



Temporal and spatial variations of low-molecular-weight organic acids in Dianchi Lake, China

Min Xiao, Fengchang Wu*, Runyu Zhang, Liying Wang,
Xinqing Li, Rongsheng Huang

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences,
Guiyang 550002, China. E-mail: xiaomin@mails.gyig.ac.cn

Received 18 October; revised 05 January 2011; accepted 08 January 2011

Abstract

Low-molecular-weight organic acids (LMWOAs) in eutrophic lake water of Dianchi, Southwestern China Plateau were investigated diurnally and vertically using ion chromatography. Two profiles (P1 and P2) were studied due to the difference of hydrochemical features. Lactic, formic, pyruvic and oxalic acid were detected as major components at P1 and P2 which were on average 7.98 and 6.53 $\mu\text{mol/L}$, respectively, corresponding to their proportions of 2.68% and 2.48% relative to DOC. Pyruvic acid was regarded as the uppermost species at P1 and P2, reaching up to 3.82 and 3.35 $\mu\text{mol/L}$ and accounting for 47.9% and 51.3%, respectively, in individual TOA. Although humus were of biogenetic production at both sites, the significant negative correlation between diurnal variations of TOAs, fluorescence intensity (FI) of protein-like components and humic-like components at P1 indicated LMWOAs were greatly originated from bacterioplankton excretion and degradation. However, correlations between diurnal variations of humic-like FI and physicochemical parameters demonstrated algal origination of LMWOAs at P2. Although content of humus was high, TOA at P2 was 1.45 $\mu\text{mol/L}$ lower than that at P1, due to the co-influence of more intense photo-oxidation and aggregation at P2. Therefore, TOAs exhibited quite opposite diurnal variation trends of increasing-decreasing and decreasing-increasing at P1 and P2, respectively. Except for impact of solar radiation, bacterial decomposition and assimilation rendered shifts of maximal LMWOAs along water column at P1. Covering with massive algae, UV rays penetrated shallower depth than LMWOAs assembled in surface layer water before 18:00 at P2 and represented decreasing profiles.

Key words: Dianchi Lake, humus, algae; solar radiation; low-molecular-weight organic acids

DOI: 10.1016/S1001-0742(10)60567-0

Citation: Xiao M, Wu F C, Zhang R Y, Wang L Y, Li X Q, Huang R S, 2011. The temporal and spatial variations of low-molecular-weight organic acids in Dianchi Lake, China. *Journal of Environmental Sciences*, 23(8): 1249–1256

Introduction

In general, DOM (dissolved organic matter) mostly exists in form of humus (about 50%–90%) in lakes and this part of DOM can reside in aquatic environment for a long time and is difficultly to be biodegraded (Sondergaard and Middelboe, 1995). Recent study suggested that terrigenous humus did not accumulate significantly in oceans and humic-like substances were more sensitive to photodegradation (Mopper et al., 1991; Moran et al., 2000). Moreover, bacterioplankton decomposed components of humus under UV radiation and transformed part of carbon into compounds of higher trophic level through microbic cycles to stimulate productivity of ecosystem (Bushaw-Newton and Moran, 1999; Brinkmann et al., 2003; De Lange et al., 2003), mainly because photochemical reactions played an important role in chemical and biological processes in upper layer waters of sea and other water column

(Morris and Hargreaves, 1997). Photochemical processes were kind of catalytic mechanisms that modified the chemical components even the bioavailability of natural organic matter (De Lange et al., 2003; Christian and Lind, 2007). Previous publications have confirmed that carbonyl compounds and low-molecular-weight (LMW) carboxylic acids were important intermediate degradation products of bioavailability, which were apt to be biologically assimilated and degraded (Kieber et al., 1989; Mopper et al., 1991; Dahlen et al., 1996). Bacteria employed extracellular enzymes to cleave the macromolecules into monomers or oligomers that were subsequently transported across the cell membrane (Chrost and Siuda, 2006). The combined photochemical-biological degradation proved to be more important than the pure photochemical mineralization and biodegradation of dissolved humic materials was enhanced after photolysis (Tranvik et al., 1999). On the other hand, low molecules, vulnerable to exploitation by microbes were also removed by photooxidation, or consumed by

* Corresponding author. E-mail: wufengchang@vip.skleg.cn

aggregation or condensation under UV radiation where the number of enzymatic sites decreased (Tranvik et al., 1999; Lindell et al., 2000; Tranvik and Bertilsson, 2001). Moreover, during the formation of reactive intermediate induced by photochemical processes, some harmful physiological effects on plankton were occurred because of enhanced UV-B penetration (Smith, 1992). Researchers have increasingly realized that photochemical transformation of DOM was very important for global carbon cycle, biogeochemical behavior of carbon and ecological environment effect (Kieber et al., 1989; Moran and Zepp, 1997; Zhang et al., 2009). As an important intermediate, sources of LMWOAs and their transformation mechanisms during photochemical degradation bio-assimilation and mineralization of DOC in lake aquatic environment needed further investigation.

This study mainly aimed to discuss the origins and transformation of LMWOAs under solar radiation in Dianchi Lake water, content variation of organic acids in time-scale and water depth, as well as the main influencing factors in these processes. Moreover, the effects of photochemical and biological reactions on biogeochemical cycles of carbon in lacustrine ecosystems were the key issues to speculate tentatively. In addition, environmental effects during microbial processes mediated by UV radiation were evaluated.

1 Sampling and analysis

1.1 Geographic location of Dianchi Lake

Dianchi Lake is the largest lake in southwestern China with the geographic location of 102°36′–102°47′E, 24°40′–25°02′N and elevation of 1885.5 m. Dianchi situates in the center of Yunnan Province and southern suburbs of Kunming City. The lake area is 300 km² and drainage area of 2920 km², with an average water depth of 4.4 m and a largest water depth of 10 m, and the storage capacity of 12.9 × 10⁸ m³. Because many source rivers inflowed and only one outflowed, Dianchi Lake had relative strong closure and long water residence period which would exacerbate retention and accumulation of nutrients in the lake. With the development of social economy and population explosion, pollution pressure to the lake was increasing and the lake was seriously eutrophic since 70s of 20th century, mainly because that pollutants loaded into the lake was far greater than the water environmental capacity (Gui et al., 2003).

1.2 Sample collection

Water samples were collected at 1.5 m intervals with a Niskin water sampler in July 2008. Profiles 1 and 2 in this limnetic ecosystem were chosen to sample and analyze geographically locating at 102°45.7′E, 24°50.8′N for P1 and 102°40.004′E, 24°56.144′N for P2. These two sampling sites were of weak hydrodynamic characteristic, and sufficiently exposure to sunlight. In addition, P1 was comparatively far from effluent inlet sump and connected with river as Luolong, Laoyu and Yangliu, with relatively low

algae and high water transparency comparing to P2 near Haigeng. Thus, these different hydrologic characteristics between P1 and P2 were conducive to obtain comparable results. The sampling time-scale lasted 8 hr from 10:00 in the morning to 18:00 in the afternoon excluding the nighttime due to restriction of field sampling conditions and sampled every 2 hr. Water samples were immediately filtered through pre-washed cellulose acetate membrane filters and instantly determined various physicochemical parameters as electrical conductivity (EC), alkalinity, pH, dissolved oxygen (DO), temperature in the field. The surplus were collected directly into an acid-cleaned, pre-combusted brown glass bottles (550°C, 5 hr) and chilled in fridge at 4°C to further detect LMWOAs, fluorescent properties and DOC.

1.3 Experimental methods

Ion chromatography (IC) technology takes the advantages of less injection amount of sample, low detection limit, simple and rapid operation, good reproducibility, simultaneous detection of multi low-molecular-weight organic acids (LMWOAs), overcoming the inconvenience brought with other technologies. Ion chromatograph (Dionex ICS-90 model, USA) was used in this study, and the detector was a suppressed conductivity detector, an IonPac®AS11-HC (4 × 250 mm) high-capacity column, an IonPac®AS11-HC 4 mm protection column, an ASRS automatically renewable suppressor and a Dionex RFC-30 online eluent generator was used in the experiment. Peaknet 6 software was used for data processing.

Catalytic oxidation was used to quantify DOC with OI Analytical-TOC 1030 model analyzer (USA), and high-grade purity of potassium hydrogen phthalate was taken as standard substance with detection limit of 0.2 mg/L, RSD less than 2% Hitachi F-4500 (Japan) model molecular fluorescence spectrometer was used to scan three-dimensional excitation emission matrix fluorescence spectroscopy (3DEEM). Acid standard solution titration was utilized to determine alkalinity.

2 Results and discussion

2.1 Contents of organic acids and their contributions to DOC

Generally, four main organic acids have been detected in water of Dianchi Lake including lactic, formic, pyruvic and oxalic acid. In a few samples, propionic, methanesulfonic, trifluoroacetic and sorbic acid were detected at low micromole concentrations as well, but, due to their inconsistent presence, these data were not presented here. Samples for studying diurnal variation trends of LMWOAs were collected from P1 and P2 in east-central and northern Dianchi Lake. The organic acids including lactic, formic, pyruvic and oxalic acid were pervasive and concentrations were on average 3.69, 0.42, 3.82, 0.05 μmol/L, respectively at P1. Pyruvic acid took the highest proportion 48% in total organic acid (TOA). The contribution of TOA relative to DOC averaged out to 2.68%, so that pyruvic

acid also had the highest share of 1.33% in DOC. The TOA was 6.53 $\mu\text{mol/L}$ at P2, and the concentrations were 2.55, 0.63, 3.35, respectively for lactic, formic, pyruvic acid. Similar to P1, pyruvic acid at P2 also took the highest proportion in TOA with 51%, and among the total contribution of 2.48% relative to DOC, pyruvic acid also shared the highest proportion with 1.36% in DOC. More and more evidences suggested that preferable bioavailability of high-molecular-weight organic matter of high aromaticity and complicated structure in humic lakes was conducted by photochemical processes (Moran and Zepp, 1997; Bertilsson and Tranvik, 2000; Lepane et al., 2003). It has been clarified that large amount of carboxylic acids as oxalic, malonic, formic and acetic acid were photochemically produced in humic lake Skarshult and clear water lake Fiolen with TOA 1.55 and 1.54 $\mu\text{mol/L}$, respectively, and acetic acid dominated in these two types of lakes (Bertilsson and Tranvik, 1998). The TOA values detected at P1 and P2 (7.98 and 6.53 $\mu\text{mol/L}$) were nearly five times of that in Skarshult Lake and Fiolen Lake. The differences in content and species of organic acids may be attributed to that the origins of organic acid and abundance of precursors, DOM in Dianchi was mainly autochthonous production from bacterioplankton and algae, which reduced their bio-availability and ultimately inhibited microbial activity after solar radiation (Tranvik and Kokalj, 1998). It was argued that bacterial productivity decreased by 62%–80% when exposed to solar radiation, photochemical production rate of carboxylic acids was relatively high compared to uptake and mineralization by bacterial assemblages with photochemical yield one magnitude higher than bacterial conversion of carboxylic acids (Bertilsson and Tranvik, 1998). Overall, our monitoring time-scale was just limited to daytime when fierce sunlight scattered on lake surface and organic acids accumulated significantly. However, DOM in Skarshult and Fiolen Lake was mainly derived from photodecomposition of allochthonous materials as plant detritus that bacteria were stimulated much and the uptake of organic acids was enhanced, resulting in less organic acids in Skarshult and Fiolen Lake. In addition, Bertilsson and Tranvik (1988) primarily focused on pure bacterial cultivation where photo-degradation and bio-assimilation of organic acids were more intense under extended exposure to constant steady illuminant. In the bog lake water, formic, acetic, pyruvic, oxalic, malonic and succinic acid were identified as important photo-degraded products, and their contribution to DOC rose from 0.31% before to 6.4% after 24 hr irradiation (Brinkmann et al., 2003). In Dianchi Lake water, the highest contribution of LMWOAs to DOC was at 12:00 with 4.11% at P1 and the contents of LMWOAs and their contributions to DOC fluctuated with prolonged exposure to solar UV light, not as did in previous publication (Brinkmann et al., 2003) where the proportions relative to DOC increased linearly within hour radiation scale. The significant difference between the results of bog lake and Dianchi lake water was probably due to differentiation of radiation level in these two studies. A stable and constant radiation source was utilized in

bog lake research, but transient and intense solar light was amenable to less LMWOAs production and lower contributions of LMWOAs to DOC in Dianchi Lake water. A number of LMW carboxylic acids such as formic, acetic, malonic and oxalic acid were photochemically produced at high rates in research of photochemical transformation of DOM in 38 Swedish lakes (Bertilsson and Tranvik, 2000). The combined photoproduction of these four compounds ranged from 0.5 to 158.5 $\mu\text{g C/L}$, and formic acid was the major photoproduct constituting on average 42.2% of the total photoproduced carbon retrieved in the four quantified carboxylic acids, with the contribution of them to DOC of 0.2%–11.1% (av. 4.7%) (Bertilsson and Tranvik, 2000). In this study, the total carbon content of carboxylic acids ranged from 151.0 to 426.6 $\mu\text{g C/L}$, pyruvic acid as the main species took up the average proportion of 52.3% in the total carbon quantified in four photoproduced carboxylic acids, with total carboxylic acid several times higher than that reported by Bertilsson and Tranvik (2000), and the proportions of main species in total carboxylic acids were of the same order of magnitude between Dianchi Lake and the lake environments referred in Bertilsson and Tranvik (2000). Contributions of LMWOAs relative to DOC in Dianchi Lake ranged from 1.7%–4.1% (av. 2.6%). The inherent property as UV absorbance of DOM and extrinsic attributes as physicochemical parameters of surrounding water appeared to affect the complete photochemical mineralization of the DOM, and the existing results showed that photodegradation of DOM in rivers was strongly influenced by acidity (Wu et al., 2005). In other words, these internal and external factors affected the structure and speciation of organic matter. The large differences of organic acids between Bertilsson and Tranvik (2000) and our research were presumably related to different parameters, which expounded a higher transformation level of DOM to inorganic carbon in 38 lakes than that in Dianchi Lake. Bertilsson and Tranvik (2000) concluded that refractory DOC was more easily photomineralized from oligotrophic humic lakes than from eutrophic lakes with high algal production. It was speculated that higher LMWOAs in Dianchi Lake probably resulted from its relative oligotrophic characteristic in comparison with the lacustrine environment referred in Bertilsson and Tranvik (2000).

2.2 Diurnal variation trends of organic acids

Fluorescence index $f_{450/500}$ can be used as an indicator to evaluate the sources of DOM (McKnight et al., 2001). The values of $f_{450/500}$ ranged from 1.44–1.81, mostly apt to the end source of 1.9, revealing that DOM in Dianchi Lake water was mainly biogenetically derived. $r_{(B,D)}$ at P1 and P2 were about 0.6 and 0.8, revealing that protein-like fluorescence substances mainly originated from the same sources, as algal excretion and decomposition of bacterial residues (Coble, 1996). As illustrated in Table 1, NOM was at a state of synthesis before 14:00, indicating solar radiation affected organic matter in lake water greatly, beneficial to phytoplankton photosynthesis as well as humus photodegrade. DOM before 14:00 was replenished

Table 1 Water quality parameters at profiles 1 and 2

	Profile	Time				
		10:00	12:00	14:00	16:00	18:00
pH	P1	9.36	9.43	9.54	9.49	9.49
	P2	8.55	8.99	9.02	9.21	9.20
DO ($\mu\text{mol/L}$)	P1	493.62	541.60	607.85	600.66	577.22
	P2	331.11	491.91	538.94	633.63	587.22
EC ($\mu\text{S/cm}$)	P1	384.25	382.25	382.75	382.25	383.75
	P2	412.25	401.25	400.25	394.25	394.25
Alkalinity ($\mu\text{mol/L}$)	P1	1724.58	1727.10	1724.58	1815.48	1787.70
	P2	1939.20	1903.85	1893.75	1812.95	1878.60
Temperature ($^{\circ}\text{C}$)	P1	20.50	20.88	21.25	21.23	20.93
	P2	20.80	21.55	22.33	22.18	21.65

DO: dissolved oxygen; EC: electrical conductivity.

continuous decomposition of POM. Bio-refractory organic matter was sensitive to solar radiation, the photodegradation extent of DOM deepened with radiation intensifying and time prolonging (Fu et al., 2006). In this study, high-molecular-weight organic components was degraded into low-molecular substances under solar radiation from 3DEEM of peak C because of stronger fluorescent effect caused by lower molecular weight organic compounds (Fig. 1). The lowest fluorescence intensity (FI) of peak C was the result of maximal photodegradation of bio-refractory humus.

FI of humic-like components diurnally varied in opposite correlations with that of protein-like fluorescence ($R^2 = 0.75$, $P \leq 0.05$), suggested that photodegradation of humus stimulated bioactivity. It was confirmed in our research that TOA was highest in the time scale of 12:00–14:00 at P1, with the average concentration of 11.57 $\mu\text{mol/L}$, whereas, the humic FI was lowest on average 217.73 a.u. and decreased sharply from 219.9 at 10:00 to

217.7 a.u. at 14:00. The significant negative relationship ($R^2 = 0.84$, $P \leq 0.01$) between TOA and FI of humus during the entire monitoring period indicated that organic acids were the photo-degraded products from humus. This result was in good concert with that of previous publications (Dahlen et al., 1996; Herndl et al., 1997; Bushaw-Newton and Moran, 1999). TOA tended to cumulate promptly from 5.25 $\mu\text{mol/L}$ at 10:00 to 12.15 $\mu\text{mol/L}$ at 12:00 and maintained a high concentration level of 11.57 $\mu\text{mol/L}$ (av.) within the time paragraph of 12:00–14:00. Likewise, FI of protein-like peak B also accumulated to the highest value at 14:00, which showed definite consistency with the diurnal variation trend of TOA, further confirming that microbial activity fluctuated with abundance of micromolecular substances and LMWOAs derived from humus photodegradation promoted microbial activity. Carboxylic acids were major bacterioplankton substrates, and the metabolic processes influenced distribution of these carboxylic acids (Bertilsson and Tranvik, 1998), thus,

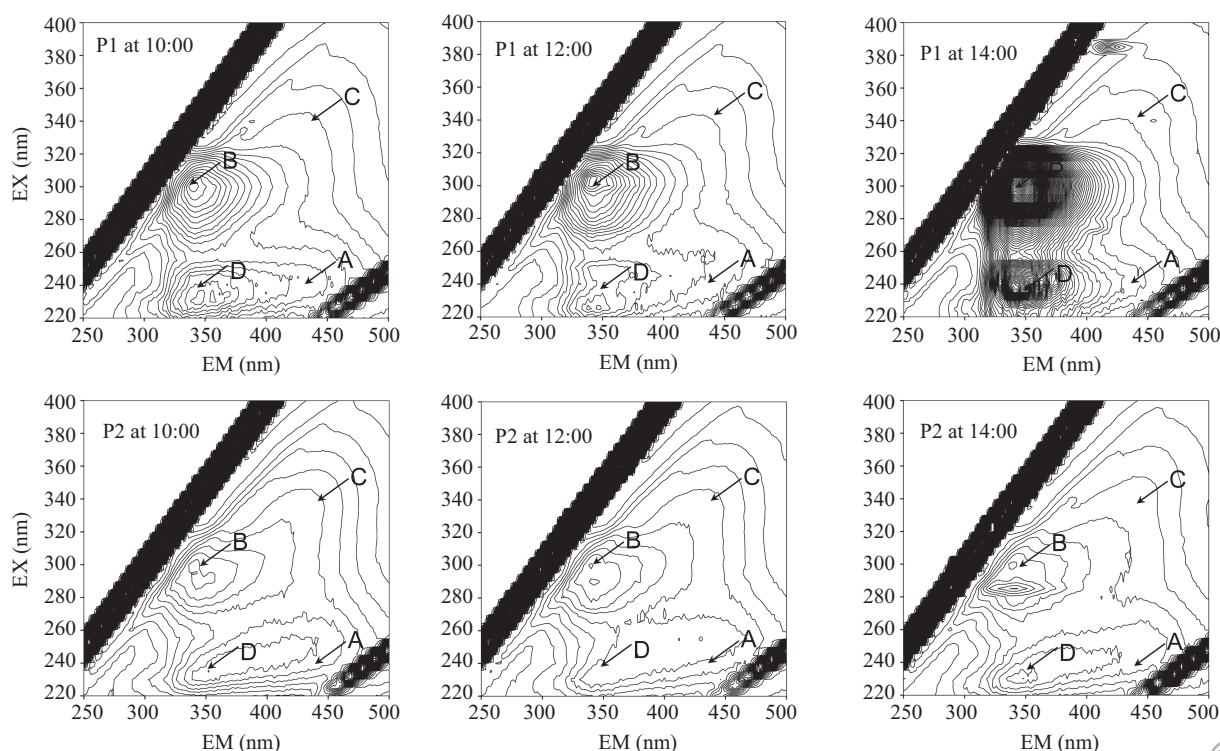


Fig. 1 3DEEMs of surface water samples at different times in Dianchi Lake. A, C: fluorescent peak of fulvic-like, humic-like structures; B, D: fluorescent peak of protein-like structures.

bacterioplankton origination of LMWOAs predominated in photochemical production of LMWOAs

LMWOAs were one category of multitudinous components of bioavailability in DOC, but combining the analysis of diurnal variation consistency between TOA and FI of protein-like structure, it was proposed that LMWOAs constituted the major fraction in bioavailable components. It is similar to the results of Bertilsson and Tranvik (1998) that LMWOAs constituted about 33% of DOM photoproducts. It was deduced from the above narration that organic acids originated from photodegradation of humus and greatly interacted with bacterioplankton.

Although TOA decreased rapidly to 6.27 $\mu\text{mol/L}$ at 16:00 and subsequent 5.22 $\mu\text{mol/L}$ at 18:00, FI of humic-like peak C increased rapidly after 14:00 and exhibited a cumulative trends, which probably due to the photoaggregation of LMWOAs. Once the bioavailable organic matter accumulated to a certain level, they might largely polymerize after extensive exposure to solar radiation (Obernosterer et al., 1999; Lindell et al., 2000). However, DOC after 14:00 was degraded into inorganic carbon, inferring that LMWOAs might also be photodegraded directly into inorganic carbon other than the impacts of photo-polymerization. Content of LMWOAs at midday was 2 times of that in dusk time and showed a cumulative tendency until 14:00, demonstrating that production of LMWOAs from photodegradation of DOM had an advantage over their consumption by bio-assimilation and photo-oxidation. And then, LMWOAs decreased sharply mainly due to their direct photooxidation into inorganic carbon or photo-polymerization into macromolecular bio-refractory compounds. During the whole monitoring time-scale, formic acid was 8.4 times of oxalic acid with the average concentrations of 0.42 and 0.05 $\mu\text{mol/L}$, respectively. However, there was a significant negative relationship ($R^2 = 0.88$, $P \leq 0.01$) between the diurnal variation trends of them. In cloud water, production and release of pyruvic and fumaric acid were related to the transformation of lactic and succinic acid by the influences of micro-organisms (Amato et al., 2007). In Dianchi Lake, formic acid increased with time, having the highest and lowest contents of 0.48 and 0.35 $\mu\text{mol/L}$ at 18:00 and 16:00, respectively. Oxalic acid slightly decreased diurnally in reverse with formic acid ($R^2 = 0.89$, $P \leq 0.01$), suggesting that oxalic acid might act as the precursor of partial formic acid.

It could be proposed that the algae at P2 was always at photosynthesis until 16:00, and then it was degraded largely. From various physicochemical parameters shown in Table 1, DOC accumulated rapidly from 16:00 to 18:00. The content of TOA at P2 decreased promptly from 8.75 $\mu\text{mol/L}$ at 10:00 to 5.1 $\mu\text{mol/L}$ at 12:00 (Fig. 2), which was coupled with FI of protein-like peak B decreasing sharply from 805 a.u. to 410.9 a.u., indicating that bioavailable micro-molecular substances exerted an important influence on bacterial activity. However, decreasing FI of humic-like substances was accompanied by decrease of TOA during this time interval instead of increase of TOA, indicating that LMWOAs probably were directly photo-oxidized into

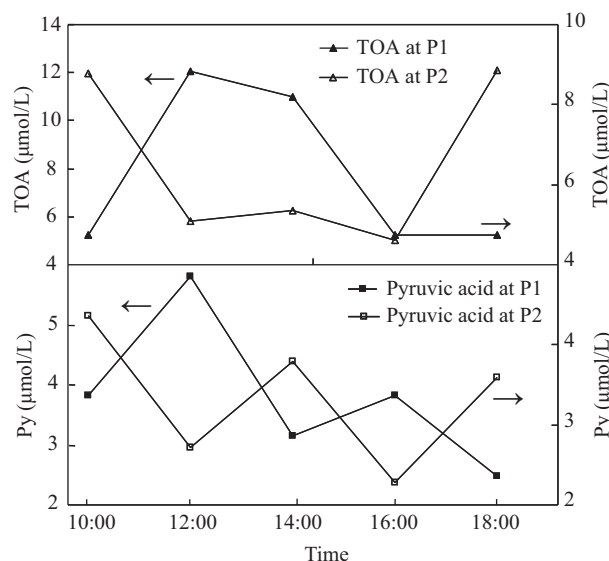


Fig. 2 Diurnal variation trends of total organic acid (TOA) and pyruvic acid (Py^-) in water of Dianchi Lake.

inorganic carbon morphology during photodegradation of humus, which led to the lowest microbial activity. TOA attenuated to the lowest 4.6 $\mu\text{mol/L}$ at 16:00 and then increased rapidly to 8.85 $\mu\text{mol/L}$ at 18:00. FI of protein-like substances rebounded to and maintained at a high level after 12:00, indicated that influence of LMWOAs on microbial activity was minor. FI of humic-like substances decreased slightly with time, which was found in reverse with pH and DO significantly ($R^2 = 0.87$, $P \leq 0.01$) and in appreciable positive correlation with EC, dissolved inorganic carbon (DIC) ($R^2 = 0.83$, $P \leq 0.05$), demonstrating that humus had much to do with photosynthesis and degradation of algae, and humus was derived from algae greatly. Photoproducts from photodegradation of humus were recycled in photosynthesis of algae again. According to Tranvik and Bertilsson (2001), LMW components of algal origination were susceptible to photo-aggregation. Therefore, it was deduced that relative low content of LMWOAs 5.01 $\mu\text{mol/L}$ between 12:00 and 16:00 could also be polymerization-related. Once photosynthesis of algae attenuated and photodegradation enhanced after 16:00, humus tended to increase, resulting from condensation of LMW organic compounds of algal source under solar radiation. LMWOAs increased rather than decreased from 16:00 to 18:00, mainly because that their accumulation from excretion and degradation release from algae surpassed their loss caused by aggregation and photo-oxidation. DOC increased constantly and positively with the diurnal variation of Cl^- as time continued at P2 ($R^2 = 0.91$, $P \leq 0.01$), revealing that other than autochthonous production of DOC, anthropogenic input affected DOM as well. This influencing factor could not be excluded, which might contribute to significant increase of TOA from 16:00 to 18:00 at P2. Pyruvic acid exhibited gradual decrease variation trends at both sampling sites (Fig. 2). It was reported that photochemical production of pyruvic acid was strongly coupled with its bioassimilation (Kieber et al., 1989; Mopper et al., 1991). Kinetic experiments confirmed that direct photo-oxidation of LMWOAs

occurred simultaneously during exposure to the irradiation of ultraviolet rays, and alpha-oxo LMWOAs were more amenable to these mineralization processes (Brinkmann et al., 2003). The decreasing diurnal variation trend of pyruvic acid at P1 was mainly related with bio-assimilation into higher biomass and bio-mineralization into inorganic carbon pyruvic acid at P2 was not only produced from humus photodegradation and algal excretion, but also consumed by photo-oxidation and aggregation. For formic acid at P2, it increased firstly with the highest value of 0.73 $\mu\text{mol/L}$ at 14:00 and then decreased. It varied diurnally in a significant positive correlation with H_2PO_4^- ($R^2 = 0.92$, $P \leq 0.01$), indicating that they might be the photoproducts of the same source materials in accordance with Moran and Zepp (1997) who concluded that bio-labile photo-products included LMW organic compounds and compounds rich in N, P.

FI of humus at P2 was slightly higher than that at P1, but TOA was 1.45 $\mu\text{mol/L}$ lower at P2 than P1, which was also inconsistent with maximal degradation of humus that the FI reduced by 10.3% at P2 and 5.3% at P1. The outcome was mainly because that excessive photochemical mineralization and aggregation predominated in consumption of organic acids at P2. Apparently, microbial biomass was not so abundant as P1 from FI of protein-like substances, following the result of Jones (1998), where presumably differentiation of community structure became another important ingredient resulting in great consumption of LMWOAs. FI of protein-like peak at P1 was 2.4 times of that at P2, mainly because that the decisive stipulation factors responsible for organic acids production differentiated largely, further demonstrating that photodegradation of algae-derived DOC inhibited bacterial growth (Benner and Biddanda, 1998; Obernosterer et al., 1999; Lindell et al., 2000). NO_3^- was the important influencing factor on degradation of organic acids and higher NO_3^- could lead to lower LMWOAs (Brinkmann et al., 2003). NO_3^- as photosensitizer was seven times higher at P2 than that at P1 and took responsibility for the lower LMWOAs at P2 in

Dianchi Lake water. As referred in Bertilsson and Tranvik (2000) that less eutrophic aquatic environment at P1 should account for the higher content of LMWOAs than that at P2. In conclusion, different origination and discriminatory influencing factors were decisive during kinetic processes of production and consumption of LMWOAs. It was suggested that the content level of organic acid was markedly related to photochemical formation of LMWOAs from humus and algal release, biotic assimilation and abiotic mineralization, rather than content of humus.

2.3 Profile variation trends of organic acids

The highest content of TOA at P1 at 10:00 was 6.99 $\mu\text{mol/L}$, appearing at 3 m water depth. Profile of TOA at this moment was in accordance with FI of protein-like peak (Fig. 3), indicating that mutual effect between LMWOAs and microbes was relatively significant in whole water column during the early stage of phytoplankton photosynthesis. Although most LMWOAs was directly derived from humus photodegradation, contribution from bacterioplankton excretion and biomass decomposition itself to LMWOAs at 10:00 in ultraviolet rays transmissive region in this shallow water lake shouldn't be ignored.

Profile of DOC at 14:00 was similar with that of TOA, with highest contents of 959.8 $\mu\text{mol C/L}$ and 22.5 $\mu\text{mol/L}$, respectively at 3 m depth, showing the same influencing factors regulated DOC and TOA in the water column. Both TOA and DOC were subjected to strong solar radiation and microbial activity in surface water and maximums of them transferred downward. TOA at 18:00 tended to increase along the water column down with the highest content 10.55 $\mu\text{mol/L}$ at 3 m water depth, and TOA was consistent with FI of humic substances in profile trends, revealed that under attenuating solar radiation, production of LMWOAs was mainly dependent on photodegradation of humus and decrease of chromophoric dissolved organic matter in surface water was conducive to deeper penetration of UV rays. Bertilsson and Tranvik (1998) concluded that photochemical cleavage of macromolecules was perhaps

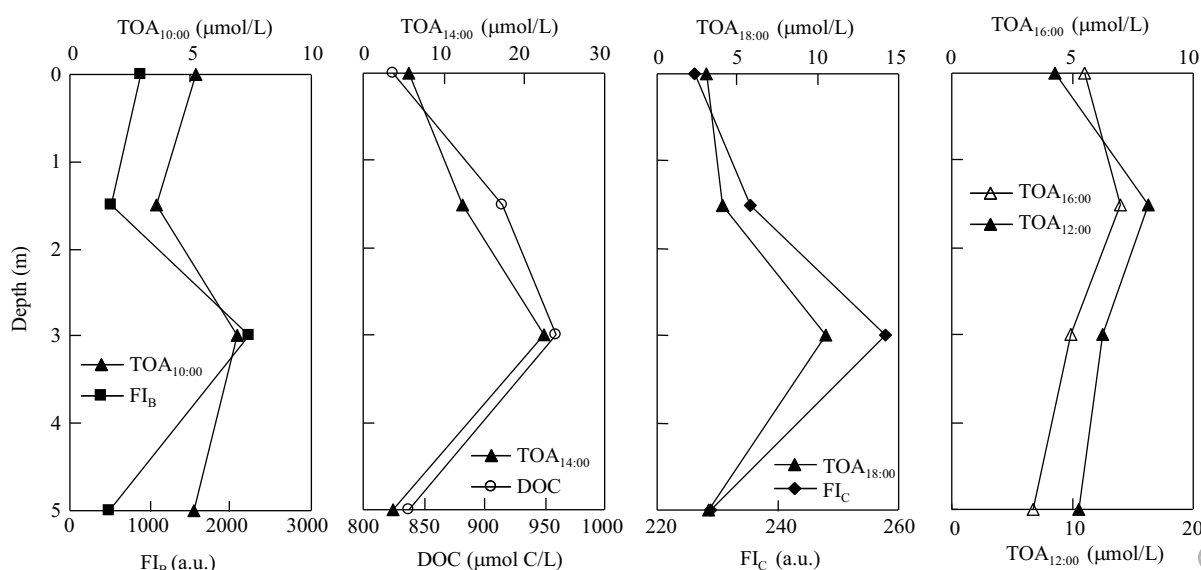


Fig. 3 Profile variation trends of total organic acid at P1 at different time. FI_B, FI_C: fluorescent intensity of protein-like, humic-like substances.

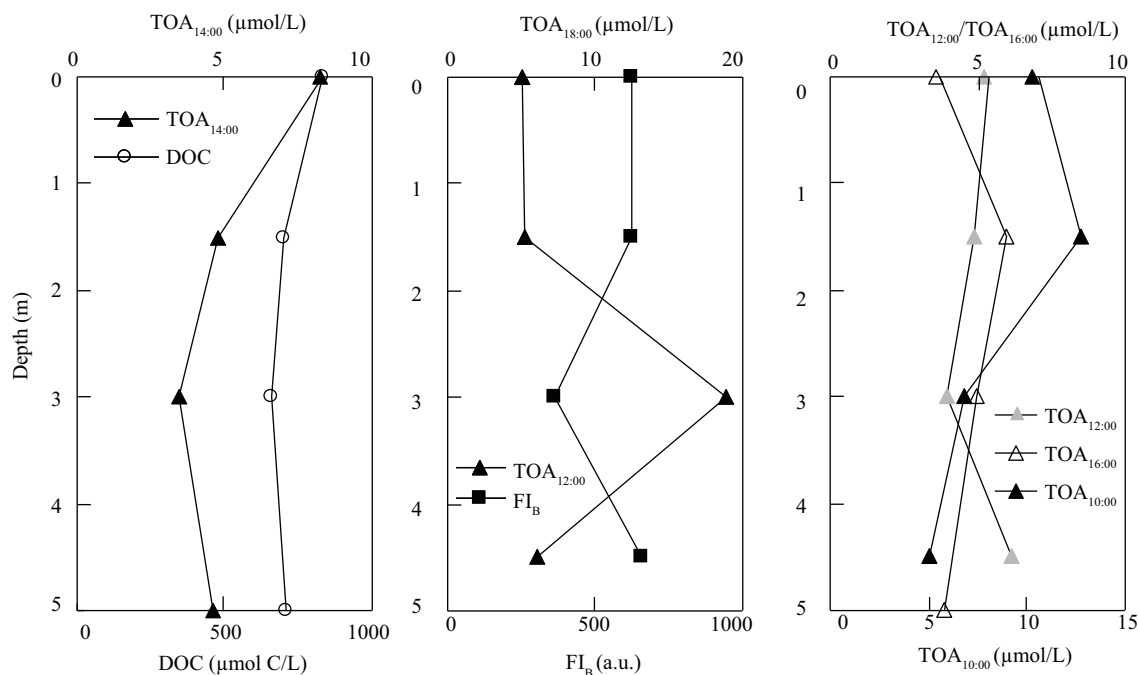


Fig. 4 Profile variation trends of total organic acid at P2 at different time. FI_B: fluorescent intensity of protein-like substances.

assisted by bacteria after strong radiation. TOAs at 12:00 and 16:00 both exhibited a decreasing profile with highest contents of 16.43 μmol/L and 7 μmol/L at 2 m depth, mainly because that bio-assimilation was intense at 12:00 in bottom water from the FI of protein-like peak. Photo-oxidation receded since 14:00 and maximal TOA shifted upwards at 16:00 relative to 18:00.

TOA all decreased with depth before 18:00 at P2 (Fig. 4), because LMWOAs was mainly at photosynthesis-based stage of algae in most of the day that slight transformation from POM to DOC and fast photo-oxidation of organic acids both resulted in slow diffusion of LMWOAs downwards. Otherwise, massive algal substances just permitted ultraviolet rays to penetrate into shallow water layer, which resulted in an intensive decomposition of humus and higher LMWOAs focusing at upper layer water. Furthermore, organic acids were mainly algal source that the highest contents of TOA all concentrated in surface water where algae enriched in. In addition, it was also found that profile variation trend of TOA at 14:00 correlated positively with that of DOC ($R^2 = 0.99$, $P \leq 0.01$) (Fig. 4), with the highest contents of 8.4 μmol/L and 840 μmol C/L in surface layer under strong solar radiation, respectively, revealing that they resembled in influencing factors and sources at this moment, mainly derived from excretion and decomposition of massive algae and gradually decreased with water depth (Fig. 4).

Unlike the above profile trends, TOA at 18:00 was highest with 19.01 μmol/L at 3 m water depth, quite reverse to profile trend of FI of protein-like substances ($R^2 = 0.97$, $P \leq 0.01$), indicating that algal excretion and decomposition made a good contribution to production and cumulation of LMWOAs at this profile depth with the assistance of anaerobic bacteria. LMWOAs increased with reduction of microbial productivity down the water column.

3 Conclusions

Two water column (P1 and P2) samples with different trophic characteristics were collected for analysis of variations of LMWOAs in Dianchi Lake, Southwest China. The results showed that macromolecular weight humus and phytoplankton were considered as the initial photochemical sources of bio-available substrates in the Lake. LMWOAs were predominantly influenced by biological behavior at P1, whereas, they were mainly related to metabolic mechanism of algae at P2. Simultaneously, bio-assimilation and mineralization, photo-oxidation and aggregation mainly caused consumption of LMWOAs at these two sampling sites. Different sources and impact factors resulted in contrasts of content and diurnal variations of LMWOAs. Besides, shallower penetration of ultraviolet rays at P2 became the main controlling factors in profiles of LMWOAs. Environmental effects stemmed from photoproduction of LMWOAs were mainly reflected in differentiation of microbial activity and depth of ultraviolet rays penetration, distribution patterns, structure and morphology of compounds, except for the influences on carbon cycle flux in lakes.

This research on sources of LMWOAs and their influencing factors during solar radiation provided basic theoretical foundation and scientific proof for sunlight penetrating into lake water, as well as for research of the influenced microbial activity by radiation. The results had important environmental implications, particularly for planktonic-web-food. The dynamic research of LMWOAs in various lake ecosystems should not be ignored and needs further investigation.

Acknowledgments

This work was jointly supported by the National Basic Research Program (973) of China (No. 2008CB418000,

2008CB418200), the National Natural Science Foundation of China (No. 41003055, 40903051, U0833603, 40632011, 40873080) and the Chinese Research Academy of Environmental Sciences (No. 2007KYYW01).

References

- Amato P, Demeer F, Melaouhi A, Fontanella S, Martin-Biesse A-S, Sancelme M et al., 2007. A fate for organic acids, formaldehyde and methanol in cloud water: their biotransformation by micro-organisms. *Atmospheric Chemistry and Physics*, 7: 4159–4169.
- Benner R, Biddanda B, 1998. Photochemical transformations of surface and deep marine dissolved organic matter: Effects on bacterial growth. *Limnology and Oceanography*, 43: 1373–1378.
- Bertilsson S, Tranvik L J, 1998. Photochemically produced carboxylic acids as substrates for freshwater bacterioplankton. *Limnology and Oceanography*, 43(5): 885–895.
- Bushaw-Newton K L, Moran M A, 1999. Photochemical formation of biologically available nitrogen from dissolved humic substances in coastal marine systems. *Aquatic Microbial Ecology*, 18: 285–292.
- Bertilsson S, Tranvik L J, 2000. Photochemical transformation of dissolved organic matter in lakes. *Limnology and Oceanography*, 45(4): 753–762.
- Brinkmann T, Horsch P, Sartorius D, Frimmel F H, 2003. Photoformation of LMW organic acids from brown water dissolved organic matter. *Environmental Science of Technology*, 37: 4190–4198.
- Coble P G, 1996. Characterization of marine and terrestrial DOM in seawater using excitation – emission matrix spectroscopy. *Marine Chemistry*, 51(4): 325–346.
- Chrost R J, Siuda W, 2006. Microbial production, utilization, and enzymatic degradation of organic matter in the upper trophogenic layer in the pelagial zone of lakes along a eutrophication gradient. *Limnology and Oceanography*, 51(1): 749–762.
- Christian B W, Lind O T, 2007. Multiple carbon substrate utilization by bacteria at the sediment-water interface: seasonal patterns in a stratified eutrophic reservoir. *Hydrobiologia*, 586: 43–56.
- Dahlen J, Bertilsson S, Pettersson C, 1996. Effects of UV irradiation on dissolved organic matter in humic surface waters. *Environment International*, 22(5): 501–506.
- De Lange H J, Morris D P, Williamson C E, 2003. Solar ultraviolet photodegradation of DOC may stimulate freshwater food webs. *Journal of Plankton Research*, 25(1): 111–117.
- Fu P Q, Wu F C, Liu C Q, Xu C, Wang J, Bai Y C et al., 2006. Effect of sunlight irradiation on fluorescent properties of dissolved organic matter. *Spectroscopy and Spectral Analysis*, 26(3): 471–474.
- Gui M, Zhu W P, Yu G, Zhang P Y, 2003. Release regularity of agricultural non-point pollution in drainage area in Dianchi region. *Agro-environmental Protection*, 22(1): 1–5.
- Herndl G J, Bruggner A, Hager S, Kaiser E, Obernosterer I, Reitner B et al., 1997. Role of ultraviolet-B radiation on bacterioplankton and the availability of dissolved organic matter. *Vegetatio*, 128: 43–51.
- Jones D L, 1998. Organic acids in the rhizosphere – A critical review. *Plant and Soil*, 205: 25–44.
- Kieber D J, Daniel J Mc, Mopper C, 1989. Photochemical source of biological substrates in sea water: implications for carbon cycling. *Nature*, 341: 637–639.
- Lindell M J, Graneli H W, Bertilsson S, 2000. Seasonal photoreactivity of dissolved organic matter from lakes with contrasting humic content. *Canadian Journal of Fisheries and Aquatic Sciences* 57: 875–885.
- Lepane V, Persson T, Wedborg M, 2003. Effects of UV-B radiation on molecular weight distribution and fluorescence from humic substances in riverine and low salinity water. *Estuarine, Shelf and Coastal Science* 56: 161–173.
- Mopper K, Zhou X, Kieber R J, Kieber D J, Sikorski R J, Jones R D, 1991. Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle. *Nature*, 353: 60–62.
- Moran M A, Sheldon Jr W M, Zepp R G, 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnology and Oceanography*, 45(6): 1254.
- Moran A M, Zepp R G, 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography*, 42(6): 1307–1316.
- Morris D P, Hargreaves B R, 1997. The role of photochemical degradation of dissolved organic carbon in regulating the transparency of three lakes on the Pocono Plateau. *Limnology and Oceanography* 42(2): 239–249.
- McKnight D M, Boyer E W, Westerhoff P K, Doran P T, Kulbe T, Andersen D T, 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. *Limnology and Oceanography*, 46: 38–48.
- Obernosterer I, Reitner B, Herndl G, 1999. Contrasting effects of solar radiation on dissolved organic matter and its bioavailability to marine bacterioplankton. *Limnology and Oceanography*, 44(7): 1645–1654.
- Smith R C, Prezelin B B, Baker K S, Bidigare R R, Boucher N P, Coley T, 1992. Ozone depletion: Ultraviolet radiation and phytoplankton biology in Antarctic waters. *Science*, 255: 952–959.
- Sondergaard M, Middelboe M, 1995. A cross-system analysis of labile dissolved organic carbon. *Marine Ecology Progress Series*, 118: 283–294.
- Tranvik L, Kokalj S, 1998. Decreased biodegradability of algal DOC due to interactive effects of UV radiation and humic matter. *Aquatic Microbial Ecology*, 14: 301–307.
- Tranvik L J, Olofsson H, Bertilsson S, 1999. Photochemical effects on bacterial degradation of dissolved organic matter in lake water. In: *Microbial Biosystems: New Frontiers, Proceedings of the 8th International Symposium on Microbial Ecology* (Bell C R, Brylinsky M, Johnson-Green P, eds.). Atlantic Canada Society for Microbial Ecology, Halifax, Canada.
- Tranvik L J, Bertilsson S, 2001. Contrasting effects of solar UV radiation on dissolved organic sources for bacterial growth. *Ecology Letters*, 4: 458–463.
- Wu F C, Mills R B, Cai Y R, Evans R D, Dillon P J, 2005. Photodegradation-induced changes in dissolved organic matter in acidic waters. *Canadian Journal of Fisheries and Aquatic Sciences*, 62: 1019–1027.
- Zhang M L, Liu M L, Qin B Q, Feng S, 2009. Photochemical degradation of chromophoric-dissolved organic matter exposed to simulated UV-B and natural solar radiation. *Hydrobiologia*, 627: 159–168.