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Comparison of Relationships Between pH, Dissolved Oxygen and Chlorophyll *a* for Aquaculture and Non-aquaculture Waters

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Abstract The relationships between pH, dissolved oxygen (DO) and chlorophyll *a* in aquaculture and non-aquaculture waters are assessed in this paper. The research includes the evaluation of field and experimental studies at the Panjiakou Reservoir (between Aug and Oct 2009) and the review of international data covering two decades. The results indicated that typical eutrophic non-aquaculture water had mean concentrations of chlorophyll *a* of higher than 10 μg L^{-1}, and significant positive correlations were found between pH, DO and chlorophyll *a*. When the mean concentration of chlorophyll *a* was less than 10 μg L^{-1}, no correlation was found between DO and chlorophyll *a* for waters with a high exchange rate or heavily organically polluted natural waters. Diurnal variations were found for both pH and DO. A corresponding significant positive correlation was found between both water quality parameters. In general, when the mean concentration of chlorophyll *a* was less than 10 μg L^{-1} within aquaculture waters of low exchange rate, only a weak or no correlation at all was found between pH, DO and chlorophyll *a* during summer and autumn. On the other hand, a significant positive correlation between pH and chlorophyll *a* and a significant positive correlation or no correlation between DO and chlorophyll *a* were found for aquaculture waters with a high exchange rate during summer and autumn. Strong diurnal variations for both pH and DO were identified. A significant positive linear correlation between pH and DO was found for field enclosure experiments.

Keywords Aquaculture · Carp · Correlation analysis · Diurnal water quality variations · Eutrophic waters · Organic pollution

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1 Introduction

1.1 Background and Problem Identification

Due to the rapid development of industry and agriculture in the last decade, large amounts of nitrogen and phosphorus associated with fertilizers were discharged to oceans, rivers, lakes, reservoirs and other waters, subsequently causing eutrophication (Albay et al. 2003; Domaizon and Devaux 1999; Scholz 2006). Accelerated eutrophication has become one of the world's most serious environmental problems (Fisher et al. 1995; Nixon 1995; Nyenje et al. 2010), and associated symptoms, including the growth of attached and planktonic algae, can be identified in about 75% of the global closed waters (Freedman 2002).

The pH is a key chemical water indicator (Lin 1990; Howland et al. 2000). Its value can rise up to 9 or 10 for eutrophic waters (Scholz 2006). A high pH may inhibit the photosynthesis of algae (Bowmer and Muirhead 1987; Jin 1992; Dai 2009). The DO is one of the limiting factors for aquatic physiological metabolism, and its value is an indicator of aquatic growth conditions and pollution status (Bolton et al. 1978; Snieszko 1974). For eutrophic waters, the DO concentration shows diurnal variations due to algal photosynthesis and aquatic respiration (Ansa-Asare et al. 2000; Scholz 2006).

Chlorophyll *a* is an important indicator for the presence of algae, and it is often considered as the dominant factor for assessing eutrophication (Jayaweera and Asaeda 1995; Yung et al. 1997; Zhou et al. 2004). Algal growth is closely related to a variety of environmental water quality parameters such as total nitrogen, total phosphorus, light intensity, water temperature, pH and DO (Lovell and Konopka 1985; Scholz 2006; Smith 1983). Changes in the number and composition of algae often relate to these parameters (Zhou and Gao 2000). Wang et al. (2000, 2004) have reported that there is a strong correlation between the pH and the amount of algae, and the DO and the amount of algae for eutrophic waters. If pH and/or DO could be regularly monitored as part of a long-term study, correlations between water quality parameters could be identified, and a severe algal bloom may subsequently be forecasted early (Wang et al. 2001).

1.2 Correlations Between pH and Chlorophyll *a*

The pH value is governed by the amount of carbon dioxide, which can react with water, as well as carbonate and bicarbonate to form complex but reversible carbonate systems. Different components of the system interrelate according to the equilibria shown in Eqs. 1 to 4. Note that the equilibria between carbonate and metal ions together with effects of carbonate solids have not been considered in this study.

$$CO_2(g) \Leftrightarrow CO_2(aq); K_H = 10^{-1.5} \quad (1)$$

$$CO_2(aq) + H_2O \Leftrightarrow H_2CO_3; K_1 = 10^{-2.8} \quad (2)$$

$$H_2CO_3 \Leftrightarrow HCO_3{}^- + H^+; K_2 = 10^{-3.5} \quad (3)$$

$$HCO_3{}^- \Leftrightarrow CO_3{}^{2-} + H^+; K_3 = 10^{-10.3} \quad (4)$$

The pH value is influenced by changes of the ion concentration in the above equilibria (Eqs. 1 to 4). The carbon dioxide concentration is also influenced by algal photosynthesis, aquatic respiration, water temperature and oxidative decomposition of organic matter. Algal photosynthesis can transform carbon dioxide into organic matter ($C_6H_{12}O_6$; Eq. 5) and oxygen, while aquatic respiration uses organic matter, resulting in the production of carbon dioxide. Photosynthesis and respiration may be characterized by Eqs. 5 and 6 (Zhang et al. 2009).

$$6CO_2 + 6H_2O + E \xrightarrow{\text{light}} C_6H_{12}O_6 + 6O_2 \quad (5)$$

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy} \quad (6)$$

Due to photosynthetic activities, carbon dioxide is quickly taken up by algae, which results in a shift of the equilibrium (Eq. 7) in favour of $HCO_3{}^-$ decomposition and increase of the pH value. Reversely, the increase of carbon dioxide produced by aquatic respiration processes can inhibit the $HCO_3{}^-$ decomposition and causes subsequently the decrease of the pH value. The dissociation reaction of HCO_3^- is shown in Eq. 7 (Welch 1992; Wetzel 1983).

$$HCO_3^- \Leftrightarrow OH^- + CO_2 \tag{7}$$

The water temperature indirectly controls the rate of algal photosynthesis and aquatic respiration through enzymes, leading to changes in the carbon dioxide content due to metabolic activities as shown in Eqs. 5 and 6. Previous studies showed that water temperature can promote algal photosynthesis and aquatic respiration at certain temperature ranges (Konopka and Brock 1978; Masaki and Seki 1984; Qi et al. 2008). The solubility of carbon dioxide within water is also affected by temperature. When atmospheric pressure is constant, a rise of water temperature results in the kinetic rate of carbon dioxide to increase. This allows for carbon dioxide to escape easily from the water surface, leading to a lower solubility. As the water temperature decreases, the solubility of carbon dioxide increases at the same time (Liu et al. 1998).

Algal debris and other organic pollutants can be converted into carbon dioxide, HNO_2 and HNO_3 (Eqs. 9 and 10) under biochemical oxidation, resulting in a decrease in pH. The corresponding oxidation reactions are shown in Eqs. 8 to 10 (Zhao 2007).

$$RCH(NH_2)COOH + O_2 \longrightarrow RCOOH + CO_2 + NH_3 \tag{8}$$

$$2NH_3 + 3O_2 \longrightarrow 2HNO_2 + 2H_2O \tag{9}$$

$$2HNO_2 + O_2 \longrightarrow 2HNO_3 \tag{10}$$

The pH value is closely related to the level of algal activity and abundance (You et al. 2007). Correlations between pH and chlorophyll *a*, as published by other researches, are summarized in Table 1. Previous research is based on non-aquaculture and aquaculture water and has been undertaken for laboratory micro-ecosystems, field enclosures experimental and natural waters (aquaculture waters).

1.3 Correlations Between Dissolved Oxygen and Chlorophyll *a*

Re-aeration and photosynthetic oxygen production are the main oxygen inputs, while aquatic respiration is the main oxygen sink. Changes in DO concentration are calculated according to Eqs. 11 and 12 (Ansa-Asare et al. 2000).

$$dC/dt = k_a(C_{sat} - C) + P - R_g \tag{11}$$

where C is the concentration of dissolved oxygen (milligrams per litre); k_a is the re-aeration constant (per day), which is related to hydrological conditions and water temperature; C_{sat} is the DO saturation concentration (milligrams per litre); P is the photosynthetic rate (milligrams per litre per day), which is a function of temperature, light and chlorophyll *a* and R_g is the aquatic respiration (milligrams per litre per day).

$$R_g = R + k_1(\text{BOD}) \tag{12}$$

where R_g is the aquatic respiration (milligrams per litre per day); R is the plant or algal respiration (milligrams per litre per day); k_1 (per day) is a constant, which depends on the concentrations of dissolved organic carbon and nutrients and BOD is the biological oxygen demand (milligrams per litre).

Equation 13 (Talling 1957) can be used to characterize the photosynthetic rate of both plants and algae. A typical value for the solar radiation measured time-dependently is 500 Ly day^{-1}.

$$P_t = P_{max}\frac{\frac{I_t}{I_k}}{\sqrt{1+\left(\frac{I_t}{I_k}\right)^2}} \tag{13}$$

where P is the photosynthetic rate at time t, P_{max} is the maximum photosynthetic rate, I_t is the solar radiation measured time-dependently (lights per day) and I_k is the optimal light intensity for plant or algal growth.

Therefore, the DO concentration is also linked to the activities of algae (Odum 1956). Correlations between DO and chlorophyll *a* for published research are shown in Table 2. Research on both non-aquaculture and aquaculture waters were undertaken. Findings are separated into laboratory-based micro-ecosystems, experimental field enclosures and natural waters.

1.4 Correlations Between pH and Dissolved Oxygen

Changes in pH and DO are both affected by algal photosynthesis, aquatic respiration, water temperature and oxidative decomposition of organic matter (Scholz 2006). Moreover, the consumption or production of

Table 1 Correlation and regression analysis for relationships between pH and chlorophyll *a*

Water type	Water type	Researcher	Research site	Regression equation	Correlation coefficient *r*
Non-aquaculture water	Laboratory micro-ecosystem	You et al. (2007)	Laboratory cylinder	pH=8.89+0.05Chl-a	0.93** (n=9)
		Li et al. (2007)	Laboratory aquarium	5 treatments	0.51*–0.77* (n=16)
	Experimental field enclosure	Kaya et al. (2005)	Enclosure at the Dianchi Lake	pH=7.38+0.45ln (Chl-a−0.26) (Encl. C)	0.92** (n=6)
		Original work reported in this paper	Enclosure at the Panjiakou Reservoir	pH=4.20+1.21ln (Chl-a+2.55) (Encl. 1)	0.73** (n=23)
				pH=9.03−0.11Chl-a (Encl. 0)	−0.92** (n=23)
		Jak et al. (1998)	Enclosure at the North Sea	pH=8.00+0.03Chl-a (C_{TBT}=0 μg L^{-1})	0.53* (n=15)
				C_{TBT}=0.05 μg L^{-1}	0.33 (n=15)
	Natural waters	López-Archilla et al. (2004)	Santa Olalla lake	pH=6.37+0.64ln (Chl-a−10.94)	0.84** (n=16)
		Ruan et al. (2008)	Shallow lakes of Suzhou	pH=7.23+0.03Chl-a	0.53** (n=128)
		Zhang (2009)	Dashahe Reservoir	pH=4.48Chl-$a^{0.22}$	0.50* (n=23)
		Li et al. (2009)	Dianchiwaihai Lake		0.45** (n=480)
Aquaculture water	Experimental field enclosure	Original work reported in this paper	Enclosure at the Panjiakou Reservoir	Encl. 2–4	n=23
	Other aquaculture waters	Ruan and Xu (1998)	Bingzhou of Tong an Bay		0.70* (n=10)
		Porrello et al. (2005)	Orbetello fish farm		−0.54 (n=6)
		Original work reported in this paper	Panjiakou Reservoir		n=23

Aquaculture water includes waters used for artificial breeding of fish, shrimps and shellfish

Chl-a chlorophyll *a* (micrograms per litre), C_{TBT} tributyltin concentration, *Encl* enclosure, *n* number of samples

*p<0.05 (correlation coefficient); **p<0.01 (correlation coefficient)

carbon dioxide is often accompanied by the production or consumption of oxygen. It follows that there is a link between both dissolved gases.

Clean water has oxidation–reduction properties that are related to its acidity (Wang et al. 2001; Inorganic Chemistry Preparation Group 1978) as shown in Eqs. 14 and 15.

$$2H^{+} + 2e^{-} \Leftrightarrow H_2(g); E_0 = 0 \tag{14}$$

$$O_2(g) + 4H^{+} + 4e^{-} \Leftrightarrow 2H_2O(aq); E_0 = +1.23V \tag{15}$$

As pH decreases (i.e. the concentration of H^+ or the activity increases), the redox reaction is shifted to the right. Hydrogen ions and oxygen react with water, which results in a decrease of the DO. An increase of the pH value can shift the redox reaction to the left. However, a high pH might inhibit algal photosynthesis at certain conditions, which does not result in DO increases (Jin 1992). Moreover, published correlations between pH and DO are shown in Table 3. Research studies covered both non-aquaculture and aquaculture waters.

1.5 Rationale and Aims

During the past two decades, many studies have been carried out to describe the relationships between pH, DO and chlorophyll *a*. These studies were mainly undertaken for natural waters such as oceans and

Table 2 Correlation and regression analysis for relationships between DO and chlorophyll *a*

Water type	Water type	Researcher	Research site	Regression equation	Correlation coefficient *r*
Non-aquaculture water	Laboratory micro-ecosystem	You et al. (2007)	Laboratory cylinder	C_{DO}=7.16+0.44Chl-a	0.89** (n=9)
		Li et al. (2007)	Laboratory aquarium	Five treatments	0.55*–0.74* (n=16)
	Experimental field enclosure	Fukushima et al. (2004)	Enclosure at the Kasumigaura Lake	Encl. 1	0.64* (n=13)
		Original work reported in this paper	Enclosure at Panjiakou Reservoir	C_{DO}=−31.0+10.96ln (Chl-a+2.55) (Encl.1)	0.74** (n=23)
				C_{DO}=13.61−0.77Chl-a (Encl. 0)	−0.82** (n=23)
		Song et al. (2008)	Enclosure at the Yellow Sea	C_{DO}=9.38+0.50Chl-a (Encl. M1)	0.98** (n=9)
		Jak et al. (1998)	Enclosure at the North Sea	C_{DO}=5.99+0.38Chl-a (C_{TBT}=0 μg L^{-1})	0.61* (n=15)
				C_{TBT}=0.05 μg L^{-1}	0.44 (n=15)
	Natural waters	Ruan et al. (2008)	Shallow lakes of Suzhou	C_{DO}=2.44+0.23Chl-a	0.45** (n=128)
		Zhang (2009)	Dashahe Reservoir	C_{DO}=1.001Chl-a$^{0.0005}$	0.49* (n=23)
		Luo (2002)	Shenhu Bay	C_{DO}=−0.46Chl-a^2+ 1.87Chl-a+5.05 (May)	±0.77** (n=12)
				C_{DO}=−0.31Chl-a^2+ 3.23Chl-a−1.60 (Sep.)	±0.56 (n=11)
		Li and Wang (2006)	Liaodong Gulf and Seaport of Daliaohe		0.21 (n=22)
		Li et al. (2009)	Dianchiwaihai Lake		0.15 (n=480)
Aquaculture water	Experimental field enclosure	Fukushima et al. (2004)	Enclosure at the Kasumigaura Lake	Encl. 2–6	0.11–0.31 (n=13)
		Original work reported in this paper	Enclosure at the Panjiakou Reservoir	Encl. 2–4	n=23
	Other aquaculture waters	Ruan and Xu (1998)	Bingzhou of Tong an Bay		0.75* (n=10)
		Porrello et al. (2005)	Orbetello fish farm		−0.33 (n=6)
		Xie et al. (2009)	Liusha Bay	Aug.	n=14
				Nov.	n=13
		Original work reported in this paper	Panjiakou Reservoir		n=23

C_{DO} concentration of DO (milligrams per litre), *Chl-a* chlorophyll *a* concentration (micrograms per litre), C_{TBT} tributyltin concentration, *Encl* enclosure, *n* number of samples

*p<0.05 (correlation coefficient), **p<0.01 (correlation coefficient)

lakes, while the study of reservoirs was rather neglected.

In view of the importance of studying the relationships among pH, DO and chlorophyll *a* and the shortcomings of previous studies, the objectives of this paper were to assess the data based on experimental field studies of aquaculture waters, laboratory-based micro-ecosystems and natural waters and to summarize the relationships among pH, DO and chlorophyll *a* in both non-aquaculture and aquaculture waters. This study aims to identify the general relationships between these parameters and provides support for water monitoring, early warning systems and timely strategies for the management and control of eutrophication.

However, a discussion on biomanipulation impacting water quality parameters is beyond the scope of this paper. Readers may refer to relevant and recent literature such as An et al. (2010).

Table 3 Correlation and regression between pH and DO

Water type	Water type	Researcher	Research site	Regression equation	Correlation coefficient r
Non-aquaculture water	Laboratory micro-ecosystem	You et al. (2007)	Laboratory cylinder	C_{DO}=76.91+9.45pH	0.97** (n=9)
	Experimental field enclosure	Jak et al. (1998)	Enclosure at the North Sea	C_{DO}=−72.63+9.87pH (C_{TBT}=0 μg L^{-1})	0.77** (n=15)
		Original work reported in this paper	Enclosure at the Panjiakou Reservoir	C_{DO}=68.55+9.11pH (Encl. 1)	0.97** (n=23)
				C_{DO}=54.52+7.54pH (Encl. 0)	0.89** (n=23)
	Natural waters	Sheng and Xu (1993)	East Sea (shallow station)	C_{DO}=7,802.88+1.27pH	0.97** (n=8)
			East Sea (deep station)	C_{DO}=7,644.07+1.37pH	0.89** (n=13)
		Luo (2002)	Shenhu Bay	C_{DO}=−87.18+11.57pH (May)	0.80** (n=12)
				C_{DO}=−41.59+5.93pH (Sep.)	0.84** (n=11)
		Zhang and Sun (2004)	New Ocean Lake of Yan Tai	C_{DO}=−281.64+27.78pH	0.93** (n=10)
		Zhang (2009)	Dashahe Reservoir		0.51* (n=23)
		Luis et al. (2010)	Itaipu Reservoir	C_{DO}=−10.21+2.47pH	0.63* (n=12)
Aquaculture water	Experimental field enclosure	Original work reported in this paper	Enclosure at the Panjiakou Reservoir	C_{DO}=60.77+8.19pH (Encl. 2)	0.97** (n=23)
				C_{DO}=57.41+7.92pH (Encl. 3)	0.94** (n=23)
				C_{DO}=68.51+9.18pH (Encl. 4)	0.97** (n=23)
	Other aquaculture waters	Wang et al. (1999)	Honghai Bay		0.74* (n=20)
		Xu et al. (2008)	Ponds of Xiangshan Bay	C_{DO}=−31.77+4.76pH (with *Gracilaria lichenoides*)	0.65* (n=13)
		Wang et al. (2009)	From Hukou to Sanmenxia Section of the Yellow River	$C_{DO}=3.322e^{0.064}$pH	0.13 (n=9)
		Original work reported in this paper	Panjiakou Reservoir		n=23

C_{DO} DO concentration (milligrams per litre), C_{TBT} tributyltin concentration, *Encl* enclosure, n number of samples

*p<0.05 (correlation coefficient); **p<0.01 (correlation coefficient)

2 Materials and Methods

2.1 Experimental Setup

In situ enclosure experiments were carried out within the representative culturing water area of the Panjiakou Reservoir, which is about 10 m away from the nearest reservoir bank. The dimensions of the enclosures 0 to 2 were 2.9 m (length) × 2.9 m (width) × 1.5 (depth). In comparison, enclosures 3 and 4 were 0.3 m deeper to allow for the stocking of carp, which prefers deeper water than the bighead carp. Enclosures were fixed to the reservoir bank with the help of anchors and steel ropes. Furthermore, enclosures were designed not to hit the sediment and surrounding reservoir banks.

Enclosures 1 to 4 were designed to examine the relative impacts of bait and fish on the growth of algae: bait (enclosure 1), bighead carp (*Aristichthys novilis*) with bait (enclosure 2), carp (*Cyprinus carpio*) with bait (enclosure 3) and bighead carp and carp with bait (enclosure 4). Enclosure 0 was the experimental control containing neither fish nor bait (Table 4). All

Table 4 Experimental enclosure with different designs

Enclosures		Culturing conditions			Bait dosage (g)
Number	Volume (m^3)	Fish species (–)	Number stocked (–)	Stock density (g fish/m^3 water)	
1	12.6	N/A	N/A	N/A	16.7×3/day
2	12.6	Bighead carp	4	95.24	16.7×3/day
3	15.1	Carp	16	67.22	20.0×3/day
4	15.1	Bighead carp Carp	2 7	66.23	20.0×3/day
0	12.6	N/A	N/A	N/A	N/A

Bait was added with a frequency of three times a day

N/A not applicable

fishes used for this experiment were obtained from a local fishery utilizing the reservoir. The fishes for the same species had similar weights: 250±20 g (mean ± standard deviation) for the bighead carp and 63±9 g for carp. Soybean meal bought from a local fish farm was used as bait. The organic matter, total nitrogen and total phosphorus contents of the soybean meal were 88.20%, 4.67% and 0.83%, respectively.

The enclosures were filled with reservoir water using a submerged pump. After 2 days of acclimation and stabilization, bighead carp and carp were stocked within the enclosures according to the list in Table 4. Bait was added three times per day at dosages of 16.7 g to the enclosures 1 and 2 and 20.0 g to the enclosures 3 and 4. The selected dosages and feeding frequencies were comparable to that of the nearby fish farm. During the study period, no fish jumped in or out of the cages and no predation by birds was recorded. Fish mortality was also monitored every day. Fortunately, all fishes survived the experiment and no dead fish was detected during the whole study period.

2.2 Water Sampling and Analysis

Enclosure and reservoir water samples were collected 0.5 m below the water surface every second day between 18 August and 6 October 2009. Reservoir water samples were assessed to determine the background values for algal biomass and water quality parameters.

All collected water samples were analysed directly for the following parameters: chemical oxygen demand (COD), ammonia nitrogen (NH_4^+-N), nitrate nitrogen (NO_3^--N), dissolved total nitrogen (DTN), total nitrogen (TN), electric conductivity, total dissolved solids, chlorophyll *a*, DO, water temperature (T) and pH. Water quality parameters including COD, NH_4^+-N, NO_3^--N, DTN and TN were determined according to standard methods (APHA, 1998), if not stated otherwise. Water temperature, pH, DO, total dissolved solids, conductivity and chlorophyll *a* were examined by the multi-meter YSI6600 (Beijing SYTF Science and Development Company, Beiyuan Road, Chaoyang District, Beijing, China).

Water samples were also analysed to investigate the variation in dominant algal species. A JKY/FluoroProbe-BBE was used to measure the biomass of total algae, *Cyanophyta* (blue algae), *Chlorophyta* (green algae), *Bacillariophyta* (diatom) and *Cryptomonas*. Furthermore, 7.5 mL of a 1% of Lugool's iodine solution was added to 500 mL of a water samples, and subsequently, the sample was concentrated to 30 mL after sedimentation for 24 h. After full sedimentation, 0.1 mL of a concentrated sample each was used to identify the algal species. Twenty-three valid data points were used for statistical analysis.

2.3 Statistical Analysis

All statistical tests were performed using the Statistical Package for the Social Sciences (SPSS) software package (SPSS 2003). Significances were defined as $p<0.05$, if not stated otherwise.

3 Results and Discussion

3.1 Correlation Between pH and Chlorophyll *a* for Non-aquaculture Waters

The mean concentration of chlorophyll *a* in enclosure 1 was calculated to be 27.5 μg L^{-1}, which is higher than the threshold of 10 μg L^{-1}. The mean chlorophyll *a* concentration of enclosure 0 was only 3.4 μg L^{-1}, which is lower than 10 μg L^{-1}.

Figure 1a shows a logarithmic relationship between pH and chlorophyll *a* for enclosure 1. The correlation coefficient *r* was 0.73 at $p<0.01$. This was mainly due to the rapid growth of algae caused by high concentrations of nitrogen and phosphorus released from continuously dosed bait. Algal photosynthesis consumed large quantities of carbon dioxide resulting in a significant increase of the pH value. Similar research has been performed by Kaya et al. (2005) at the Dianchi Lake. However, the mean chlorophyll *a* concentration for the Dianchi Lake was higher than 10 μg L^{-1}. As shown in Table 1, a corresponding significantly positive logarithmic correlation ($r=0.92$) was found between pH and chlorophyll *a* concentration.

High concentrations of chlorophyll *a* within aquatic environments can consume large amounts of carbon dioxide via photosynthesis. A positive correlation should therefore be identified between the pH value and the concentration of chlorophyll *a* (see above). However, Fig. 1b shows a more significant negative linear correlation ($p<0.01$) between pH and chlorophyll *a* for enclosure 0. This contradicted results possibly because the chlorophyll *a* concentration for enclosure 0 was rather low, and some data were only slightly higher than or even below the detection limit (0.1 μg L^{-1}). Therefore, the detection accuracy may not be high.

You et al. (2007) carried out a similar study with the help of eight cylinders located within a self-built room lit by artificial lighting. The raw water source came from Shichahai Lake. The YSI6600 auto-analyser was used to continuously monitor pH, DO and chlorophyll *a* within a period of 24 h. The pH and chlorophyll *a* data associated with the fifth cylinder were analysed for the purpose of this paper. Daily samples were always taken at 19:00 hours. A correlation and regression analysis was performed, and the corresponding results are shown in Fig. 2.

As the hydrological and meteorological conditions were constant and nutrients were sufficiently abundant in the micro-ecosystem, the mean concentration of chlorophyll *a* was higher than 10 μg L^{-1}, and pH was mainly affected by algal photosynthesis. With an increase in the algal biomass, the consumption of carbon dioxide caused by photosynthesis has increased and subsequently resulted in an increase value of pH. Therefore, a more significant positive linear correlation between pH and chlorophyll *a* was found (Fig. 2). This was broadly consistent with the experimental aquarium-based results performed by Li et al. (2007) as shown in Table 1.

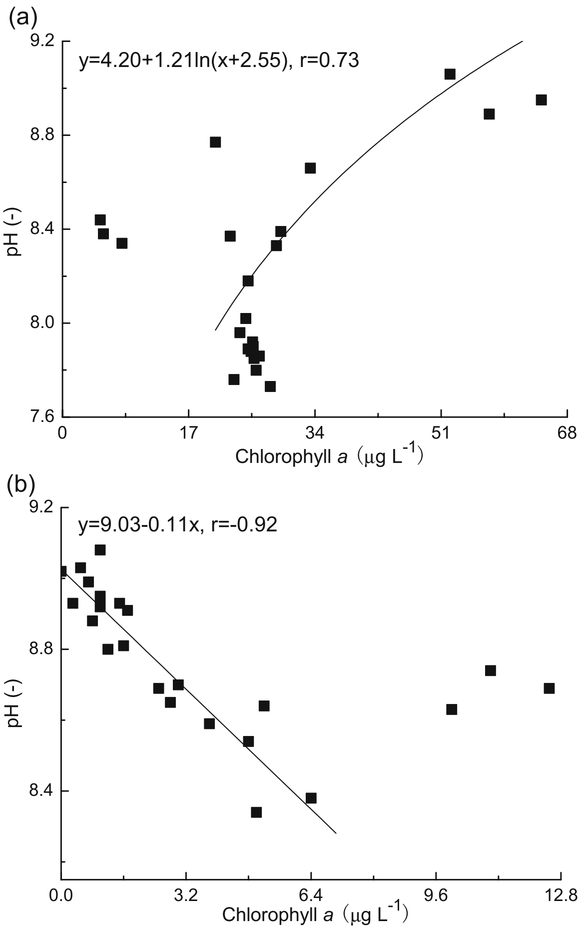

Fig. 1 Regression curves for pH and chlorophyll *a* for **a** enclosure 1 and **b** enclosure 0

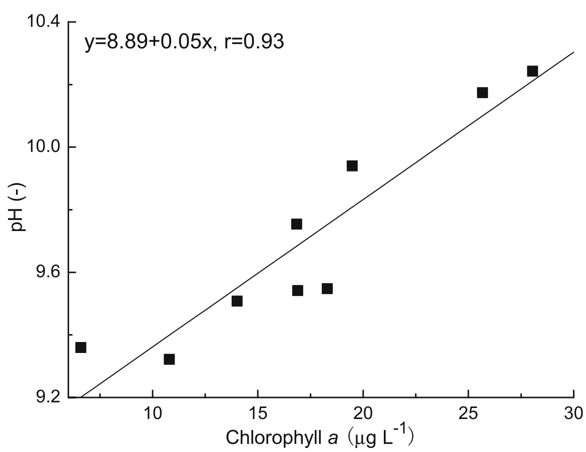

Fig. 2 Regression curve for pH and chlorophyll *a* regarding cylinder 5 (after You et al. 2007)

Jak et al. (1998) have constructed enclosures in the relatively clean North Sea. Even though the mean chlorophyll *a* concentrations of the two enclosures were both lower than 10 μg L^{-1} during the study period, correlations between pH and chlorophyll *a* were not the same. The former one showed a significant positive linear correlation, while no obvious correlation was found for the other enclosure (Table 1). This observation can be explained by the fact that tributyltin, a kind of toxic compound to marine copepod species, was not introduced into the first enclosure at the pre-stage of the experiment (Jak et al. 1998). However, at the post-stage of the experiment, copepods fed on phytoplankton bloomed; thus, the phytoplankton biomass decreased and the consumption of carbon dioxide declined, which resulted in a pH decrease.

In comparison, tributyltin was added to the second enclosure, inhibiting the increase of copepod biomass; thus, the phytoplankton biomass was higher than that for the former and was stable at the post-stage (Jak et al. 1998). The pH consequently decreased. This might be due to the result of zooplankton respiration or oxidative decomposition of organic matter, which generated carbon dioxide to promote a shift of the equilibrium to the left.

Regarding natural waters, as the environmental conditions of natural waters are complex, the relationships between pH and chlorophyll *a* are not of consistent nature. Ruan et al. (2008) concluded that there was a significant positive linear correlation between pH and chlorophyll *a*. They demonstrated that with the increase of phytoplankton biomass, the consumption of carbon dioxide caused by photosynthesis promoted an increase of the pH value. As shown in Fig. 3, a significant positive logarithmic relationship between the pH value and the growth of phytoplankton at favourable temperatures (20–30°C) was found within the hypereutrophic Santa Olalla Lake by López-Archilla et al. (2004). Similarly, Zhang (2009) found a significant positive exponential relationship between pH and chlorophyll *a* for the eutrophic Dashahe Reservoir (Table 1). This can be explained by significant photosynthetic activities consuming large amounts of carbon dioxide, which consequently resulted in a significant increase in pH. Therefore, significant positive correlations were found between pH and chlorophyll *a* for the eutrophic water with a mean chlorophyll *a* concentration higher than 10 μg L^{-1}.

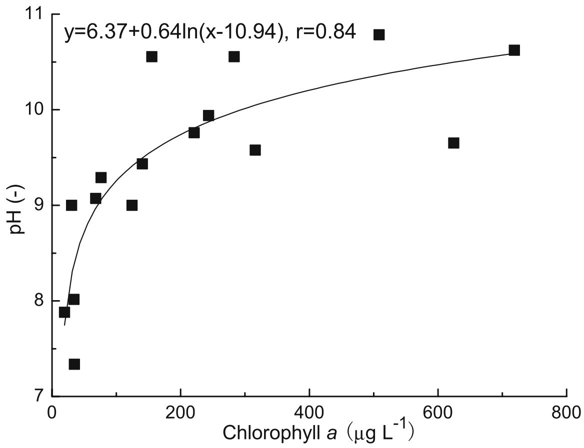

Fig. 3 Regression curve for pH and chlorophyll *a* in Santa Olalla Lake (after López-Archilla et al. 2004)

Li et al. (2009) concluded that the mean chlorophyll *a* concentration for the Dianchiwaihai Lake was lower than 10 μg L^{-1} between 2003 and 2007, although some areas were polluted by industrial and agricultural effluents and domestic sewage. However, the pH was not significantly affected. During the 5-year period of study, Dianchiwaihai Lake had a mean pH of 8.8, which is very favourable for algal growth. As algal numbers increased, the carbon dioxide concentration decreased, and thus, the pH increased. The results showed that a significant positive correlation was found between pH and chlorophyll *a* (Table 1).

For eutrophic non-aquaculture waters, the mean concentration of chlorophyll *a* is usually higher than 10 μg L^{-1}. Although the relationships between pH and chlorophyll *a* were not consistent with respect to the laboratory micro-ecosystems, general findings for experimental field enclosures and natural waters show a significant positive correlation between both parameters. When the mean concentration of chlorophyll *a* was less than 10 μg L^{-1}, the combined effects of algal photosynthesis, aquatic respiration, organic pollutants and other parameters for the field studies and natural waters led to unclear relationships between pH and chlorophyll *a* due to the high system complexities.

3.2 Correlation Between pH and Chlorophyll *a* for Aquaculture Waters

The enclosure experiment in Panjiakou Reservoir was carried out during summer and autumn. The mean concentrations of chlorophyll *a* for enclosures 2 to 4 (all containing fish) were 52.0, 89.0 and 57.0 μg L^{-1}, respectively. Furthermore, the chlorophyll *a* concentration of enclosure 3 containing carp was significantly higher than that of enclosure 2 used for bighead carp and enclosure 4, which comprised both bighead carp and carp ($p<0.01$). As can be seen in Fig. 4, there are no correlations between pH and chlorophyll *a* for enclosures 2 to 4. This was assumed to be the result of complex ecosystems containing fish.

The following paragraphs are concerned with aquaculture waters. During the experiment at the Panjiakou Reservoir, the mean chlorophyll *a* concentration was only 5.4 μg L^{-1}. As shown in Fig. 5, no correlation was found between pH and chlorophyll *a*. Likely reasons were that pH was affected not only by algal photosynthesis but also by aquatic respiration, oxidative decomposition of organic matter in bait residue and high amounts of fish waste brought about by the nature of the large-scale cage culture within the reservoir.

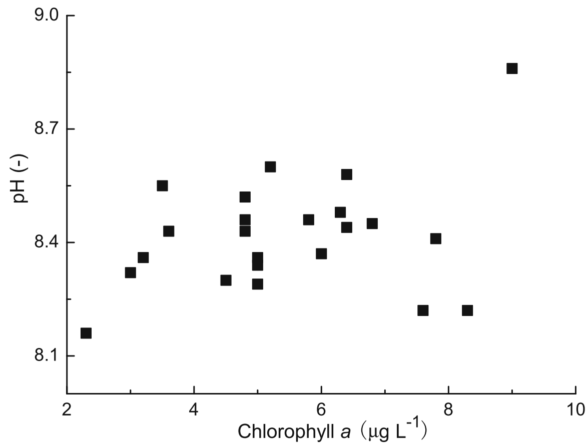

Fig. 5 Regression curve for pH and chlorophyll *a* for the Panjiakou Reservoir

Limited water self-purification due to the relatively high depth of the Panjiakou Reservoir was anticipated. This phenomenon contributed to the complex relationship between pH and chlorophyll *a*. Moreover, Porrello et al. (2005) concluded that the mean chlorophyll *a* concentration of a closed marine fish farm was less than 10 μg L^{-1} during the period between June and November. They also found no obvious correlation between pH and chlorophyll *a* (Table 1).

The mean chlorophyll *a* concentration in the Bingzhou aquaculture waters of Tongan Bay was only about 3 μg L^{-1} during summer and autumn (Ruan and Xu 1998). In contrast to reservoirs and closed fish farms with a limited potential for regular water exchange, gulf aquaculture waters have high water exchange rates due to water currents and waves. This results in organic pollutants such as bait residue and excreta to be rapidly dispersed. Thus, the production of carbon dioxide declines and affects HCO_3^- dissociation, and subsequently, pH is weakened. Therefore, the consumption of carbon dioxide caused by algal photosynthesis controlled HCO_3^- dissociation, and a significant positive correlation was found between pH and chlorophyll *a* (Table 1).

Concerning general aquaculture waters on a field scale, if the mean concentration of chlorophyll *a* is less than about 90 μg L^{-1} during summer and autumn, no correlation can be found between pH and chlorophyll *a*. When the mean concentration of chlorophyll *a* was less than 10 μg L^{-1}, no correlation

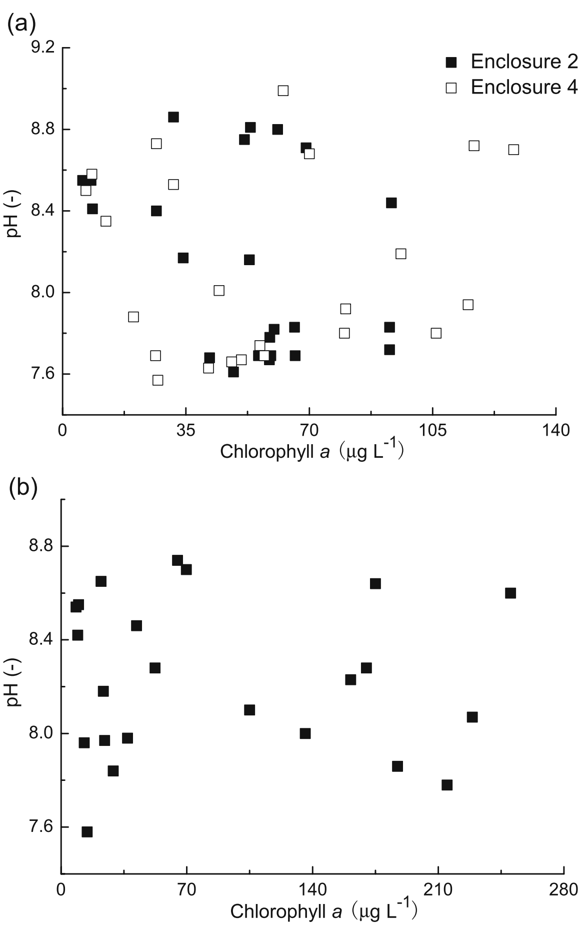

Fig. 4 Regression curves for pH and chlorophyll *a* for **a** enclosures 2 and 4 and **b** enclosure 3

or no obvious correlation has been identified between pH and chlorophyll *a* for water with a low exchange rate. For high rate exchangeable aquaculture waters, a significant positive correlation between pH and chlorophyll *a* can be found. However, there is currently a lack of reliable data obtained from controlled laboratory experiments.

3.3 Correlation Between Dissolved Oxygen and Chlorophyll *a* for Non-aquaculture Waters

Figure 6a shows a logarithmic relationship between DO and chlorophyll *a* for enclosure 1 located within Panjiakou Reservoir. The correlation coefficient *r* was 0.72 at $p<0.01$. This significant correlation was the result of the rapid growth of algae. Corresponding photosynthetic activities led to the production of large amounts of oxygen causing an increase in DO, as evident from Eq. 11. Fukushima et al. (2004) performed a similar study to that of enclosure 1 but in the Kasumigaura Lake, where the mean chlorophyll *a* concentration was higher than 10 μg L^{-1}. Moreover, a significant positive correlation was also found between DO and chlorophyll *a*.

As a general rule of thumb, high phytoplankton activity within waters (i.e. the higher the chlorophyll *a* concentration) can produce a large amount of oxygen. Therefore, changes in DO closely follow adjustments in chlorophyll *a* concentration, and a positive relationship was found between them (see above). However, Fig. 6b shows a more significant negative linear correlation ($p<0.01$) between DO and chlorophyll *a* for enclosure 0. This observation contradicts current study findings, and no explanation can currently be found.

Concerning laboratory micro-ecosystems, You et al. (2007) merely analysed experimental data for cylinder 5. Only daily DO and chlorophyll *a* data determined at 19:00 hours for this cylinder have been used for a subsequent correlation and regression analysis (Fig. 7).

For laboratory-based micro-ecosystems, when the mean concentration of chlorophyll *a* was higher than 10 μg L^{-1}, the DO was mainly affected by algal photosynthesis. With the increase of algal biomass, the production of oxygen subsequently increased the DO. Considering Eq. 11, significant positive linear correlations can be found between DO and chloro-

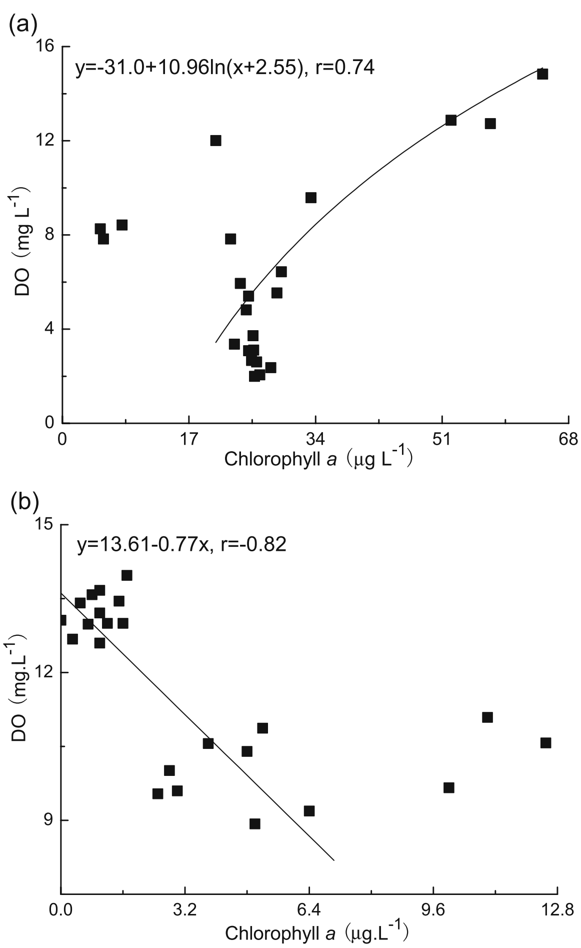

Fig. 6 Regression curves for dissolved oxygen (*DO*) and chlorophyll *a* for **a** enclosure 1 and **b** enclosure 0

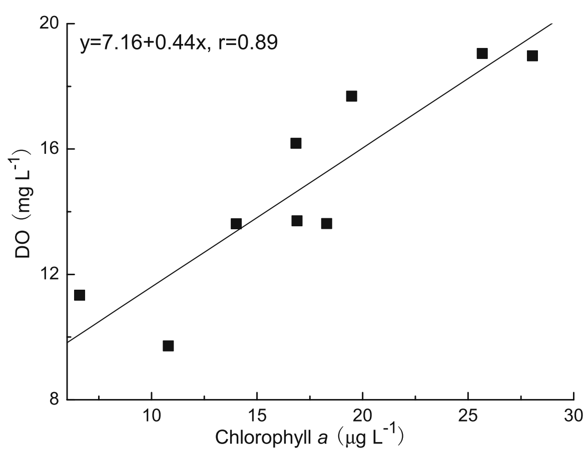

Fig. 7 Regression curve for dissolved oxygen (*DO*) and chlorophyll *a* regarding cylinder 5 (after You et al. 2007)

phyll *a* as summarized in Table 2 (Li et al. 2007; You et al. 2007).

The observed correlations between DO and chlorophyll *a* for two enclosures located in the North Sea were not same (Jak et al. 1998) as shown in Table 2. The possible reason for this was that tributyltin was introduced to one enclosure at the pre-stage of the experiment. This led to an increase of oxygen produced by phytoplankton photosynthesis. While at the post-stage of the experiment, phytoplankton biomass decreased due to the blooming of copepods, which fed on phytoplankton. The production of oxygen consequently declined, and the DO concentration therefore decreased.

Tributyltin is known for inhibiting the increase of copepod biomass. Thus, the phytoplankton biomass was high and stable at the post-treatment stage. However, the DO concentration reduced. This might be a consequence of zooplankton respiration or oxidative decomposition of organic matter depleting oxygen.

Enclosures constructed in the Yellow Sea had relatively clean water (Song et al. 2008). During the study period, phytoplankton growth of enclosure M1 was relatively slow, and the mean chlorophyll *a* concentration was less than 10 μg L^{-1}. Song et al. (2008) pointed out that the DO of this enclosure was mainly affected by phytoplankton photosynthesis. Therefore, the DO concentration increased with an increase of oxygen produced by photosynthesis. A significant positive linear correlation was found between DO and chlorophyll *a* (Table 2).

With respect to natural waters, the significant positive linear (Ruan et al. 2008) and exponential relationship (Zhang 2009) were found between DO and chlorophyll *a*. The former finding demonstrates that with an increase in phytoplankton biomass, the amount of oxygen produced by photosynthesis increases. This subsequently leads to an increase of the concentration of DO. However, the latter one was due to the exponential growth of phytoplankton at an appropriate temperature. Associated photosynthetic activity produced large quantities of oxygen, which resulted in an obvious increase in DO. For the cases where a significant positive correlation was found between DO and chlorophyll *a*, the status of waters was eutrophic and the mean concentrations of chlorophyll *a* were higher than 10 μg L^{-1}.

When the mean concentration of chlorophyll *a* was less than 10 μg L^{-1}, either a quadratic parabola relationship (Luo 2002) or no obvious relationship (Li et al. 2009; Li and Wang 2006) was found between DO and chlorophyll *a*. Luo (2002) showed that as the initial number of phytoplankton within Shenhu Bay was low, photosynthesis produced less oxygen, which was virtually completely absorbed by the sea. This led to a rapid increase in DO.

When the phytoplankton biomass was high and the corresponding production of oxygen increased, the DO increased slowly (Wang et al. 1996). This is because the water became supersaturated with oxygen and only a small part of the oxygen produced by the phytoplankton was absorbed by the sea. However, the research found a weak correlation between DO and chlorophyll *a* for September (Table 2), which might be due to the fact that a frequent occurrence of typhoons has considerably increased the water exchange rate within the whole bay, and re-aeration became a controlling factor for the DO concentration.

The DO of the Dianchiwaihai Lake (Li et al. 2009), Liaodong Gulf and the Seaport of Daliaohe (Li and Wang 2006) were greatly affected by industrial, agricultural and domestic sewage. Decomposition of organic matter subsequently led to the depletion of oxygen (Eq. 11).

For non-aquaculture waters, when the mean concentration of chlorophyll *a* was higher than 10 μg L^{-1}, a significant positive correlation was found between DO and chlorophyll *a* for the experimental field enclosures, laboratory-based micro-ecosystems and natural waters. In comparison, if the mean concentration of chlorophyll *a* was less than 10 μg L^{-1}, only a weak correlation was observed between DO and chlorophyll *a* for both waters with a high exchange rate and for natural waters that were heavily polluted with organic matter. The relationship between DO and chlorophyll *a* for experimental field enclosure waters was not assessed due to a lack of data.

3.4 Correlation Between Dissolved Oxygen and Chlorophyll *a* for Aquaculture Waters

The following two paragraphs are merely concerned with experimental field enclosures. Regarding to the enclosure experiment at Panjiakou Reservoir during summer and autumn (Fig. 8), no correlations between DO and chlorophyll *a* were calculated for enclosures 2 to 4 containing rather complex ecosystems. On one

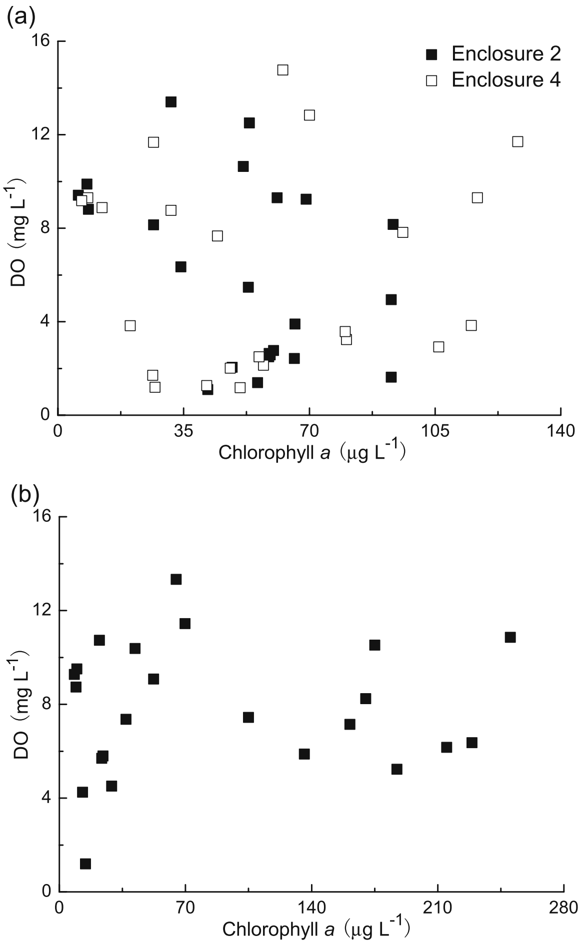

Fig. 8 Regression curves for dissolved oxygen (*DO*) and chlorophyll *a* for **a** enclosures 2 and 4 and **b** enclosure 3

hand, changes in DO concentration are affected by algal photosynthesis and the subsequent production of oxygen. On the other hand, changes in DO concentration are affected by aquatic respiration, oxidative decomposition of organic matter in bait residue, fish waste and the nature of the bottom sediment.

It is likely that the complex interactions between the above processes lead to a more multifaceted link between DO and chlorophyll *a*. Fukushima et al. (2004) concluded that there was no correlations between DO and chlorophyll *a* for fish located within enclosures 2 to 6 of the experiment in the Kasumigaura Lake, where the mean chlorophyll *a* concentration was less than 90 μg L^{-1} (Table 2).

Concerning aquaculture waters such as those applied for the experiment at the Panjiakou Reservoir, there is no correlation between DO and chlorophyll *a* (Fig. 9). This can be explained by the fact that DO was not only affected by algal photosynthesis but also by aquatic respiration, oxidative decomposition of organic matter associated with bait residue and fish waste due to the adverse affects of the large-scale cage culture in the reservoir (see above). Meanwhile, the waters had a certain self-purification capacity. The combined effects of these factors made the relationship between DO and chlorophyll *a* rather complex. Porrello et al. (2005) also concluded that no obvious correlation was found between DO and chlorophyll *a* in a closed marine fish farm during a trial period from June to November (Table 2).

In contrast to reservoirs with a low water exchange rate or closed fish farms, organic pollutants within the Bingzhou aquaculture waters of the Tongan Bay were rapidly dispersed due to water currents and waves. It turns out that the consumption of oxygen declined. Thus, changes in DO concentration were mainly affected by algal photosynthesis, and there was subsequently a significant positive correlation between DO and chlorophyll *a* (Ruan and Xu 1998). Xie et al. (2009) carried out an experiment on aquaculture waters of the Liusha Bay, which is characterized by a high water exchange rate during summer and autumn. The results showed that there was no correlation between DO and chlorophyll *a*, which indicated that findings might also be influenced by specific habitat conditions, different aquaculture species and varying densities.

In general, for experimental aquaculture waters with a mean concentration of chlorophyll *a* less than 90 μg L^{-1} during summer and autumn, no or only a very weak correlation was found between DO and

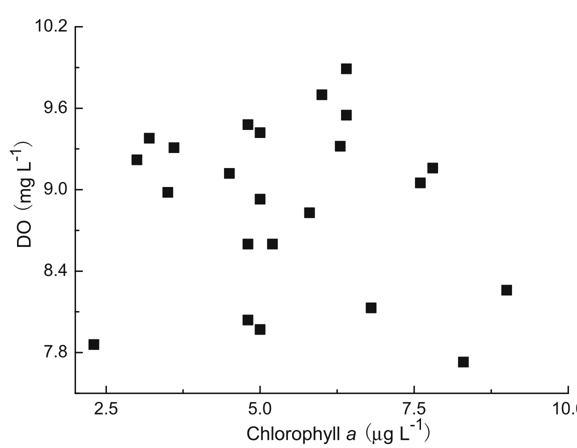

Fig. 9 Regression curve for dissolved oxygen (*DO*) and chlorophyll *a* for the Panjiakou Reservoir

chlorophyll *a*. When the mean concentration of chlorophyll *a* was less than 10 μg L^{-1}, no or only a relatively weak correlation was found between DO and chlorophyll *a* for aquaculture waters with a low water exchange rate during summer and autumn. In comparison, aquaculture waters characterized by a high water exchange rate show a significant positive correlation or no correlation at all between DO and chlorophyll *a*. There is currently a lack of laboratory data to allow for a better assessment of these findings.

3.5 Correlations Between pH and Dissolved Oxygen for Non-aquaculture Waters

Figure 10 indicates that there is a significant positive linear correlation ($p<0.01$) between pH and DO for enclosure 1 of the Panjiakou Reservoir experiment. This was consistent with findings of the North Sea enclosure if $C_{TBT}=0$ μg L^{-1} as reported by Jak et al. (1998), which is summarized in Table 3. However, Fig. 10b shows a significant positive linear correlation ($p<0.01$) between pH and DO for enclosure 0. The negative correlations between both pH and chlorophyll *a* and DO and chlorophyll *a* for enclosure 0 cannot be easily explained with the current knowledge base.

In laboratory micro-ecosystems, pH and DO showed diurnal variations because they were both affected by algal photosynthesis within eutrophic waters. The minimum DO concentration was noted at 07:00 hours and the maximum value was recorded at 17:30 hours (You et al. 2007; Cui et al. 2008).

You et al. (2007) analysed daily experimental pH and DO data for a cylinder at 19:00 hours (Fig. 11). The result shows a more significant positive linear correlation between pH and DO, which is due to the influence of both parameters by algal photosynthesis.

Regarding to the experimental field enclosures, Li et al. (1994) concluded that diurnal variations of pH and DO for eutrophic enclosures of the Dongzhou Reservoir were closely related to the corresponding metabolic activities of algae. The minimum DO was noted for 06:00 hours. After that time point, the DO continuously increased until a maximum was reached at about 18:00 hours.

For natural waters, both pH and DO can have obvious diurnal variations (Moheimani and Borowitzka 2006; Song et al. 2008; Zhang and Sun 2004). Zhang and Sun (2004) analysed a 24-h continuously monitored pH and DO data set for the New Ocean Lake of Yan Tai on

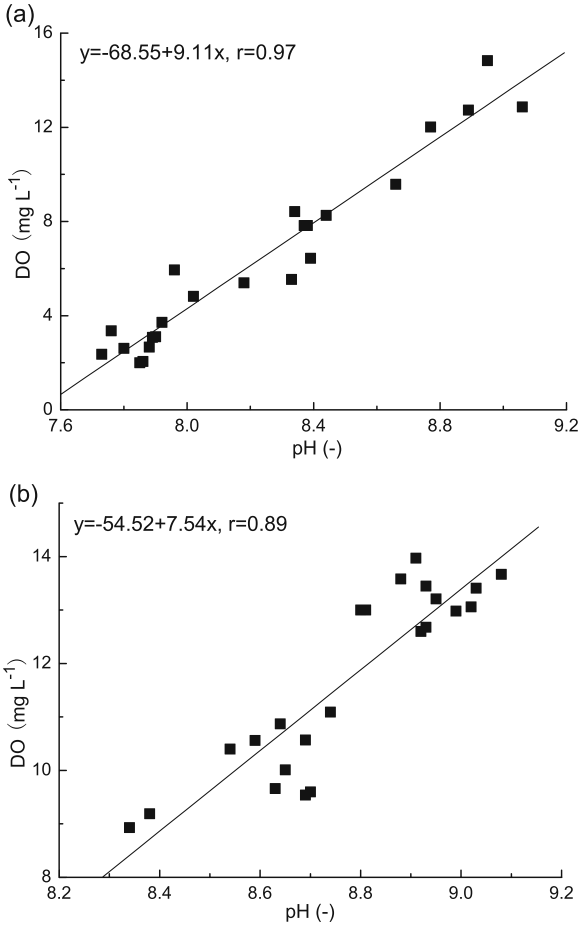

Fig. 10 Regression curves for pH and dissolved oxygen (*DO*) for **a** enclosure 1 and **b** enclosure 0

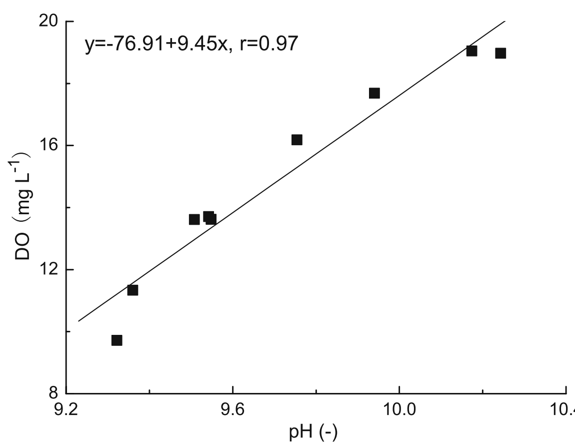

Fig. 11 Regression curve for pH and dissolved oxygen (*DO*) regarding cylinder 5 (after You et al. 2007)

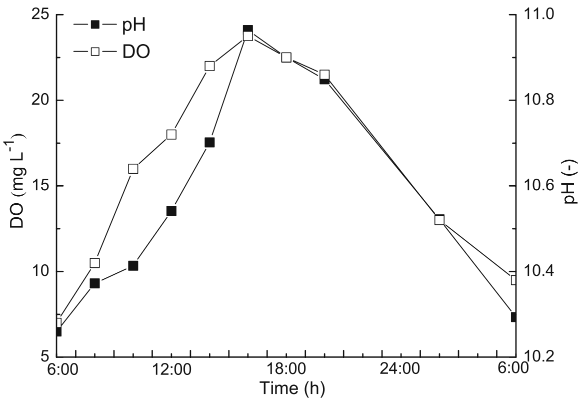

Fig. 12 Distribution of pH and dissolved oxygen (*DO*) for a 24-h experiment (after Zhang and Sun 2004)

17 June 1994. Figure 12 shows that minimum pH and DO values were recorded at 06:00 hours. Both pH and DO continuously increased until 16:00 hours. This can be explained by algal photosynthesis during daylight. The rapid consumption of carbon dioxide resulted in an increase of the pH value. Although aquatic respiration consumed oxygen during the day, the amount of oxygen produced by photosynthesis was much higher. Both pH and DO reached a maximum at around 16:00 hours. Algae and other aquatic organisms started to consume oxygen at night. The accumulated carbon dioxide inhibited HCO_3^- decomposition, promoting a shift of the equilibrium to the left. Both pH and DO reached a minimum at 06:00 hours in the following morning. A significant positive linear correlation was therefore found between pH and DO (Table 3).

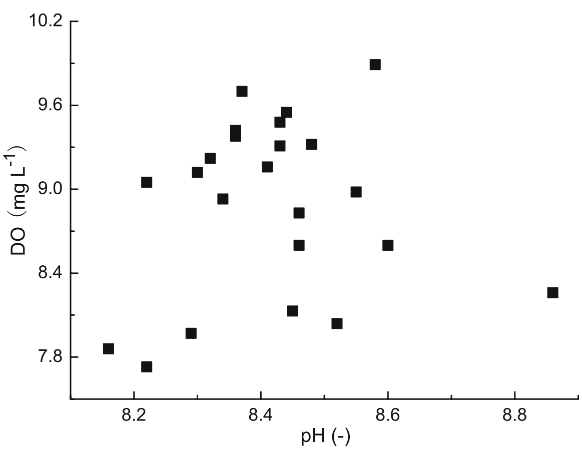

Fig. 13 Regression curve for pH and dissolved oxygen (*DO*) for the Panjiakou Reservoir

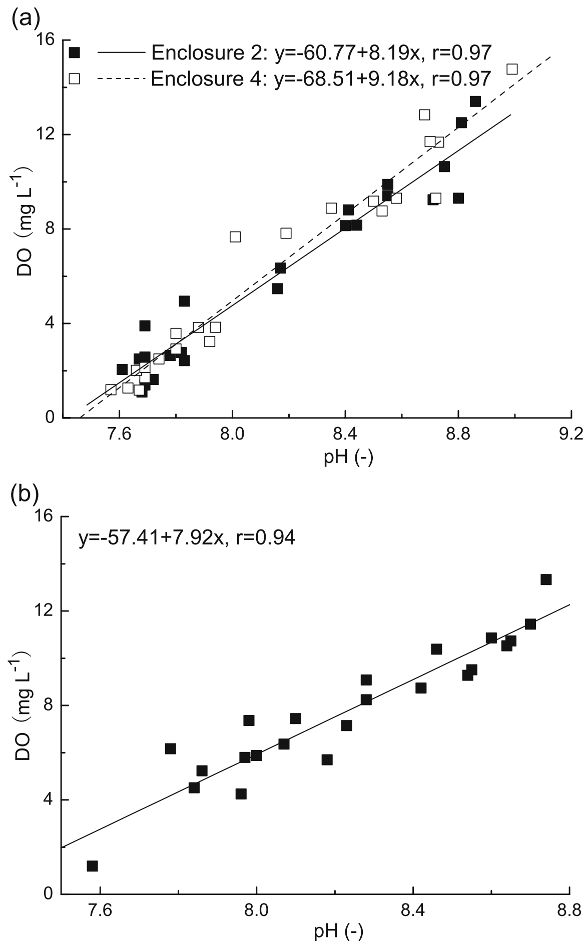

Fig. 14 Regression curves for pH and dissolved oxygen (*DO*) for **a** enclosures 2 and 4 and **b** Enclosure 3

Many studies on correlations between pH and DO indicated significant positive linear correlations (Luis et al. 2010; Luo 2002; Sheng and Xu 1993; Zhang 2009) as summarized in Table 3. In general, diurnal variations were observed for both pH and DO, and a significant positive correlation was found for all non-aquaculture waters.

3.6 Correlations Between pH and Dissolved Oxygen for Aquaculture Waters

Figure 13 shows that there is no correlation between pH and DO for the Panjiakou Reservoir. This can be explained by the fact that both pH and DO were affected not only by algal photosynthesis but also by oxidative decomposition of organic matter related to bait residue and fish waste due to the large-scale cage culture practiced at this reservoir.

Concerning experimental field enclosures in general, Li et al. (1994) found diurnal variations for both pH and DO regarding field enclosure waters of the Dongzhou (see above). In comparison, during the enclosure experiment at Panjiakou Reservoir, significant positive linear correlations (r=0.94–0.97; p<0.05) were found between pH and DO for enclosures 2 to 4 (Fig. 14). This may be the result of complex interactions between algal photosynthetic processes, respiration and oxidative decomposition of organic matters.

Diurnal variations of pH and DO were characteristic of aquaculture waters (Johnston et al. 2002). Wang et al. (1999) and Xu et al. (2008) concluded that there were significant positive linear correlations between pH and DO. Changes in pH and DO were mainly affected by algal photosynthesis (Wang et al. 1999). *Gracilaria lichenoides*, a marine alga, could effectively use metabolic waste from fish and shrimp to purify water, while both pH and DO remained stable (Xu et al. 2008).

Wang et al. (2009) studied a stretch of the Yellow River located between Hukou and Sanmenxia, which was severely polluted by organic matter and had a relatively high alkalinity. The results showed that the chemical oxygen demand was a major factor in controlling DO. Moreover, a high alkalinity inhibited algal growth; thus, the impact of pH on DO was weakened, resulting in only a relatively weak correlation between both parameters.

Characteristic diurnal variations in pH and DO were seen in aquaculture waters as well. A significant positive linear correlation was found between pH and DO for field enclosures, while the relationships between pH and DO for aquaculture waters were rather complex, requiring further research.

4 Conclusions and Further Research Recommendations

The correlation results between pH and chlorophyll *a* for non-aquaculture waters show a significant positive correlation, if the mean concentration of chlorophyll *a* was higher than 10 μg L^{-1}. A significant positive correlation between pH and chlorophyll *a* was also found for aquaculture waters with a strong exchange rate during summer and autumn.

A significant positive correlation between DO and chlorophyll *a* was found for non-aquaculture waters with a chlorophyll *a* concentration greater than 10 μg L^{-1}. In comparison, findings for aquaculture waters were inconclusive, i.e. significant positive correlations could be found occasionally for waters with a strong exchange rate, if the mean concentration of chlorophyll *a* was less than 10 μg L^{-1}.

In aquaculture and non-aquaculture waters, diurnal variations were found for both pH and DO. In addition, a significant positive correlation exists between both parameters. In comparison, diurnal variations for both pH and DO were identified for fieldwork and aquaculture waters. A significant positive linear correlation between pH and DO was found for experimental field enclosures.

The study highlighted further research needs for more complex natural waters with relatively low chlorophyll *a*. Moreover, waters with a high exchange rate should be studied under controlled laboratory conditions.

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