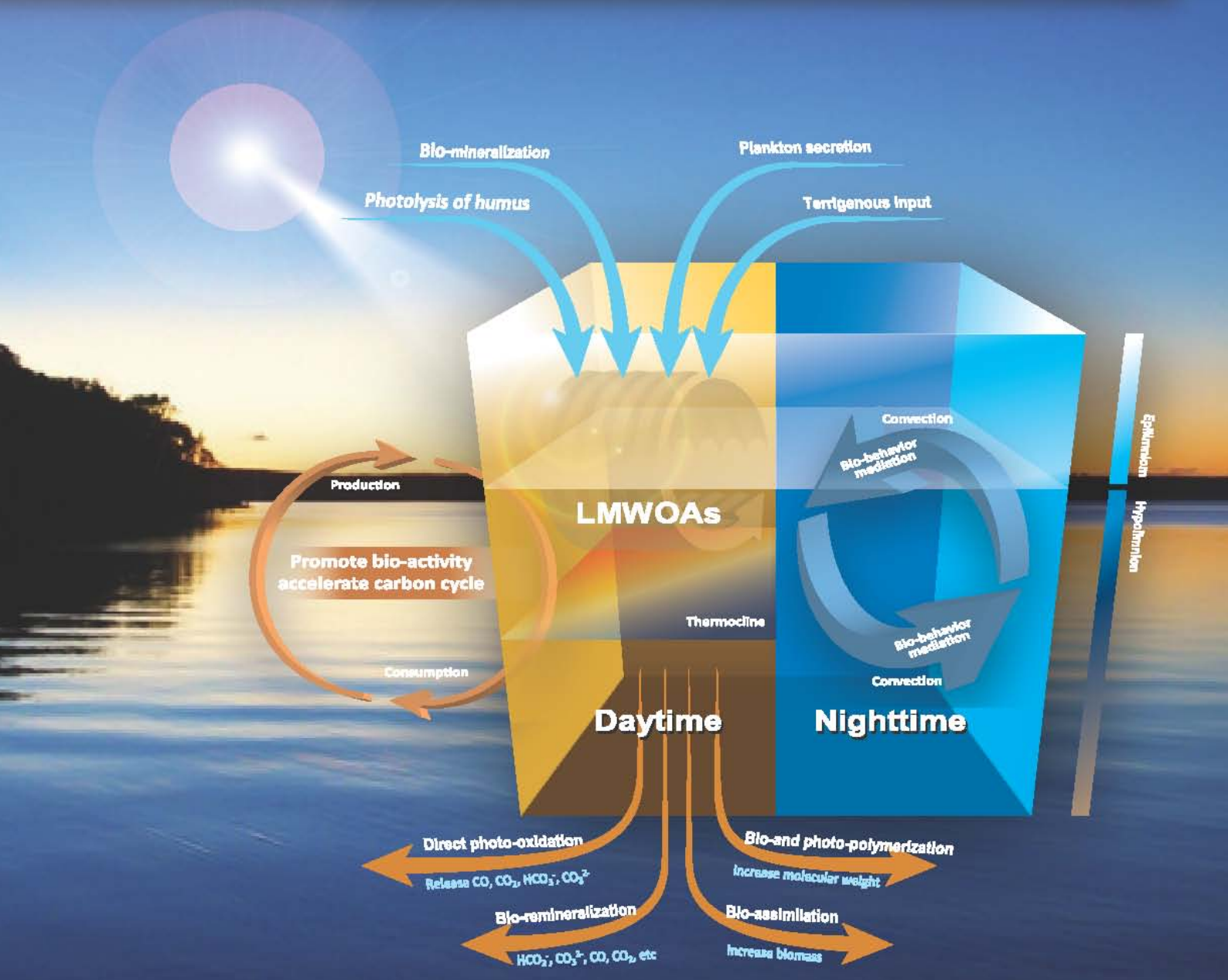
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Investigation of low-molecular weight organic acids and their spatiotemporal variation characteristics in Hongfeng Lake, China

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Abstract

The identities and concentrations of low-molecular-weight organic acids (LMWOAs) were determined by ion chromatography throughout a 20-m water column in Hongfeng Lake, China. The spatiotemporal variations of LMWOAs and their contributions to dissolved organic matter (DOM) in a research period of 24 hr were also investigated. The results demonstrated that five LMWOAs (lactic, acetic, pyruvic, sorbic, oxalic acid) were detected, and their total concentration and proportion in DOC were 6.55 μmol/L and 7.47%. Their average levels were 2.50, 0.65, 2.35, 0.96 and 0.09 μmol/L, respectively. LMWOAs were higher during daytime (10:00–18:00 on Jun 13, 2008) than nighttime (21:00–6:00 the next morning), in particular 4.99 μmol/L high in the epilimnion (⩽ 1 m water depth), reflecting the fact that direct import from terrigenous sources and photochemical production from humic materials were dominant during LMWOAs' origin and accumulation. The same factors caused LMWOAs to be 0.63 μmol/L in the epilimnion higher than in the hypolimnion. The rapid decrease of total organic acid (TOA) up until 18:00 mainly resulted from bio-uptake and mineralization in the hypolimnion (>1 m water depth). Pyruvic acid increased with time in the epilimnion and decreased in the hypolimnion, largely related to the two contrary processes of continuous degradation and synthesis of macromolecular organic matter during life materials' cycle mediated by organisms. Simultaneously, plankton behavior and thermal stratification played a pivotal role in LMWOAs' behavior in the water column, causing decreasing and increasing profiles. The distribution of LMWOAs represents an interesting resource for biogeochemical research of DOM in aquatic ecosystems.

Key words: Hongfeng Lake; low-molecular-weight organic acids; photochemical production; spatiotemporal variations; thermal stratification

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Introduction

It has been demonstrated that 50%–90% of dissolved organic matter (DOM) in lakes stained with organic matter is comprised of dissolved humic substances (Thurman, 1985), most of which originates from terrestrial sources, but a small part can form in the water itself through the condensation of smaller molecules (Steinberg, 2003). Humic substances, sensitive to light and easily photodegraded in natural water, are the main source material for photochemically-produced low-molecular-weight (LMW) carbonyl compounds due to the cleavage of large organic molecules and aromatic structures into smaller and potentially more labile and less absorbing entities; for example, the photodegradation of humic acid in Luther Marsh was found to be 3–4 times higher than that of the fulvic component (Mopper and Stahovec, 1986; Kieber et al., 1990; Winter et al., 2007). Photochemical reactions shoulder an important responsibility for the transformation of organic matter in the lake water column: 40%–70% of the organic matter annually imported into lake water is preserved in sediments or lost into the atmosphere through photodegradation processes (Gennings et al., 2001). Photochemical and microbial processes are two critical pathways for altering and removing DOM in aquatic systems (Wiegner and Seitzinger, 2001). As early as the 1980s, there was documented evidence that photochemical alteration fulfills an important function in chemical and biological processes in the sea where chemical composition is affected by light-induced processes (Zafiriou et al., 1984). As a result, DOM and its photo-products can be taken up by bacteria and phytoplankton, and then incorporated into the biological

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cycle through the secretion of exoenzymes and cell surface oxidation. During direct photochemical alteration of DOM to release inorganic compounds, dissolved inorganic carbon and CO, biological remineralization can also not be neglected during DOM transformation (Francko and Heath, 1982; Pantoja and Lee, 1994). Finally, heterotrophic bacteria are stimulated and their utilization of DOM or bioavailability of DOM is enhanced (Lindell et al., 1995; Mopper and Kieber, 2002). Even so, photo-oxidation still mostly mediated during natural organic matter (NOM) degradation compared with bacterial degradation (Hernes and Benner, 2003). However, the earlier studies reported that the biological reactivity of DOM after being exposed to solar radiation is inversely related to the initial bioavailability of the DOM prior to its exposure (Obernosterer et al., 2001). Research has previously demonstrated that the exposure of terrigenous DOM to light in estuaries resulted in the decrease of DOC and variation of fluorescence properties and decreased molecular weight of organic matter (Moran et al., 2000; Helms et al., 2008). Low-molecular-weight organic acids (LMWOAs) were found to be the major components in photodegradation products of DOM, highly labile constituents in DOC and easily absorbed or decomposed by organisms (Kieber et al., 1989, 1990; Bertilsson and Allard, 1996; Moran and Zepp, 1997; Bertilsson and Tranvik, 1998; Clark and Zika, 2000; Brinkmann et al., 2003). For example, in an investigation of LMWOAs' formation in a peat bog, about 33% of bioavailable photoproducts were comprised of LMWOAs (Brinkmann et al., 2003). LMWOAs produced in these processes are an important index to evaluate the levels of photochemical and biological behavior in aquatic environment.

Therefore, the impacts of photochemical processes on the biogeochemical cycling of carbon, especially on the dynamic conversion of LMW organic compounds, should not be ignored. However, little has been known about the mechanisms and influencing factors in relation to the transformation of large molecules into LMW compounds. In order to make these interrogations clear, Hongfeng Lake in the Guizhou Plateau was selected as the study object to study the fluctuations of LMWOAs, investigate the influence of solar irradiation on the formation and conversion of LMWOAs in lake water and behavior of LMWOAs in photo-radiation and microbial processes, and further survey the environmental effects associated with them. However, no studies have explicitly examined the discrimination of LMWOAs over temporal and spatial scales.

1 Materials and methods

1.1 Study area

Hongfeng Lake (HF, 106.24°E, 26.32°N) is situated at 31 km west of Guiyang City, at the upper stream of the Maotiaohe River in the Wujiang river water system. The lake covers an area of 57.20 km^2, its reservoir storage capacity is 6.01×10^8 m^3, the drainage area is 1596 km^2, the water retention time is about 0.33 a (annum) with a recharge coefficient of 49.60, the maximum water depth is 45 m, and the average deposition rate is 0.17 $g/(cm^2\cdot a)$ (Chen et al., 2008). It is an intermountain lake, the largest artificial lake of karstic features in the Guizhou Plateau so far and one of the main water sources with strong hydrodynamic force in the Guizhou Plateau. Karstic landforms developed in this territory where limed and yellow soil is widely distributed. HF fulfills may functions such as drinking water, power generation, agricultural irrigation, aquaculture, flood control, climatic regulation, and eco-environment improvement (Wu et al., 2004).

1.2 Sampling and analysis

A Niskin water sampler was utilized to collect water samples at different depths and time intervals in Jun 2008 in the north open aquatorium of HF in Guiyang. The water surface was relatively calm, not significantly disturbed and exposed to sunlight sufficiently that it was the ideal water area to investigate effect of photochemical mechanisms on LMWOAs. The entire sampling process lasted 24 hr, with time points of 10, 12, 14, 16, 18, 21, 24, 3, 6, 8, 10 o'clock and water depths at 0, 1, 2, 4, 6, 8, 10, 15, 20 m. Various physicochemical parameters were determined as soon as water was collected in the field. Water samples were filtered immediately through pre-combusted (450°C, 5 hr) Whatman glass-fiber filters. The filtrate was collected directly into an acid-cleaned, pre-combusted (550°C, 5 hr) brown glass bottle and preserved in refrigeration at 4°C to quantify LMWOAs and DOC. A fluorescence fingerprint technique was used to characterize the DOM in HF.

1.3 Experimental methods

High performance liquid chromatography (HPLC), capillary zone electrophoresis and gas chromatography (GC) techniques have previously been used to measure LMWOAs in sea water, plant extracts and soil (Kieber et al., 1990; Obernosterer et al., 1999; Rivasseau et al., 2006), but for these methods the compounds must be combined with 2,4-dinitrophenylhydrazine to form hydrazone, which has high UV absorption, or they require careful electrolyte pH adjustment and correct selection of chromophores during pretreatment, etc. These detection methods are time-consuming as well as cumbersome, may incur problems with incomplete reaction or by-product formation, suffer from low sensitivity and make the determination of minor components difficult. Ion chromatography (IC) measurement has been widely used to quantify LMWOAs in the atmosphere, glaciers, rainwater, seawater and soil. In comparison with GC and HPLC, IC technology takes advantage of low sample quantity requirement, low detection limit, simple and rapid operation, good reproducibility, and

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simultaneous detection of multiple LMWOAs, overcoming the inconvenience of other technologies. IC, which used to be widely applied in the study of ice cores, was described by Li et al. (2001) and adopted in this study to detect LMWOAs in lake water. An IC (Dionex ICS-90 model, USA) was used in this study, equipped with 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. Peaknet 6 software was used for data processing and the detection limits of this method and other various detection conditions were reported by Xiao et al. (2010).

The fluorescence was determined on a spectrofluorometer (F-4500, Hitachi, Japan) at room temperature (20°C) with a 150-W ozone-free xenon arc lamp and a 1-cm quartz cell. The excitation-emission matrix (EEM) fluorescence data were collected every 2 nm in emission and every 5 nm for excitation. The spectrofluorometer was operated under the conditions of 5 nm slit width for excitation and 5 nm slit width for emission, photomultiplier voltage of 700 V, scan speed of 2400 nm per minute and auto response time. The scan range was 220–400 nm for excitation and 250–550 nm for emission. Duplicate measurements of each sample were carried out with averaged results reported. Replicate scans were generally within 2% agreement in terms of intensity. The spectra were corrected with Milli-Q water (18.2 MΩ·cm, Millipore) as a blank. The software of SigmaPlot (Systat Software Inc., SSI) was applied for the visualization of EEM data, and the fluorescence intensity (FI) was expressed in arbitrary units (a.u.). For comparative purposes, the water Raman scattering peak intensity recorded under these conditions was 48.60 a.u. at Ex/Em = 290/336. The protein-like fluorescence appearing at Ex/Em = 275–305/326–350 nm was used to characterize biological activity, including bacterioplankton and macroalgae excretion, and to evaluate the influence of microbial behavior on LMWOAs.

Catalytic oxidation was used to quantify DOC with an O·I· Aurora model 1030 Analytical-TOC analyzer (USA), and high-grade purity potassium hydrogen phthalate was used as the standard. 5% (*V/V*) phosphoric acid and 100 g/L sodium persulfate solution were instrumentally added to each sample to remove the dissolved inorganic carbon and oxidize DOC. After removing dissolved inorganic carbon by bubbling with high purity nitrogen, 10 mL of each sample was injected into a non-dispersive infrared analyzer. The relative standard deviation of the replicate measurements (n = 5) of DOC was less than 2% with detection limit of 16.70 μmol C/L. Portable gauges were used to measure the four parameters of pH, dissolved oxygen (DO), electrical conductivity and temperature. Acid standard solution titration was utilized to determine alkalinity. Pearson correlation coefficients were determined using SPSS Base 7.5 (SPSS Inc., USA) to understand potential relationships between LMWOAs and various physicochemical parameters of HF water.

2 Results and discussion

2.1 LMWOAs concentrations

As shown in **Table 1**, five organic acids were detected in HF water, as lactic, acetic, pyruvic, sorbic and oxalic acid. The content of DOC in our study ranged from 179.94 to 664.70 μmol C/L, and averaged 291.64 μmol C/L. The TOA concentration was up to 10.82 μmol/L, with an average value of 6.55 μmol/L and proportion of 7.47% in DOC. These five organic acids averaged 2.50, 0.65, 2.35, 0.96 and 0.09 μmol/L, respectively, with lactic and pyruvic acid in the majority and accounting for 38.20% and 35.90% in TOA. For the spatial and temporal scales, TOAs were 7.03 and 6.40 μmol/L respectively in epilimnion and hypolimnion, as well as 7.52 and 6.06 μmol/L during daytime and nighttime. Pyruvic acid was on average 2.58 and 2.30 μmol/L in the epilimnion and hypolimnion, and 2.52 and 2.37 μmol/L during nighttime and daytime. Referring to daytime and nighttime, TOA were 10.15 and 5.16 μmol/L in the epilimnion, as well as 7.03 and 6.20 μmol/L in the hypolimnion. However, pyruvic acid was 2.52 and 2.74 μmol/L in the epilimnion, 2.34 and 2.48 μmol/L in the hypolimnion.

The value of the fluorescence indexes $f_{450/500}$ in the epilimnion and hypolimnion were on average 1.60 and 1.74, respectively. Values and FI of proteinaceous materials can be used to indicate the origination of proteinaceous materials and the frequency of bio-activity. The $r_{(B/D)}$ values were about 0.60 in HF water. It was shown that the FI of proteinaceous materials during daytime in the epilimnion

Table 1 Concentrations of LMWOAs in the spatiotemporal frame and their proportions in DOC

		DOC (μmol/L)	Lactic (μmol/L)	Acetic (μmol/L)	Pyruvic (μmol/L)	Sorbic (μmol/L)	Oxalic (μmol/L)	TOA (μmol/L)	
Epilimnion	Day	376.25	1.49 (1.19%)*	4.71 (2.50%)	2.52 (2.01%)	1.26 (2.01%)	0.16 (0.09%)	10.15 (7.80%)	7.03 (6.49%)
	Night	287.96	1.78 (1.85%)	0.20 (0.14%)	2.74 (2.86%)	0.44 (0.92%)	– (–)	5.16 (5.77%)	
Hypolimnion	Day	304.3	2.66 (2.63%)	0.57 (0.37%)	2.34 (2.31%)	1.31 (2.57%)	0.15 (0.10%)	7.03 (7.98%)	6.40 (7.66%)
	Night	262.36	3.19 (3.65%)	0.18 (0.14%)	2.48 (2.84%)	0.34 (0.78%)	– (–)	6.20 (7.41%)	
Whole water column		291.64	2.50 (2.58%)	0.65 (0.44%)	0.44 (2.41%)	0.96 (1.98%)	0.09 (0.06%)	6.55 (7.47%)	

* Data in the bracket represent LMWOAs proportion in DOC, –: not detected.
TOA: total organic acid.

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was 2464.13 a.u., 2.5 times higher than that of 964.68 a.u. during nighttime. Moreover, the FI of proteinaceous materials in the epilimnion was on average 1907.29 a.u., much higher than that of 1100.66 a.u. in the hypolimnion.

For the physicochemical parameters, pH and DO in the epilimnion exhibited an increasing trend until 21:00 and then decreased until 6:00 the next morning. In the hypolimnion, pH and DO increased from 10:00–14:00 and then decreased abruptly until 24:00. Whether in the epilinion or hypolimnion, electrical conductivity and dissolved inorganic carbon demonstrated an inverse variation trend compared with the individual pH and dissolved oxygen.

2.2 Origin of LMWOAs and influencing factors in HF

The observed results of the various physicochemical parameters suggested that NOM was at the status of synthesis until 21:00 in the epilimnion. However, the time range of NOM synthesis in the hypolimnion was relatively transient within 10:00–14:00. The value of the fluorescence indexes f450/500 in the epilimnion in HF mostly inclined towards the low value end of 1.40 in the epilimnion, indicative of the terrestrial sources of DOM. However, the fluorescence index in the hypolimnion was most close to the high value end at 1.90, suggesting autochthonous sources of DOM. Low $r_{(B/D)}$ values in HF water reflected the fact that the protein-like fluorescence was brought about by algae exudation and decomposition of bacteria detritus. The higher FI of proteinaceous materials in the epilimnion or during daytime reflected the fact that algae and bacterioplankton in the epilimnion were active. Intense bio-behavior was triggered by photochemical reactions such that photoproduction of LMW compounds was relatively intensive in the epilimnion, especially during daytime.

Significant photodegradation of humus to produce LMWOAs made TOA 0.63 μmol/L higher in the epilimnion than in the hypolimnion and 1.46 μmol/L higher during daytime than nighttime. Carbon of terrestrial sources was more abundant in the epilimnion, where DOC was 58.82 μmol C/L higher than in the hypolimnion, encouraging photodegradation and benefiting the assemblage of LMWOAs. In addition, the lesser difference between TOAs spatially was also caused by the physical motion of water. Firstly, vertical mixing of water above the thermocline brought about strong and periodic fluctuations in irradiance that reduced differences of LMWOAs between the epilimnon and hypolimnion (Zagarese et al., 2001). Secondly, LMWOAs in the epilimnion would be transferred to the hypolimnion through water convection during the night, which also shrank the gap between the epilimnion and hypolimnion. TOAs were basically balanced between production and consumption in the epilimnion except for an unexpectedly high value of 19.36 μmol/L at 18:00 (**Fig. 2**) when acetic acid was 13.90 μmol/L, probably related to the maximum degradation of humus as illustrated in **Fig. 1**. As has been indicated in Lake Diktar-Erik that direct

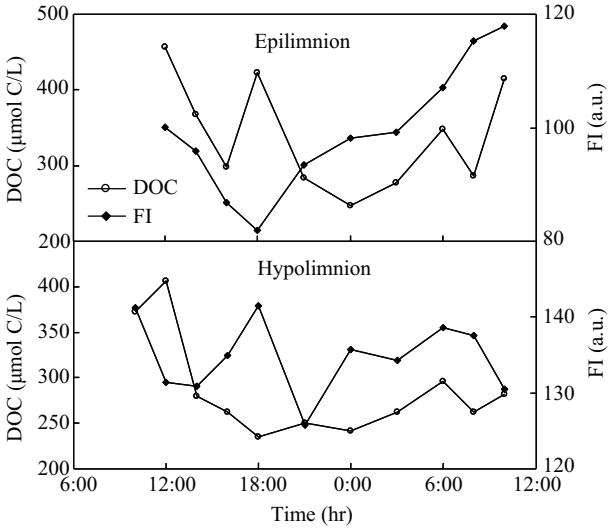


Fig. 1 Diurnal variations of DOM in the epilimnion and hypolimnion. FI: fluorescent intensity of humic materials.

terrestrial import influenced much of LMWOAs in lake water (Jonsson et al., 2007), thus large terrigenous sources resulted in the unusual increase of LMWOAs, as DOC did at 18:00 (**Fig. 1**). Due to allochthonous sources, acetic acid and TOA in the epilimnion of HF which received sufficient sunlight were 4.71 and 10.15 μmol/L, nearly 7 times and 10 times higher than those in solar radiation cultivation experiments in both humic lake Skarshul and clearwater lake Fiolen, where acetic acid was 0.70 and 0.77 μmol/L, and TOAs were 1.55 and 1.54 μmol/L (Bertilsson and Tranvik, 1998). Of course, the influencing factors which caused remarkable differences of LMWOAs between these two studies could be complicated, as varying microbial community structure, humification degree, radiance intensity, even DOC in oligotrophic humic lakes were more prone to photodegradation (Bertilsson and Tranvik, 2000).

Contrary to TOA, pyruvic acid was always higher during nighttime whether in the epilimnion or hypolimnion, because keto acids can be photolyzed and bio-assimilated rapidly once they are photo-produced from bio-refractory DOM: the photochemical flux of pyruvic acid was reported to be 2.00%–4.00% of total carbon flux to bacteria on a daily basis (Grosjean, 1983; Kieber et al., 1989). Based on this reason, pyruvate was found to be only 4.00 and 0.50 nmol/L during daytime and nighttime in a field study of seawater (Kieber, 1988). As the most abundant organic acid in HF, pyruvic acid was still one order of magnitude lower than the most abundant glycolic acid, at 35.50 μmol/L in Lake Diktar-Erik (Jonsson et al., 2007). The remarkable difference between these two studies probably lies in the sources except for the above explanation. Pyruvic acid is closely bound up in life materials and plays a pivotal role in the metabolic interconversion of saccharides, fats and amino acids by acetyl CoA during Kreb's cycle. Combining analysis of the diurnal variation trends of physicochemical parameters and that of pyruvic

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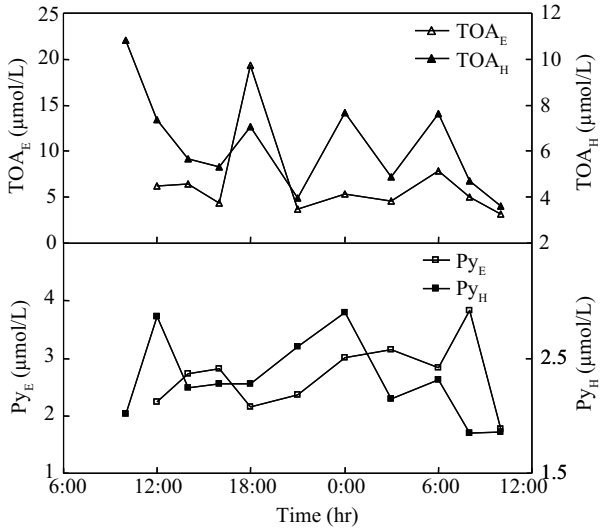


Fig. 2 Diurnal variations of TOAs and pyruvic acid in HF in the spatiotemporal frame. TOA_E, TOA_H: total organic acid in epilimnion, hypolimnion; Py_E, Py_H: pyruvic acid in epilimnion, hypolimnion, respectively.

acid in both the epilimnion and hypolimnion, it was observed that pyruvic acid had an opposite variation relation to NOM during nighttime and pyruvic acid increased with NOM degradation (**Fig. 2**), suggesting that pyruvic acid largely derived from bio-degradation of NOM and planktonic secretion (autochthonous biogenetic sources). For this reason, pyruvic acid in the epilimnion of HF was 2.52 and 2.74 μmol/L during daytime and nighttime, which is a few orders of magnitude higher than that reported by Kieber (1988). During the Kreb's cycle of life materials, lactic acid mainly originating from pyruvic acid through anaerobic transformation could accumulate due to its relative stability. Therefore, lactic acid was analogous to pyruvic acid and was also higher during nighttime rather than during daytime. Pyruvic and lactic acid even had the similar cumulative ratios (concentration, night/day) of 1.10 and 1.20 (**Table 1**). Nevertheless, TOA was 1.04 μmol/L higher in the hypolimnion than in the epilimnion during nighttime, mainly due to conversion of pyruvic acid to lactic acid during transportation downwards.

The contribution of TOA to DOC ranged widely from 0.31% to 6.40% in an investigation of the formation of LMWOAs in a peat bog after 24 hr UV irradiation (Brinkmann et al., 2003), whereas the contribution increased from 5.17% at 10:00 to 10.97% at 18:00 over 8 hrs' radiation in the epilimnion in HF. The results of the two studies are close to each other because LMWOAs in the epilimnion in HF were similar to that in the peat bog originating from the photochemical degradation of bio-refractory humus. Yet because of the two additional sources of terrigenous input and autochthonous biogenetic origination, the contribution of LMWOAs to DOC in the HF epilimnion had an initial value of 5.17%, much higher than that of 0.31% in the peat bog.

2.3 Spatiotemporal variation characteristics of LMWOAs in HF Lake

2.3.1 Variation trends of LMWOAs in time scale

In the whole time frame of the research, diurnal variation trends of TOAs after 21:00 between the epilimnion and hypolimnion were well positively correlated ($R^2 = 0.72$, $p \leqslant 0.05$), and it was revealed that the vertical current mainly reconciled TOAs' behavior after 21:00 in these two water layers and that LMWOAs originating from bio-degradation of NOM were influenced by planktonic behavior.

Decrease and increase of organic acids during time-course irradiation depended on rates of consumption and production. TOA decreased from 10.82 μmol/L at 10:00 to 5.01 μmol/L at 16:00, which was caused mainly by the sharp decrease of LMWOAs in the hypolimnion. NOM during this time interval was at a stage of synthesis, thus, LMWOAs were largely absorbed as substrate by phytoplankton to improve productivity or involved in aggregation into large molecules through successive condensation and structural rearrangement (Parlanti et al., 2000). However, TOA fluctuated around 5.34 μmol/L after 21:00, which was chiefly caused by the balance between release of LMWOAs and their bio-aggregation with vertical mixing as thermal stratification attenuated. Meanwhile, LMWOAs' release originated from algae secretion and macro molecules' decomposition with the help of bacterioplankton. Taken as a whole, the behavior of LMWOAs with time was mainly controlled by bio-behavior and the physical motion of water.

In the epilimnion, accompanying NOM degradation, pyruvic acid promptly increased during nighttime without the rapid photo-oxidation and intense phytoplankton phagocytosis which exclusively happened during daytime. A similar phenomenon was also observed for pyruvic acid in the hypolimnion; it had its highest concentration of 2.90 μmol/L at 24:00 when NOM and plankton reached the maximum degradation and secretion. Afterwards, rapid bio-aggregation and assimilation of pyruvic acid with NOM synthesis was observed through analysis of physicochemical parameters in the hypolimnion (**Fig. 2**). All of these observations further revealed in detail that autochthonous biogenetic derivation by way of bacterioplankton degradation of NOM and phytoplankton exudation predominated in the origination and conversion of pyruvic acid. Therefore, pyruvic acid exhibited an increasing and decreasing diurnal variation trend in the epilimnion and in the hypolimnion respectively.

Sorbic acid was positively correlated with bromate in the epilimnion ($R^2 = 0.82$, $p \leqslant 0.05$), and this kind of organic acid was catalytically oxidized more and more with time and was exhausted after 24:00. However, bromide was in sharp contrast to sorbic acid and gradually increased. Previous study has shown that BrO_3^- could act as an oxidant to anticipate in catalytic oxidation and degraded

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humic acid (Xie et al., 2008), thus implying that bromate was probably stimulated by catalysis to oxidize sorbic acid and itself was reduced to bromide.

2.3.2 Variation trends of LMWOAs in vertical profiles

Sulfate reduction mediated by bacteria was found to always be accompanied by the oxidization of hydrocarbons (Chen et al., 1995). A significant negative relationship between the profiles of SO_4^{2-} and TOA (R^2 = 0.87, $p \leqslant 0.01$) was apparent at 10:00 in the first morning (**Fig. 3a1**) and TOA reached up to 25.10 μmol/L at 15 m water depth, revealing that SO_4^{2-} contributed a great deal during the production and consumption of LMWOAs. Photochemical reactions could also act as a consumption route for organic acid as shown by the result that about 98% ^{14}C tagged formic acid was almost exclusively mineralized to CO_2 after exposure to natural sunlight for few hours (Bertilsson and Tranvik, 1998). At 14:00 and 16:00, the maximum values of TOAs of 9.83 and 7.83 μmol/L appeared at 10 and 8 m water depths. This suggested that after intense photo-oxidation and bio-assimilation in upper-layer water (above 8 m, definition by thermocline), LMWOAs could not be immediately replenished through conveyance from lower-layer water (below 8 m) where higher contents of LMWOAs were preserved. From the FI of proteinaceous materials, stronger planktonic metabolic behavior was exhibited above 8 m depth at 10:00 the next morning and then significantly weakened with depth, resulting in a gradually increasing profile of LMWOAs, revealing that the biomineralization and phagocytosis for LMWOAs weakened with depth (**Fig. 3a3**), so that the maximums of 9.26 and 4.69 μmol/L at 8:00 and 10:00 appeared in lower-layer waters.

The highest concentrations of LMWOAs at 12:00 and 18:00 were 13.54 and 30.71 μmol/L at 2 m and 1 m water depth (**Fig. 3b1**), which was comparable to the result of

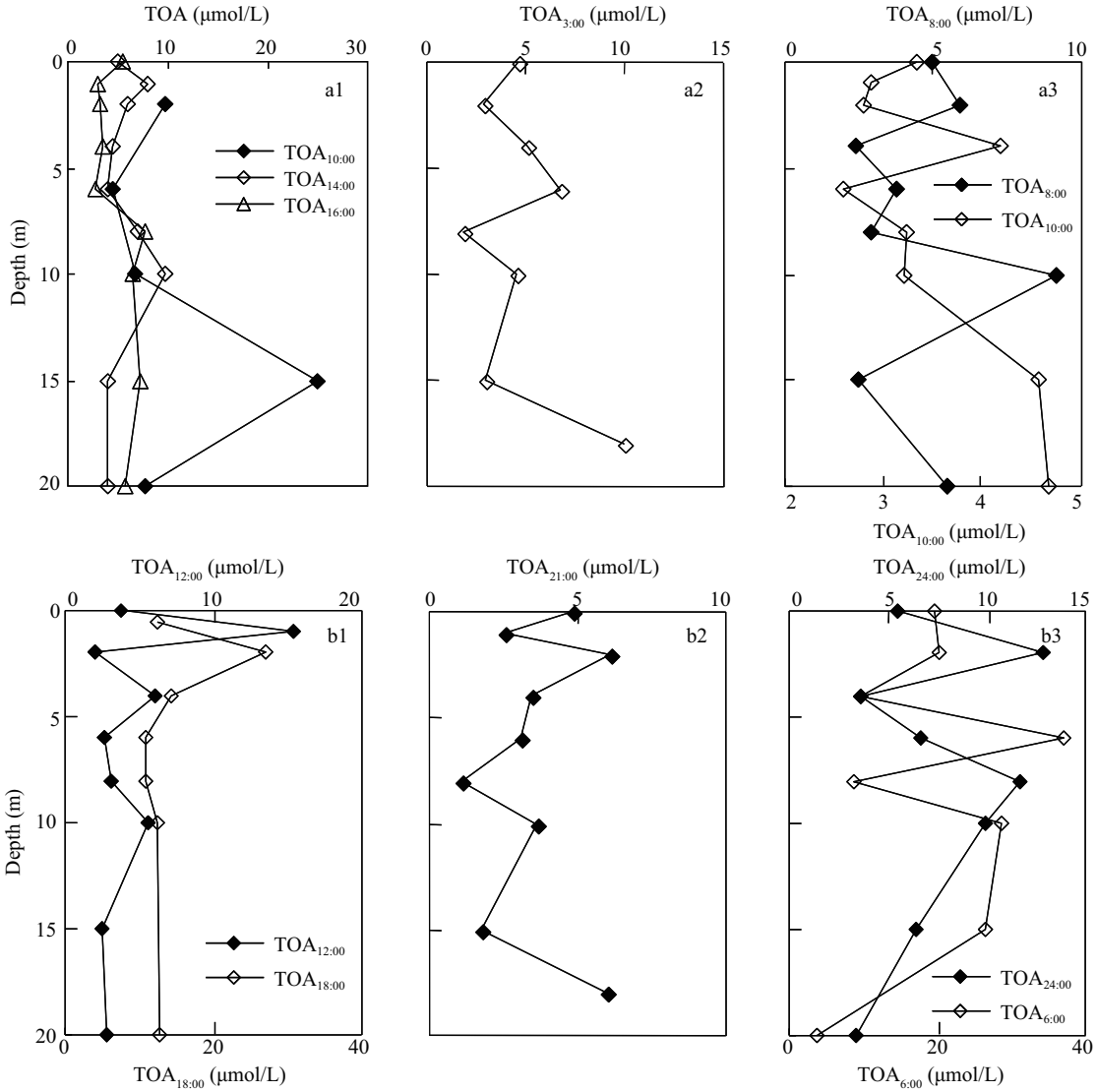


Fig. 3 Increasing (a) and decreasing (b) profiles of TOAs in the water column of HF. $TOA_{10:00}$ in a1 represents TOA in the first morning; $TOA_{10:00}$ in a3 represents TOA in the next morning.

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Jonsson et al. (2007) that abundant terrigenous input for LMWOAs was not excluded. Similarly, TOA at 24:00 was highest at 12.74 μmol/L at 2 m depth, where FI of proteinaceous materials was up to 9824 a.u. and microbial activity was most frequent, indicating that the LMWOAs originated from NOM degradation by bacterioplankton and exudation release by phytoplankton.

Pyruvic acid decreased with depth at 10:00, 14:00 and 16:00 as illustrated in **Fig. 4a1**, which shows that its highest values were in the upper-layer waters at 2.77, 3.44, 3.90 μmol/L, respectively. Similarly, pyruvic acid exhibited diffuse profiles at 3:00 and 6:00, with highest contents 4.04 and 3.03 μmol/L in the upper-layer waters, respectively (**Fig. 4a3**). These observations were all the result of biogenetic sources for pyruvic acid in the epilimnion and pyruvic acid values all presented a decreasing profile.

Pyruvic acid decreased first and then increased promptly with depth at 12:00 and 18:00 (**Fig. 4b2**). Both times exhibited the same profiles (R^2 = 0.86, $p \leqslant 0.01$) with depressions of 1.63 and 1.88 μmol/L at 8 m. Reinforced by NOM degradation, pyruvic acid gradually increased with depth, showing good negative correlation with pH, DO (R^2 = 0.68, $p \leqslant 0.05$) and coarse positive correlation with electrical conductivity, alkalinity (R^2 = 0.62) at 12:00, indicating that pyruvic acid in the vertical section was still influenced greatly by degradation and synthesis of NOM, as well as uptake and secretion of phytoplankton. These biologically relevant factors mediated during the environmental processes. Pyruvic acid at 8:00 and 10:00 in the next morning showed similar profile trends, but the highest concentration of 3.05 μmol/L of pyruvic acid at 10:00 was gently pushed downwards to 4 m water depth under photo-oxidation, bio-assimilation and decomposition in the epilimnion. Simultaneously, because NOM in the epilimnion remained at a stage of decomposition and secretion of plankton, yet NOM in the hypolimnion nearly kept at synthesis and plankton assimilation during

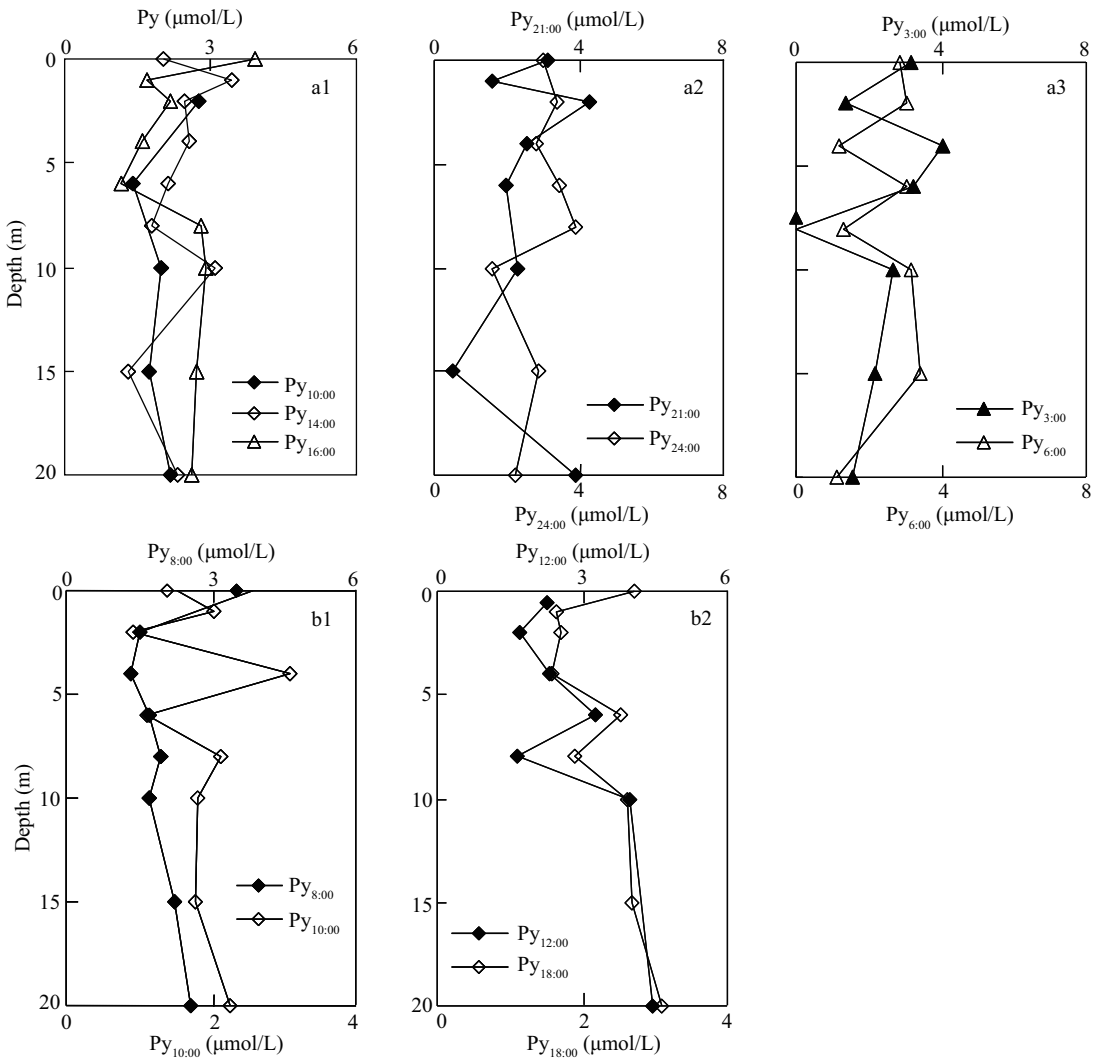


Fig. 4 Decreasing (a) and increasing (b) profiles of pyruvic acids in the water column of HF. $Py_{10:00}$ in a1 represent Py in the first morning; $Py_{10:00}$ in b1 represents Py in the next morning.

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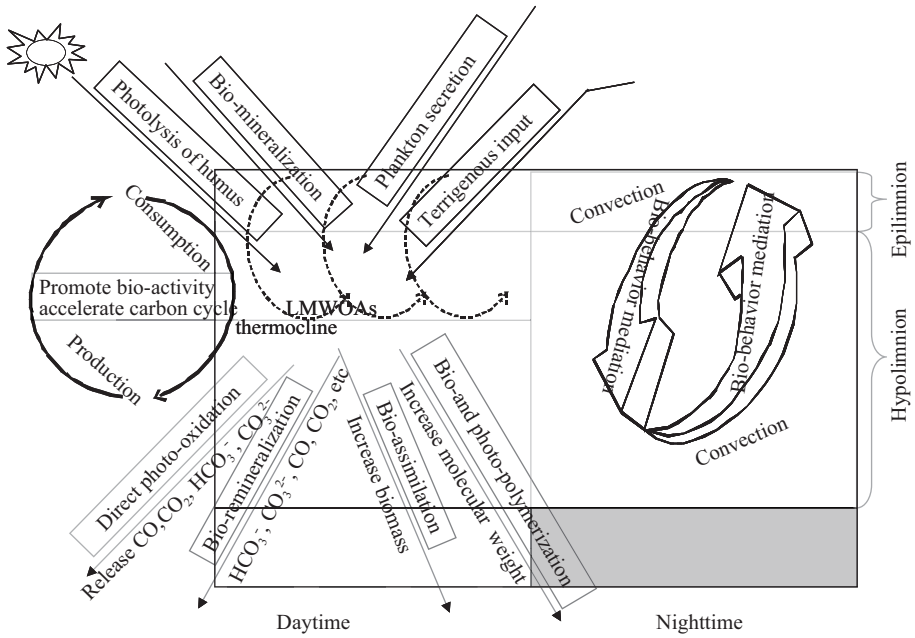


Fig. 5 Cycle mechanism contour of LMWOAs in HF lake water.

the time range of 21:00–6:00, thus, TOAs and pyruvic acid exhibited decreasing profiles during this time interval (**Fig. 3b** and **4a**). However, there was an exception at 3:00 where TOA abruptly increased from 4.74 μmol/L at 10 m to 9.98 μmol/L at 20 m, probably because the sediment-water interface was disturbed.

Through comprehensive analysis and discussion on LMWOAs' origin and conversion, a mechanism contour was sketched in **Fig. 5**.

3 Conclusions

In conclusion, natural sunlight scattering on surface lake water was found to be very conducive to LMWOAs' production and accumulation. These results from HF showed the contents of LMWOAs and their spatiotemporal variation features, as well as the main influencing mechanisms. Terrigenous input, thermal stratification and convection, photochemical reactions and polymerization, microbial remineralization and assimilation, plankton release etc.; these complicated physical, chemical and biological processes interacted in the distribution of LMWOAs in HF. However, the factors influencing spatiotemporal variations of pyruvic acid were relatively simple, especially at night, chiefly being dependent on plankton behavior. In short, accumulation of LMWOAs from terrigenous input and endogenous production exceeded their consumption by photochemical and biological reactions, so that they could be detected and successively accumulate in lake water. The results of HF are compatible with those of Bertilsson and Tranvik (1998), who found that the photochemical yield of carboxylic acids was one order of magnitude higher than their bacterial conversion. The concomitance of photo-chemical reactions and biological behavior provided an important removal pathway for DOC and bio-refractory NOM in lakes. Moreover, photo-chemical degradation played a unique role and represents a pivotal research orientation in biogeochemical circulation of carbon compounds in aquatic systems.

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