation rates were  $0.69 \text{ g cm}^{-2} \text{ y}^{-1}$  and  $0.76 \text{ g cm}^{-2} \text{ y}^{-1}$ . Because of the relatively great difference in the sediment between Station I and other lake areas (Liu, 1990), we calculated the carbon burial in Station I by multiplying the MAR of  $0.69 \text{ g cm}^{-2} \text{ y}^{-1}$  and the average TC concentration of 4.25% by the area (1.14 km<sup>2</sup>). For other lake areas carbon burial was calculated by multiplying the MAR of  $0.76 \text{ g cm}^{-2} \text{ y}^{-1}$  and the average TC concentration of 3.90% by the area (30.86 km<sup>2</sup>). The calculated total carbon burial from this was 9481 ty<sup>-1</sup> (Table 2). Based on the standard deviations of long-term sedimentation rate  $(0.39 \pm 0.17 \text{ cm y}^{-1} \text{ and } 0.46 \pm 0.18 \text{ cm y}^{-1} \text{ in Stations I}$ and II, respectively, Table 2), the minimal carbon burial was only 5756 t while the maximum peaked at 13 206 t. Considering the standard deviation of sedimentation rate and gaseous carbon exchange (752  $\pm$  407), the ratio of gas exchange to carbon burial could change between 0.03 and 0.20.

The ratio of gaseous carbon exchange across the water—air interface (752 t) to carbon burial in the sediments (9481 t) was 0.08 in Lake Donghu.

# 4. Discussion

# 4.1. Reliability of the carbon budget calculations

The first weakness in our analysis is the difference in gaseous carbon exchange between the littoral and pelagic zones, which is not accounted for in this study. In the present study, CO<sub>2</sub> and CH<sub>4</sub> were measured at Stations I, II and III in the pelagic zone of Lake Donghu (Fig. 1). A recent study in a oligotrophic, clearwater, boreal lake showed that the littoral zone may play an important role in the lake-wide carbon cycle with CO<sub>2</sub> absorbed by emergent macrophytes in the littoral zone and transported to the pelagic zone (Andersson and Kumblad, 2006). In eutrophic Lake Donghu, macrophytes almost completely disappeared from the 1980s (Ni, 1996).

In addition, Lake Donghu is a shallow lake with an average water depth of 2.5 m, so we feel justified in assuming that the lake is a homogeneous mixed reactor and that there is no great difference in the gaseous carbon exchange between the littoral and pelagic habitats. Similarly, Hanson et al. (2004) did not separate the littoral and pelagic habitats in their studies in the Northern Highlands Lake District of Wisconsin.

The floating static chamber was used to directly collect the gaseous carbon across the water-air interface during a relatively short time period while allowing for considerable spatial coverage due to the ease with which the system can be transferred from one site to another (Duchemin et al., 1999). The chamber method has been used in a large number of studies (Chan et al., 1998; Duchemin et al., 1999; Huttunen et al., 2003; Kelly et al., 1997; Xing et al., 2004; Xing et al., 2005). Some researchers have compared the results of the floating static chamber with thin boundary layer techniques finding a good agreement between the two methods (Chan et al., 1998; Duchemin et al., 1999; Kelly et al., 1997). Research in two large reservoirs has shown that the static chamber technique contained fewer analytical biases whilst the thin boundary layer method underestimated CO<sub>2</sub> and CH<sub>4</sub> emission fluxes (Duchemin et al., 1999). Some researches showed that chamber technique overestimates the fluxes relative to the thin boundary layer technique, primarily because the latter only considers diffusion across the air-water interface (Richey et al., 1988; Devol et al., 1990). Similarly, Bubier et al. (1993) also suggested the difference between chamber method and thin boundary layer technique results from the absence of ebullition, an important flux mechanism, especially to CH<sub>4</sub>, in the latter method. According to the estimation of a eutrophic lake in Priest Pot, UK, CH<sub>4</sub> 92-98% is released by ebullition and CO<sub>2</sub> 98.8-99.7% is released by diffusion (Casper et al., 2000). So, the estimation of gaseous carbon flux in our eutrophic Lake Donghu study is relatively reliable as the ebullition is included in our chamber technique.

Due to absence of the data of sedimentation rate from April 2003 to March 2004, average long-term linear accumulation rates  $0.39 \text{ cm y}^{-1}$  and  $0.46 \text{ cm y}^{-1}$  at Stations I and II were used to calculate the carbon burial in Lake Donghu. It should be noted that the linear sedimentation rate should only be regarded as the mean sedimentation rates during the last about 100 years and probably not be representative for present study period. Different time scales, especially the gaseous carbon exchange and carbon burial, is the factor contributing to some potential uncertainties in the present carbon budget research. The gaseous carbon exchange measurements are more 'instant' and the physical, chemical and biological processes take place just at the time of sampling. On the other hand, the carbon burial is a process taking place slowly and extending over long time period. Although we are uncertain about whether the about 100 years average sedimentation rate is significantly different from the sedimentation rate during the study period, the ratios of gas exchange to carbon burial (0.03-0.20) much less than 1 still clearly indicate that Lake Donghu is a great carbon sink over the study period.

4.2. Comparison of carbon source/sink functions of Lake Donghu to other freshwater lakes

Previous carbon budget studies in northern temperate mesotrophic and dystrophic lakes, using an overall mass balance method, where CH<sub>4</sub> was not taken into account, showed that lakes could be a carbon source (Carpenter et al., 1983) or carbon sink (Cole et al., 1989; Eadie and Robertson, 1976). Carbon budget studies using a gas exchange and carbon burial balance showed the ratio of gaseous carbon exchange across the water—air interface of most northern temperate lakes to be greater than 1, similar to the average global ratio for lakes which is also greater than 1 indicating that most lakes are a carbon source (Algesten et al., 2004; Cole and Caraco, 1998; Dillon and Molot, 1997; Hanson et al., 2004) (Table 3). In our study, a net carbon budget of 9955 t and a ratio of gas emission to carbon burial of only 0.08 clearly indicate that subtropical, eutrophic Lake Donghu is a great carbon sink. The model of gas exchange and carbon burial balance developed in the Northern Highlands Lake District of Wisconsin showed that lakes low in carbon loading and moderate to high in total phosphorus (TP) are net carbon sinks (Hanson et al., 2004). The average TP concentration in Lake Donghu was very high over the study period (0.173 mg  $L^{-1}$ ) (unpublished data of H. Yang). On the other hand, carbon loading was also high,  $465.8 \text{ g m}^{-2} \text{ y}^{-1}$ , due to high inputs from sewage and land runoff. It therefore seems that the model developed in north temperate lakes may not be suitable for interpreting the carbon sink function of Lake Donghu. We argue that the main reasons for the relatively high carbon sink function of Lake Donghu are due to high primary production, substantive allochthonous carbon inputs and intensive anthropogenic activity.

The subtropical climate around Lake Donghu is typically characterized by high temperatures which result in higher primary production (average NPP 1440 mg C m<sup>-2</sup> d<sup>-1</sup>, range from 254 mg C m<sup>-2</sup> d<sup>-1</sup> to 2330 mg C m<sup>-2</sup> d<sup>-1</sup> during the study period, for more details see Xing et al., 2005) than temperate lakes (Liu, 1990). In eutrophic lakes, primary production by algae is also higher than mesotrophic lakes, so aqueous CO<sub>2</sub> is depleted and atmospheric CO<sub>2</sub> diffuses into the surface waters (Schindler et al., 1997; Xing et al., 2005; Xing et al., 2006), particularly in spring and summer (Fig. 3), resulting in relatively small CO<sub>2</sub> emission in Lake Donghu.

Furthermore, eutrophic Lake Donghu receives more allochthonous carbon inputs (409.8 g m $^{-2}$  y $^{-1}$ ) than other lakes such as Mirror Lake (12.3 g m $^{-2}$  y $^{-1}$ , Cole et al., 1989) and Lake Michigan (8.0 g m $^{-2}$  y $^{-1}$ , Biddanda and Cotner, 2002) due to the high sewage influx, which amounts to 88% of the total input. Allochthonous carbon, which survives microbial attack in the watershed and in the soil system, has already been processed and decomposed to some degree by the biota, removing the most labile compounds before it enters lake. Compared to autochthonous carbon from phytoplankton primary production, allochthonous carbon is recalcitrant and difficult to assimilate (Wetzel, 1995; Cole et al., 2000) due to a relatively high molecular weight and aromaticity (Moran and Hodson, 1994). Consequently, it is likely that large

Table 3
Comparison of the ratios of gaseous carbon exchange to carbon burial in various freshwater lakes

Lake	Location	Trophic state	Ratio	Source
Lake Donghu	30°33′N, 114°23′E	Eutrophic	0.08	This study
Blue Chalk Lake	45°11′N, 78°56′W	Oligotrophic	-0.09	Dillon and Molot (1997)
Chub Lake	45°13′N, 78°59′W	Mesotrophic	2.24	Dillon and Molot (1997)
Crosson Lake	45°05′N, 77°20′W	Mesotrophic	3.43	Dillon and Molot (1997)
Dickie Lake	45°13′N, 78°59′W	Mesotrophic	1.16	Dillon and Molot (1997)
Harp Lake	45°23′N, 79°07′W	Oligotrophic	1.15	Dillon and Molot (1997)
Plastic Lake	45°11′N, 78°50′W	Oligotrophic	3.88	Dillon and Molot (1997)
Red Chalk Lake	45°11′N, 78°56′W	Oligotrophic	0.49	Dillon and Molot (1997)
Mirror Lake	43°56.5′N, 71°41.5′W	Oligotrophic	1.6	Cole and Caraco (1998)
79 536 lakes and total running water	21 major Scandinavian catchments		8	Algesten et al. (2004)
World lakes average			2.3	Mulholland and Elwood (1982), Cole et al. (1994)

amounts of allochthonous carbon entered sediment and eventually became carbon burial in Lake Donghu. It should be pointed out, however, that there is difference in the sources of allochthonous carbon in Lake Donghu and north temperate/boreal lakes. In Lake Donghu, although land runoff contributed some to the allochthonous carbon, semi-treated sewage is the most important source whereas in north temperate/boreal lakes, the allochthounous carbon is of more natural origin, which reflects the soils' processes in forested catchment areas. Compared to allochthonous carbon in north temperate/boreal lakes, allochthonous carbon in Lake Donghu is probably not very recalcitrant in nature. Further investigations into the fate of allochthonous carbon in the lake are required though to provide better evidence for this.

Anthropogenic activity also results in the high carbon burial in Lake Donghu sediments. Agriculture and other types of land-cover change (conversion of forests and farmlands to cities, residential lands, and other man-made constructions) promote soil erosion, leading to an increase in sedimentation rates (Yang et al., 2005b) and the accumulation of particular organic carbon (POC) in lake sediments (Kortelainen et al., 2004). The high percentage of carbon retained in the system is also strongly related to the long lake water residence time (Marion and Brient, 1998). The Qingshan Canal, built in 1957, has greatly reduced water exchange between Lake Donghu and the Yangtze River. Moreover, separate areas of the lake areas have little interconnection because of artificial dykes (Tang and Xie, 2000). These factors combine to increase water residence times, which facilitate carbon retention (Marion and Brient, 1998; Tang and Xie, 2000).

# 4.3. Comparison of the overall mass balance to the gas exchange and carbon burial balance

The carbon budget from the overall mass balance clearly shows that the amount of carbon entering Lake Donghu exceeded the total output, indicating that Lake Donghu is a carbon sink. The ratio of gaseous carbon emission to carbon burial, considerably less than 1, also clearly shows the carbon sink function of Lake Donghu. Both methods indicate that subtropical, eutrophic Lake Donghu is a great carbon sink and as such there is reasonable agreement between the two

methods. However, although the two methods resulted in similar results, the time and money spent for each was different. Using the overall mass balance approach, the carbon source/sink function of a lake ecosystem is not obtained unless the total inputs and outputs of carbon are known. A balance between gaseous carbon evasion and carbon burial therefore has an advantage over the overall mass balance in that sediment cores can be collected one or two times during the year, thus eliminating the need for extensive monitoring programmes. Potential disadvantages of this method though are that only a long-time average estimate of carbon burial is produced and the long-term average may be inapplicable to each year in some cases (Quay et al., 1986).

# 4.4. Importance of gaseous carbon exchange in the carbon budget

A floating static chamber technique, which can directly measure CO2 and CH4 fluxes across the water-air interface, was used to achieve a more comprehensive carbon budget in Lake Donghu from April 2003 to March 2004. The gaseous carbon fluxes obtained by static chamber technique are somewhat higher than the values from thin boundary layer method, as ebullition is absent in the latter method (Richey et al., 1988; Devol et al., 1990; Bubier et al., 1993). Although there are some shortages of static chamber technique, the gas fluxes are relatively reliable as ebullition is included in this technique. Gaseous carbon emission, often overlooked in previous studies, contributed to 15% of the total output in Lake Donghu. CH<sub>4</sub> emission, nearly always neglected in many lake carbon budget studies, accounted for 2% of the total output. Not considering the gaseous carbon emission will underestimate the total carbon output, perhaps in some cases even incorrectly reversing the calculated carbon source/sink function.

# 5. Conclusions

The net carbon budget of Lake Donghu was +9955 t, indicating that the lake acts as a net sink and retained 9955 t carbon in the water column and sediment during the study period. A relatively low ratio of gas emission across the water—air interface (752 t) to carbon burial into sediments (9481 t) of 0.08

further indicates that Lake Donghu is a significant carbon sink. Both the overall mass balance and the gas exchange and carbon burial balance showed Lake Donghu to be a carbon sink. This mainly results from the high primary production, substantive allochthonous carbon inputs and intensive anthropogenic activities in and around the lake. Gaseous carbon emission accounted for 15% of the total output, indicating that the total output from a lake can be underestimated unless gaseous carbon exchanges are fully taken into account.

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## References

- APHA, AWWA, WPCF, 1995. Standard Methods for the Examination of Water and Wastewater, 19th ed. American Public Health Associaton, Washington, DC.
- Abril, G., Guerin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., Tremblay, A., Varfalvy, L., Dos-Santos, M.A., Matvienko, B., 2005. Carbon dioxide and methane emissions and the carbon budget of a 10-year old tropical reservoir (Petit Saut, French Guiana). Global Biogeochemical Cycles 19, GB4007.
- Algesten, G., Sobek, S., Bergstrom, A.K., Agren, A., Tranvik, L.J., Jansson, M., 2004. Role of lakes for organic carbon cycling in the boreal zone. Global Change Biology 10, 141–147.
- Andersson, E., Kumblad, L., 2006. A carbon budget for an oligotrophic clearwater lake in mid-Sweden. Aquatic Sciences 68, 52-64.
- Appleby, P.G., Nolan, P.J., Gifford, D.W., Godfrey, M.J., Oldfield, F., Anderson, N.J., Battarbee, R.W., 1986. <sup>210</sup>Pb dating by low background gamma-counting. Hydrobiologia 143, 21–27.
- Biddanda, B.A., Cotner, J.B., 2002. Love handles in aquatic ecosystems: the role of dissolved organic carbon drawdown, resuspended sediments, and terrigenous inputs in the carbon balance of Lake Michigan. Ecosystems 5, 431–445.
- Bubier, J.L., Moore, T.R., Roulet, N.T., 1993. Methane emissions from wet-lands in the midboreal region of Northern Ontario, Canada. Ecology 74, 2240–2254.
- Carpenter, J.W., Green, R.H., Paterson, C.G., 1983. A preliminary organic-carbon budget for a small dystrophic lake in maritime Canada. Hydrobiologia 106, 275–282.
- Casper, P., Maberly, S.C., Hall, G.H., Finlay, B.J., 2000. Fluxes of methane and carbon dioxide from a small productive lake to the atmosphere. Biogeochemistry 49, 1–19.
- Chan, A.S.K., Prueger, J.H., Parkin, T.B., 1998. Comparison of closed-chamber and Bowen-ratio methods for determining methane flux from peatland surfaces. Journal of Environmental Quality 27, 232–239.
- Charlton, M.N., 1977. Carbon budgets in Lake Ontario. Journal of the Fisheries Research Board of Canada 34, 1240—1241.
- Cole, J.J., Caraco, N.F., 1998. Atmospheric exchange of carbon dioxide in a low-wind oligotrophic lake measured by the addition of SF6. Limnology and Oceanography 43, 647–656.
- Cole, J.J., Caraco, N.F., Kling, G.W., Kratz, T.K., 1994. Carbon-dioxide supersaturation in the surface waters of lakes. Science 265, 1568–1570.
- Cole, J.J., Caraco, N.F., Strayer, D.L., Ochs, C., Nolan, S., 1989. A detailed organic-carbon budget as an ecosystem-level calibration of bacterial respiration in an oligotrophic lake during midsummer. Limnology and Oceanography 34, 286–296.

- Cole, J.J., Pace, M.L., Carpenter, S.R., Kitchell, J.F., 2000. Persistence of net heterotrophy in lakes during nutrient addition and food web manipulations. Limnology and Oceanography 45, 1718–1730.
- Crusius, J., Anderson, R.F., 1991. Core compression and surficial sediment loss of lake-sediments of high porosity caused by gravity coring. Limnology and Oceanography 36, 1021–1030.
- Dean, W.E., Gorham, E., 1998. Magnitude and significance of carbon burial in lakes, reservoirs, and peatlands. Geology 26, 535–538.
- Devol, A.H., Richey, J.E., Forsberg, B.R., Martinelli, L.A., 1990. Seasonal dynamics in methane emissions from the Amazon River floodplain to the troposphere. Journal of Geophysical Research Atmospheres 95, 16417—16426.
- Dillon, P.J., Molot, L.A., 1997. Dissolved organic and inorganic carbon mass balances in central Ontario lakes. Biogeochemistry 36, 29–42.
- Duchemin, E., Lucotte, M., Canuel, R., 1999. Comparison of static chamber and thin boundary layer equation methods for measuring greenhouse gas emissions from large water bodies. Environmental Science & Technology 33, 350–357.
- Eadie, B.J., Robertson, A., 1976. An IFYGL carbon budget for Lake Ontario. Journal of Great Lakes Research 2, 307–323.
- Einsele, G., Yan, J.P., Hinderer, M., 2001. Atmospheric carbon burial in modern lake basins and its significance for the global carbon budget. Global and Planetary Change 30, 167–195.
- Fitzgerald, S.A., Gardner, W.S., 1993. An algal carbon budget for pelagic—benthic coupling in Lake Michigan. Limnology and Oceanography 38, 547–560
- Hanson, P.C., Pollard, A.I., Bade, D.L., Predick, K., Carpenter, S.R., Foley, J.A., 2004. A model of carbon evasion and sedimentation in temperate lakes. Global Change Biology 10, 1285–1298.
- Huttunen, J.T., Alm, J., Liikanen, A., Juutinen, S., Larmola, T., Hammar, T., Silvola, J., Martikainen, P.J., 2003. Fluxes of methane, carbon dioxide and nitrous oxide in boreal lakes and potential anthropogenic effects on the aquatic greenhouse gas emissions. Chemosphere 52, 609-621.
- Kelly, C.A., Rudd, J.W.M., Bodaly, R.A., Roulet, N.P., StLouis, V.L., Heyes, A., Moore, T.R., Schiff, S., Aravena, R., Scott, K.J., Dyck, B., Harris, R., Warner, B., Edwards, G., 1997. Increases in fluxes of greenhouse gases and methyl mercury following flooding of an experimental reservoir. Environmental Science & Technology 31, 1334–1344.
- Kortelainen, P., Pajunen, H., Rantakari, M., Saarnisto, M., 2004. A large carbon pool and small sink in boreal Holocene lake sediments. Global Change Biology 10, 1648–1653.
- Liu, J.K., 1990. Ecological Studies of Lake Donghu (1). Science Press, Beijing (in Chinese).
- Maier, W.J., Swain, W.R., 1978. Lake Superior organic-carbon budget. Water Research 12, 403–412.
- Marion, L., Brient, L., 1998. Wetland effects on water quality: input—output studies of suspended particulate matter, nitrogen (N) and phosphorus (P) in Grand-Lieu, a natural plain lake. Hydrobiologia 374, 217–235.
- Mcconnaughey, T.A., Labaugh, J.W., Rosenberry, D.O., Striegl, R.G., Reddy, M.M., Schuster, P.F., Carter, V., 1994. Carbon budget for a ground-water-fed lake calcification supports summer photosynthesis. Limnology and Oceanography 39, 1319–1332.
- Moran, M.A., Hodson, R.E., 1994. Support of bacterioplankton production by dissolved humic substances from three marine environments. Marine Ecology Progress Series 110, 241–247.
- Mulholland, P.J., Elwood, J.W., 1982. The role of lake and reservoir sediments as sinks in the perturbed global carbon-cycle. Tellus 34, 490–499.
- Muller, B., Maerki, M., Schmid, M., Vologina, E.G., Wehrli, B., Wuest, A., Sturm, M., 2005. Internal carbon and nutrient cycling in Lake Baikal: sedimentation, upwelling, and early diagenesis. Global and Planetary Change 46, 101–124.
- Ni, L.Y., 1996. Long-term change of the structure and biodiversity of aquatic vegetation of Lake Donghu, Wuhan. Acta Hydrobiologica Sinica 20 (Suppl.), 60-74 (in Chinese, with English abstract).
- Page, S.E., Wust, R.A.J., Weiss, D., Rieley, J.O., Shotyk, W., Limin, S.H., 2004. A record of Late Pleistocene and Holocene carbon accumulation and climate change from an equatorial peat bog (Kalimantan, Indonesia): implications for past, present and future carbon dynamics. Journal of Quaternary Science 19, 625–635.

- Quay, P.D., Emerson, S.R., Quay, B.M., Devol, A.H., 1986. The carbon-cycle for Lake Washington — a stable isotope study. Limnology and Oceanography 31, 596—611.
- Rantakari, M., Kortelainen, P., 2005. Interannual variation and climatic regulation of the  $\rm CO_2$  emission from large boreal lakes. Global Change Biology 11, 1368–1380.
- Richey, J.E., Devol, A.H., Wofsy, S.C., Victoria, R., Riberio, M.N.G., 1988. Biogenic gases and the oxidation and reduction of carbon in Amazon River and floodplain waters. Limnology and Oceanography 33, 551–561.
- Schindler, D.E., Carpenter, S.R., Cole, J.J., Kitchell, J.F., Pace, M.L., 1997. Influence of food web structure on carbon exchange between lakes and the atmosphere. Science 277, 248–251.
- Stallard, R.F., 1998. Terrestrial sedimentation and the carbon cycle: coupling weathering and erosion to carbon burial. Global Biogeochemical Cycles 12, 231–257.
- Tang, H.J., Xie, P., 2000. Budgets and dynamics of nitrogen and phosphorus in a shallow, hypereutrophic lake in China. Journal of Freshwater Ecology 15, 505-514
- Wang, Y.S., Wang, Y.H., 2003. Quick measurement of CH<sub>4</sub>, CO<sub>2</sub> and N<sub>2</sub>O emissions from a short-plant ecosystem. Advances in Atmospheric Sciences 20, 842–844.
- Wetzel, R.G., 1995. Death, detritus, and energy-flow in aquatic ecosystems. Freshwater Biology 33, 83–89.
- Wetzel, R.G., 2001. Limnology, Lake and River Ecosystems. Academic Press, New York.

- Wickland, K.P., Striegl, R.G., Mast, M.A., Clow, D.W., 2001. Carbon gas exchange at a southern Rocky Mountain wetland, 1996—1998. Global Biogeochemical Cycles 15, 321—335.
- Xie, P., Liu, J.K., 2001. Practical success of biomanipulation using filter-feeding fish to control cyanobacteria blooms: a synthesis of decades of research and application in a subtropical hypereutrophic lake. The Scientific World 1, 337–356.
- Xing, Y.P., Xie, P., Yang, H., Ni, L.Y., Wang, Y.S., Rong, K.W., 2005. Methane and carbon dioxide fluxes from a shallow hypereutrophic subtropical Lake in China. Atmospheric Environment 39, 5532—5540.
- Xing, Y.P., Xie, P., Yang, H., Ni, L.Y., Wang, Y.S., Tang, W.H., 2004. Diel variation of methane fluxes in summer in a eutrophic subtropical lake in China. Journal of Freshwater Ecology 19, 639–644.
- Xing, Y.P., Xie, P., Yang, H., Wu, A.P., Ni, L.Y., 2006. The change of gaseous carbon fluxes following the switch of dominant producers from macrophytes to algae in a shallow subtropical lake of China. Atmospheric Environment 40, 8034–8043.
- Yang, H., Xie, P., Xing, Y.P., Ni, L.Y., Guo, H.T., 2005a. Attenuation of photosynthetically available radiation by chlorophyll, chromophoric dissolved organic matter, and tripton in Lake Donghu, China. Journal of Freshwater Ecology 20, 575–581.
- Yang, H., Yi, C., Xie, P., Xing, Y., Ni, L., 2005b. Sedimentation rates, nitrogen and phosphorus retentions in the largest urban Lake Donghu, China. Journal of Radioanalytical and Nuclear Chemistry 267, 205-208.