Characteristics and distribution of low molecular weight organic acids in the sediment porewaters in Bosten Lake, China

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Abstract

The composition and vertical profiles of low molecular-weight organic acids (LMWOAs) and the contribution of them to dissolved organic matter (DOM) in sediment porewaters in Bosten Lake, Xinjiang, China were investigated. The results showed that total concentration of LMWOAs was up to 94.5 μmol/L and their proportion in DOM was 5.6%, suggesting that LMWOAs were important chemical components in DOM in lake sediment porewaters. Among the seven LMWOAs, pyruvic and acetic acid had the highest concentrations with 26.30 and 8.31 μmol/L, accounting for 51.4% and 14.92% of LMWOAs, respectively. Trifluoroacetic and sorbic acid had the lowest concentrations, indicating that the compositions of LMWOAs in relative reducing environments were largely different from those reported in glacier, atmosphere and soils. The concentrations of lactic, acetic, formic, sorbic and oxalic acid decreased with increasing depth, probably relating to stronger microbial activities in the initial stage of early diagenesis. Trifluoroacetic acid was mainly anthropogenic with its concentration, showing a diffusive trend from the surface to bottom sediments. The concentrations of lactic acid and nitrate generally showed a consistent profile. The increasing concentration of pyruvic acid in the vertical profile was just opposite to that of sulfate, revealing a significant negative relationship between them. Oxalic acid remained constant except for an obvious peak at 6 cm depth. The results indicated the diversities in sources and behaviors for various LMWOAs during early diagenesis in sediments.

Key words: dissolved organic matter; low molecular-weight organic acids; sediment porewaters; early diagenesis

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Introduction

Low molecular-weight organic acids (LMWOAs) generally refer to the carboxylic organic compounds whose molecular weight is lower than 500 Da, e.g., oxalic, formic, acetic, propionic, pyruvic and methanesulfonic acid. Those acids have relatively high solubility and are widely distributed in surface environments, e.g., ocean, river, lake, bog, soil, rainwater, atmosphere, snow and ice (Steinberg and Kawamura, 1996; Li et al., 2001; van Hees et al., 2005). It is commonly accepted that they are degradation products of various types of naturally occurring large-molecule organic substances, and are closely related to microbial activities. LMWOAs played an important role in various physical, chemical and biological processes in surface environments (Herlihy et al., 1987; Barth, 1987; Routh et al., 2001; Boschker et al., 2001; Wu and Tanoue., 2001; Ding et al., 2005). For instance, those acids had a strong capacity to combine with trace metals, e.g., Cu, As,

Zn, Cd, Pb and Ce (Burckhard et al., 1995; Hu et al., 2005; Ebena et al., 2007) and organic chlorine pesticides as well as other organic pollutants, which would directly affect their transport, bioavailability, toxicity and fate (Zhao et al., 2006), and can act as mediators of mineral acquisition in low-nutrient environment (Dakora and Phillips, 2002). In addition, those acids also had significant influence on soil chemical weathering and leaching (Drever and Stillings, 1997; Shan et al., 2006).

Many studies on organic acids focused on their distribution in ice core, rainwater and atmosphere with an attempt to investigate their sources and influences on their evolutionary history (Li et al., 2000; Lee et al., 2005; Niu et al., 2005; Wang et al., 2007). The contents of organic acids in atmospheric particles, $PM_{2.5}$ and PM_{10}, have been detected as 541 and 615 ng/m^3, accounting for 0.4% and 0.3% of the total aerosol amount, respectively (Wang et al., 2007). In atmospheric aerosol of Nanjing City, as the major dicarboxylic acid, oxalic acid was the product of bio-sources and mainly derived from atmospheric photochemical oxidation (Niu et al., 2005). Organic acids, e.g.,

formic, acetic, propionic, pyruvic, oxalic and methane-sulfonic acid were commonly observed in snow and ice glacier, in which, formic and acetic acid were up to 350 and 200 ng/g, and were considered as the dominant acids. Those organic acids were mostly derived from organic matter from marine planktons and atmospheric pollutants due to the forest conflagration and human activities (Li et al., 2000). However, till now ittle is known on LMWOAs in surface waters and lake sediments.

Sediment porewaters are the important media for materi-al and energy exchange between sediment and its overlying water. As one of the important chemical components in lake water environment (Thurman, 1985), dissolved organic matter (DOM) is an important factor affecting the transport, behavior, toxicity and bioavailability of many toxic pollutants, and it also plays an important role in primary productivity, photosynthesis, gas-liquid exchange and other physical, chemical and biological processes in aquatic environments (Fu et al., 2004; Wu et al., 2001, 2003; Ritchie and Perdue, 2003). However, up to now, approximately less than 25% of DOM has been detected in terms of chemical compositions, and majority is un-known (Baker and Spencer, 2004). LMWOAs are group of chemical components of DOM in sediment porewaters, but their distribution and contribution relative to DOM are still unknown. Studies on organic acids in sediment porewaters would help to reveal the composition, contents and sources of organic acids, and help to understand the influence of early diagenesis in sediments on the overlying water as well.

Taking Bosten Lake, Xinjiang as an example, this study employed ion chromatography to analyze the concentra-tions of LMWOAs in sediment porewaters, to evaluate the contributions of LMWOAs to DOM, to determine the source of LMWOAs and the relationship between them and early diagenesis.

1 Material and methods

1.1 Study area

Bosten Lake (86°40′–87°26′E, 41°56′–42°14′N) is located in the southern part of Bazhoubohu County, Xin-jiang, in the lower reaches of the Kaidu River. It is one of the largest inland fresh water lakes in China. The drainage basin is located in the center of the Eurasian continent, where the sufficient sunlight and heat with an average pre-cipitation of 68.2 mm/yr recorded from 1955 to 1989 lead it an inland desert climate (Jin, 1990). In the lake region, the annual average temperature is 8–8.6°C. The lake water surface is vast, as long as about 55 km from east to west and as wide as about 25 km from south to north, covers an area of 1100 km^2 or more. The lake surface is 1048 m above sea level and the average water depth is 9 m with the maximum depth of 17 m. The total storage capacity of the lake is 88×10^8 m^3, and the lake water retention time is 4.8 yr. The drainage basin originates from perennial rivers supplied by mixed melting ice, precipitation and groundwater in the mountainous regions of Tianshan. In

addition, there are some intermittent rivers, which account for 84.1% of the total surface runoff (Jin, 1990; Wang and Dou, 1998).

1.2 Sampling and analytical methods

Using our self-made portable sediment sampling device, sediment cores were collected as long as 45 cm in the vast deep water area in the northwest of Bosten Lake (with a water depth of 15 m) in Sep 2006. The cores collected had a distinct sediment/water interface. The sediments were well preserved with no disturbed sign, reflecting a good natural sedimentation status. Cores were cut at the intervals of 1 cm in the field and porewater was centrifuged. Porewater samples were filtered with 0.45-μm acetate cellulose membrane, and were stored at 4°C until analysis.

1.3 Experimental methods and reagents

Gas chromatography or different HPLC techniques were used to analyze LMWOAs in environmental samples (Kawamura and Kaplan, 1984; Morvai et al., 1991; Albert and Martens, 1997; van Hees et al., 1999; Jiang et al., 2002), but those techniques had some disadvantages, e.g., time-consumption and requiring derivative technology. Ion exchange chromatography and size exclusion chromatog-raphy had inappropriate capacity factors and interference remnants; therefore, they are not appropriate methods used for LMWOAs determination (Baziramakenga et al., 1995; Szmigielska et al., 1997). In contrast, ion chromatography was widely used to determine organic acids in ice core and rain samples (Li et al., 2001; Lee et al., 2005; Xu et al., 2007), and thus this analytical method was employed in measuring organic acids in Bosten Lake. The Dionex ICS-90 ion chromatograph (USA) was used with a sup-pressed 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 were used in the experiment. Peaknet 6 software was used for data processing.

The eluent was KOH prepared by adding 18.2 Ω·cm Mill-Q super-pure water into RFC-30. The standard solu-tions of organic acids were purchased from Sigma-Aldrich Co., (USA) and prepared with 18.2 Ω·cm Milli-Q ultrapure water. The gradient of KOH eluent was set at 1 mmol/L in the first 6 minutes and at 30 mmol/L from the sixth minute to the thirty-sixth minute. The flow rate of eluent was 1.5 mL/min, the temperature of CTS-10 column temperature stabilizer was kept at 39°C, and 300 μL sample was injected each time.

1.4 Chemical analysis

Figure 1a illustrates the gradient elution ion chro-matograms of the standard samples, and Fig. 1b shows the gradient elution ion chromatograms of porewaters (at 14 cm depth diluted samples). The relative standard devia-tions (RSD) and detection limits of the various ions (three times the blank standard deviation, $n = 8$) were obtained using 8 times continuous analyses, a series of mixed
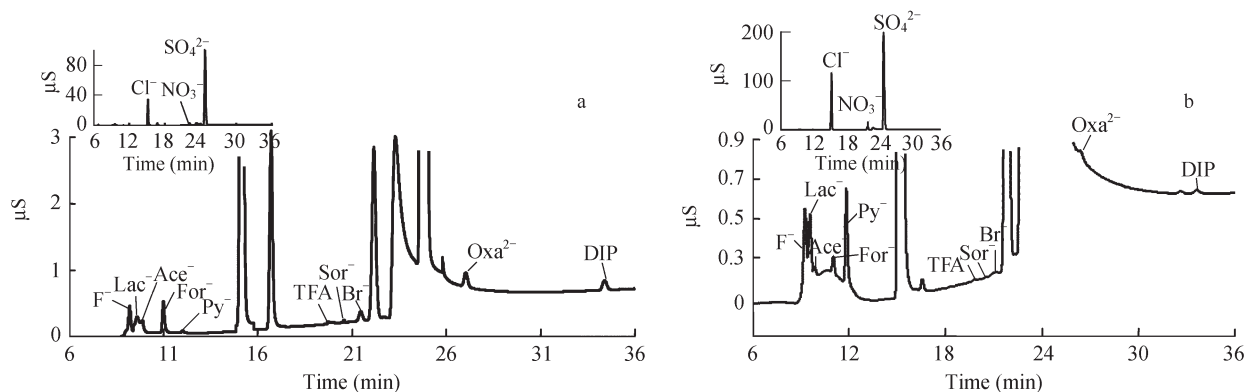
Fig. 1 Standard ion chromatogram of low molecular weight organic acids (LMWOAs) (a), and ion chromatogram of LMWOAs in sediment pore waters of Bosten Lake (diluted samples at 14 cm depth) (b). Lac⁻: lactic; Ace⁻: acetic; For⁻: formic; Py⁻: pyruvic; TFA: trifluoroacetic; Sor⁻: sorbic; Oxa²⁻: oxalic; F⁻: fluoride; Br⁻: bromide; DIP: dissolved inorganic phosphorus; Cl⁻: chloride; NO₃⁻: nitrate; SO₄²⁻: sulfate.

standard samples were analyzed and the linear correlation of each organic acid was obtained within the linear range. As shown in Table 1, RSD of standard samples determined using the gradient elution method was generally below 10%, the linear correlation coefficient $r > 0.99$, and the detection limits were less than 1 μmol/L.

Total dissolved organic carbon in water samples was analyzed using high-temperature catalytic-oxidation method (high TOC II total organic carbon analyzer, Elementar, Germany), with potassium hydrogen phthalate (highly pure) as the standard. The detection limit was 0.2 mg/L and the error was less than 2%.

2 Results and discussion

2.1 General characteristics of LMWOAs in sediment porewaters

As shown in Fig. 1b, seven of LMWOAs was detected in the sediment porewaters of Bosten Lake, as lactic, acetic, formic, pyruvic, trifluoroacetic acid (TFA), sorbic and oxalic acid with concentration ranges 1.03–7.11, 0.36–51.00, 0–14.44, 0.85–75.41, 0.51–1.79, 0.56–5.94, and 0.56–16.84 μmol/L, respectively. Average concentrations of these organic acids were 2.16, 7.69, 3.34, 24.35, 0.63, 1.29 and 2.74 μmol/L, accounting for 8.34%, 14.92%, 8.77%, 51.4%, 2.42%, 5.32% and 8.82% in the total organic acid, respectively. The concentrations of pyruvic and acetic acid out of seven organic acids were highest, whereas contents of TFA and formic acid were lowest. The total amounts of organic acids ranged between 6.9 and 94.5 μmol/L.

According to previous studies (Kawamura and Ikushi-

ma, 1993; Sempere and Kawamura, 1996; van HEES et al., 1999; Boschker et al., 2001; Tedetti et al., 2006) on organic acids in different biological environments, it is generally accepted that organic acids in different environments are different in terms of their concentrations and distributions. Pyruvic acid in sediment porewaters of Bosten Lake was the major species, while acetic acid was major in porewaters of soil, ocean and marine sediment, oxalic or formic acid was major in atmosphere and rainwater. Routh et al. (2001) detected acetic, propionic, isobutyric, butyric, isopentanoic and pentanoic acid in *in situ* sediments and acetic acid was determined as the main component with at least 200 μmol/L in the Yegua sediments. However, only less than 51 μmol/L of acetic acid was detected in porewaters of Bosten Lake. Similar to acetic acid in Yegua sediments, acetic acid in porewaters of Bosten Lake where just existed weaker activity of acetic acid-producing bacteria also mainly derived from oxidized deterioration of DOM by inorganic acid radicals or other electronic acceptors. Pyruvic acid as the major organic acid in Bosten Lake ranged between 0.85 and 75.41 μmol/L, mainly deriving from the reduction reaction of sulfate (Fig. 2). Unlike marine porewaters, the concentrations of various organic acids were relatively low, and pyruvic and acetic acid were thought to be the major components with average concentrations of 24.4 and 7.7 μmol/L, accounting for 51.4% and 14.92% in total organic acid in porewaters of Bosten Lake, respectively. In porewaters of the Cape Lookout Bight sediments, only a small amount of organic acid in winter and spring was detected. Acetic and formic acid were reported as the major components, and the maximum concentration of acetic acid was just 15 μmol/L.

Table 1 Detection limit, relative standard deviation (RSD) and linear correlation of the method

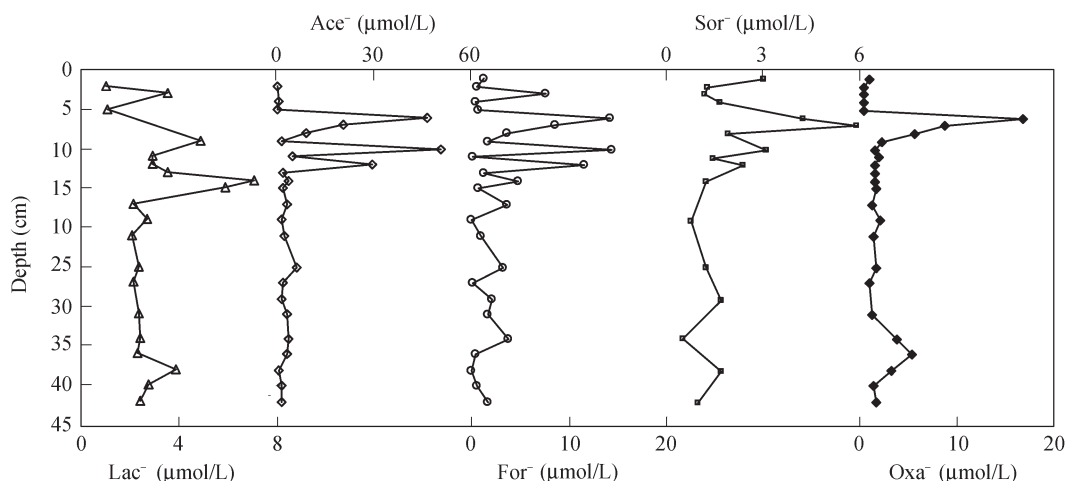| Organic acid	Linear range (× 10² μmol/L)	Standard curve equation	Linear correlation coefficient (r)	RSD (%)	Detection limit (μmol/L)
Lactic acid (CH₃CH(OH)COOH)	0.01–0.34	$1.3477X + 0.0194$	0.9802	6.7	1.01
Acetic acid (CH₃COOH)	0.01–0.51	$8.3391X + 0.0055$	0.9921	3.7	0.034
Formic acid (HCOOH)	0.01–0.22	$4.3411X − 0.0084$	0.9978	3.6	0.089
Pyruvic acid (CH₃COCOOH)	0.01–0.57	$5.6356X + 0.0034$	0.9997	8.0	0.069
Trifluoro acetic (CF₃COOH)	0.004–0.09	$5.4214X + 0.0038$	0.9998	5.1	0.027
Sorbic acid (CH₃CH=CHCH=CHCOOH)	0.001–0.09	$23.365X + 0.0033$	0.9996	18	0.01
Oxalic acid (HOOC-COOH)	0.01–0.2	$2.4805X + 0.0022$	0.9989	3.2	0.08

Fig. 2 Categories and profiles of organic acids possessing characteristic of three-stage.

However, concentrations of LMWOAs were relatively high in summer, accounting for 80%–90% of the total carboxylic acid. The dominant components were acetic and propionic acid, with the acetic acid concentration up to 2300 μmol/L (Albert and Martens, 1997). The results obtained in Bosten Lake showed some differences, reflecting that acetic acid concentration was just equivalent to those reported in winter and spring by Albert and Martens (1997). This was probably the temperature fluctuation in different seasons during districts that led to variations of microbial activity, which could impose on the production and consumption of organic acid. This may indicate that the microbial activity in Bosten Lake was similar to that in Cape Lookout Bight sediments in spring, and may also imply that microbial activity was an important factor controlling the concentrations and distributions of organic acids in sediment.

The contribution of organic acids (6.92–94.45 μmol/L) to total dissolved organic carbon (DOC) (582.3–4428.3 μmol C/L) was 0.7%–17.6% which were higher than that of organic acids in soil. LMWOAs in soils, including formic, acetic, citric, fumaric, lactic, oxalic and shikimic acid, had concentration range of 1.3–312 μmol/L. Acetic and citric acid were the main components with concentrations of 174 and 80 μmol/L, respectively. The contribution of organic acids to DOC (1.02–32.33 μmol C/L) was just up to 0.9%–3.3% in soil water extract, and decreased with increasing depth (van Hees et al., 1999). In present study, the total amount of organic acids and the maximum concentration of acetic acid were three times lower than that reported by van Hees et al. (1999), while the contribution of organic acids to DOC was six times higher than that by van Hees et al. (1999). Except for different microbial activities in the two varied ecological environments, the reason also include that the easily degradable DOM has the different proportions in total NOM which resulted in diverse contents of organic acids and their contribution to DOC in individual ecosystem.

The concentrations of organic acids in crude oil-forming water were determined by Barth (1987) to be within the range of 0.02–20 mmol/L, and among detectable species,

acetic acid was a major one with content high up to 16 mmol/L. The total concentration of organic acid in Bosten Lake is two orders of magnitude lower than the results obtained in crude oil-forming water and three orders of magnitude lower in Bosten Lake for acetic acid than that detected by Barth (1987). This was mainly caused by the abundance of organic matter and its easily degradable feature, which stirred up more frequent microbial activity and more abundant organic acids in the crude oil-forming water. Albert et al. (1995) found that in the Black Sea water the main species of organic acids were formic, acetic (up to 11.5 μmol/L) and lactic acid (up to 60 μmol/L); while in porewaters of the Black Sea the detectable organic acids were also formic, acetic and lactic acid with propionic acid in trace amount, and the concentrations of acetic and formic acid decreased downwards with the range of 0.5–3 μmol/L and 0.5–1.8 μmol/L, respectively, and the concentration of lactic acid varied between 0.25 and 7.4 μmol/L. The results in Bosten Lake are equivalent to the data of the Black Sea water except for formic and acetic acid which are 10–20 times higher in Bosten Lake than that in porewaters of Black Sea. The results of our investigation showed that the maximum concentrations of acetic and formic acid both generated at 10 cm depth, ranging 0.36–51 μmol/L and 0–14.44 μmol/L, respectively. The contents of lactic acid whose maximum concentration generated at 14 cm depth varied between 1.03 and 7.11 μmol/L. These results about formic, acetic, lactic acid in Bosten Lake differentiated from the data in Black Sea where sulfate reduction reaction occurred. The reason may be that not only sulfate-reducing bacteria provided the main driving force, but acid-producing bacteria and methane-producing microbial processes also should be responsible for the formation lactic, acetic and formic acid in Bosten Lake sediment. The content profiles of three organic acids in our investigation also showed difference from the results reported by Albert et al. (1995). This might be mainly because of no good bridge link for organic acids between the overlying lake water and the sediments. Therefore, unlike the situation in porewaters of the Black Sea that the contents of the three organic acids began to decrease

progressively from the surface sediment layer, the maximum value of them in Bosten Lake only can be observed at 10 cm sedimentation depth.

The results of this research showed that oxalic acid accounted for 8.82% of the total organic acids. In the investigations on aerosols over Tokyo, Japan, Kawamura and Ikushima (1993) found that dicarboxylic acid was the principal organic component in the atmosphere and it accounted for 37%–69% in total carboxylic acid under the influence of photochemical conditions. The abundance of oxalic acid determined in Bosten Lake was almost 10 times less than the values reported by them. The properties of short-chain dicarboxylic acid were stable in the atmospheric environment and thus can be transported over long distance. However, oxalic acid as a simplest dicarboxylic form in sediments was mainly derived from anaerobic deterioration of organic matter, sometimes probably from certain oxalic acid-bearing plants and algae and the precursor compounds to the formation of oxalic acid in sediments. Meanwhile, the catalytic factors involved in the process of its formation were relatively simple. The unique ecological environment for oxalic acid forming was a decisive factor affecting its transport distance. The factors affecting the source and formation of oxalic acid in these different environments resulted in the less abundance of oxalic acid in the sediments.

As only dicarboxylic acid in Bosten Lake, oxalic acid ranged between 49.2 and 1482.6 μg/L and its contribution to DOC was 0.24%. The total concentrations of dicarboxylic acid in rainwater samples from Western Pacific were within the range of 36–959 μg/L and its contribution to DOC (1.2–2.5 mg C/L, averaging 1.6 mg C/L) was 3% on the average, with the maximum value up to 5%. In addition, oxalic acid as the most abundant dicarboxylic acid in rainwater samples accounted for 39%–64% (averaging 50%) of the total dicarboxylic acid (Sempere and Kawamura, 1996). According to our results, the concentration of oxalic acid in porewater of Bosten Lake was 1.5 times higher than that in rainwater, its contribution to DOC in porewater was almost 20 times less than that in rainwater than that. This might be mainly due to the limitation of the source and formation mechanisms of dicarboxylic acid in porewaters. Even though the content of oxalic acid was relatively high in porewater than in rainwater, the contribution of oxalic acid to DOC still lower because of its less carbon content in the molecular structure. Generally, it is the different affecting factors under different environments that result in variable contents of organic acids and their contributions to DOC. The contents of formic and acetic acid in porewaters of Bosten Lake ranged 0–14.44 μmol/L and 0.36–51.00 μmol/L, respectively, the content of acetic acid was 4.6 times that of formic acid on average. The contents of formic and acetic acid detected in rainwater samples collected by Herlihy et al. (1987) from the Charlottesville region were 3–36 μmol/L and 2–17 μmol/L, respectively, and the content of formic acid was 3.5 times that of acetic acid on average. The obvious differences between our results and results of rainwater in Charlottesville region are probably owing to the distinct

types of organic acid-producing bacteria which affect the formation of the two organic acids in various environments, reflecting that microbial activities are ubiquitous in various environments. By comparing all results above, it is briefly summed that differences in speciation, content and distribution of organic acids root in the significant differences in their sources and biogeochemical process in different ecological environments. In addition, study results of Bosten Lake porewaters also reveal that under relatively reducing conditions, LMWOAs were precisely different in composition from those organic acids detected in ice core, seawater, sediment, pore water and soil, as well as in atmosphere and rainwater.

Both average concentration of total organic acid with (42.29 ± 27.14) μmol/L and its ratio of 5.6% relative to DOC in Bosten Lake indicated that LMWOAs in lake sediments were important components in dissolved organic matter in sediments. In the investigation for organic acids in sediment porewaters of Loch Eil, Miller et al. (1979) reported that in the case of no influence of pollution sources such as paper mills, the concentrations of acetic and butyric acid would be just as high as up to 148 and 3 μg/mL, respectively. And these two organic acids were derived from oxidation and fermented-decomposition of glucose and other volatile organic substances by microorganisms. This phenomenon reflected the early diagenesis of sediments and microbial metabolism. The contributions of various organic acids relative to DOC in porewaters of Bosten Lake were estimated to be 0.32%, 0.74%, 0.18%, 3.67%, 0.06%, 0.38% and 0.24% corresponding to lactic, acetic, formic, pyruvic, TFA, sorbic and oxalic acid, respectively. The contribution of pyruvic acid to DOC was the highest and that of TFA was the lowest. In Northwestern Mediterranean seawater, ωC_2 and C_2 compounds were the major dicarboxylic acids with total concentration in surface seawater were as high as up to (58 ± 8) μg/L, which accounted for 0.9%–2.4% of DOC with decreasing profiles for both contents of these organic species and their proportions in DOC. As the main organic acid in sea water, the content of glyoxylic acid was within the range of 8–40 μg/L (Tedetti et al., 2006). This study results in Bosten Lake showed that the total content of organic acids averaged (3380.48 ± 2133.579) μg/L within the range of 639.25–7312.28 μg/L, and their contribution to DOC ranged from 0.68% to 17.63%. As the main organic acid in Bosten Lake, the concentration of pyruvic acid was within the range of 73.8–6564.6 μg/L. The concentration of pyruvic acid reported in this study was 1–2 orders of magnitude higher than that of glyoxylic acid in seawater, and the contribution of organic acids to DOC was nine times higher than that of dicarboxylic acid in seawater mentioned above. Meanwhile, there was an increasing contribution profile for pyruvic acid presenting in porewaters of Bosten Lake. The main reason is that the activities of phytoplanktons in seawater and the photochemical degradation of DOM resulted in the increase of organic acids in the euphotic zone. Therefore, the contents of organic acids and their contributions to DOC in the seawater decreased from the surface to the bottom. In

addition, the different species of organic acids eventually originated from the discrepant behavior mechanisms for bacteria in both porewater in Bosten Lake and seawater in Tedetti et al. (2006). However, because there was no photochemical reaction occurred in the sediment, the types and contents of organic acids were mainly determined by microbial activities during the early diagenesis of organic matter. The contribution profiles of organic acids to DOC were almost determined absolutely by the content profile of pyruvic acid. The production of pyruvic acid was mainly related to the activities of sulfate-reducing bacteria. The contribution profile of total organic acid to DOC in Bosten Lake was opposite to that of dicarboxylic acid to DOC in seawater, i.e., the contribution increased with depth in Bosten Lake. By comparing the organic acids in seawater and lake porewaters, findings suggested that photochemical reactions played an important role in the formation and distribution of organic acids as well as in the path of decomposition and conversion of dissolved organic matter, and also reflected the significant differences in early diagenesis of organic matter and microbial activities between geochemical and photochemical processes.

2.2 Vertical profiles of organic acids in sediment porewaters

The contents of total organic acid and DOC had some fluctuations in the sediment profile, but on the whole they tended to increase with increasing depth. This reflected that with the extent of early diagenesis deepening, organic matter would be continuously oxidized and decomposed into low molecular-weight organic components. LMWAOs are exactly this kind of important dissolved organic components and characteristic of well water-solubility and relatively strong acid. The active radicals are few in molecular structure of LMWOAs which have strong migrating capability in surface environments and can be slightly affected by pH. Meanwhile, they are closely related to the quantity and activity of environmental microorganisms. As such, their concentrations were highly variable.

The concentrations of seven LMWOAs fluctuated in the sediment profile in Bosten Lake, but still showed some special trends. The contents of three organic acids, including acetic, formic, sorbic acid, were relatively high at top 10 cm depth in surface layer and were relatively low below 10 cm depth in sediments. In the sediment porewaters, the content of DOM relating to biological activity decreased with depth, and the decomposable and degradable DOM which was relevant to low molecular-weight organic components attenuated (Burdige, 2001), thus the amount of LMWOAs' precursors was also limited with the increasing depth. This was probably one of the reasons why these contents of organic acids decreased speedily in the surface profile. Whereas, the steady contents of these three organic acids in bottom were the results of their non-bioavailability. In addition, the increasing contribution profile of pyruvic acid to DOC was different from the decreasing contribution profiles of other organic acids to DOC. These tendencies might reflect that at least part of LMWOAs resulted from oxidized decomposition and

the conversion of organic matter. The profiles of organic acids consisted of two main categories of decreasing and increasing. The profile trends of organic acids, as TFA, lactic, acetic, formic, sorbic and oxalic acid, were classified in decreasing category, while pyruvic acid belonged to increasing type.

TFA derives from fluorocarbons (HCFCs and HFCs, hydrochlorofluorocarbons and hydrofluorocarbons) and does not have a great influence on organisms. TFA generally resistant to biodegradation in natural microbial systems tended to gradually decrease with depth in Bosten Lake. The production of TFA rooted in the microbial decomposition of fluorocarbons precursors. Along with the economic development and the growth of human's utilization for fluorocarbons, the concentration of TFA in sediment increased gradually with nearer ages. The content profile of TFA demonstrated diffusive form from surface layer to bottom. The contents of acetic, formic and sorbic acid tended to decrease rapidly with increasing depth, indicating that those three organic acids were closely related to stronger microbial activities in the surface layer.

Acetic acid was an intermediate product of organic matter mineralization, and it plays an important role during the conversion process of organic carbon. The intermediate products of anaerobic degradation of glucose were acetic acid and CO_2, and about 50%–80% of the consumed acetate was resulted from the degradation of glucose in anoxic rice filed soil (Chidthaisong et al., 1999). The content profile of acetic acid in Bosten Lake was described as follows: increasing-decreasing-stabilization (Fig. 2).

This was also consistent with the experimental results of porewater samples collected in field by Wellsbury and Parkes (1995). It was considered that the concentration of acetic acid was relatively high in upper porewater of Bosten Lake and decreased with depth. Although formic acid was significantly different from acetic acid, which the average content of acetic acid was as 5.6 times as that of formic acid, there was no difference in their profile variations. Both maximum contents for them reached at 10 cm depth and there was a significant and positive correlation between these two profiles ($R^2 = 0.91$, $P < 0.01$), indicating that they were influenced by similar factors (Fig. 3).

Lactic acid was an important product of anaerobic metabolism of saccharide. In this study, lactic acid and nitric acid showed similar variation trends in profiles and had a certain positive correlation ($R^2 = 0.44$, $P < 0.05$) (Fig. 3). According to the order in which electronic acceptors were utilized in the oxidized-degradation process of organic matter: O_2, NO_3^-, Mn, Fe, SO_4^{2-}, CO_2 (Nealson and Safarini, 1994). It might be known that lactic acid would be preferentially oxidized and decomposed during the anaerobic degradation with nitric acid as the electronic acceptor.

With the exception of an obvious peak at 6 cm depth, oxalic acid generally remained unchanged at other depths. The results in Bosten Lake indicated that there were differences in behavior for variant organic acids during early diagenesis. Oxalic acid as the simplest dicarboxylic
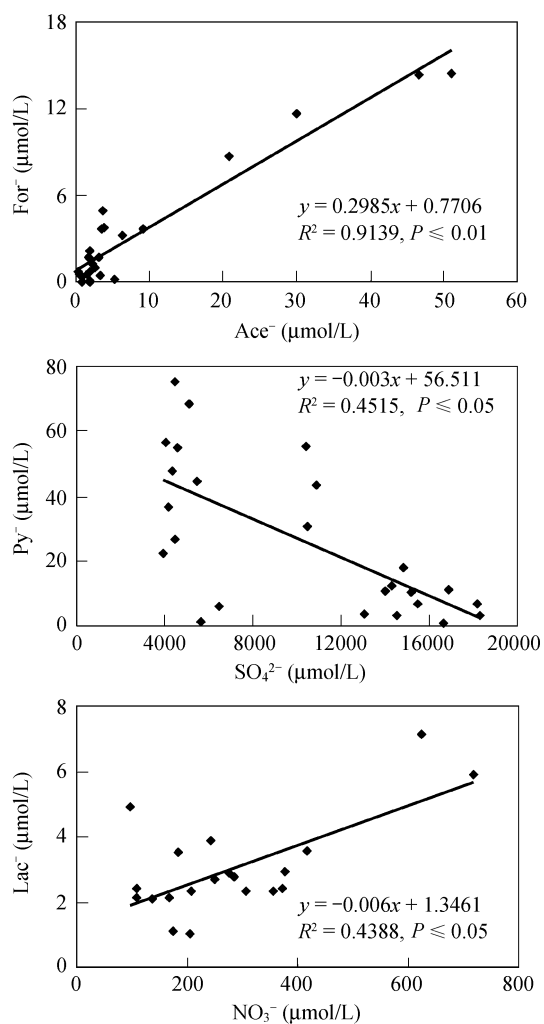
$y = 0.2985x + 0.7706$
$R^2 = 0.9139, P \leqslant 0.01$

$y = -0.003x + 56.511$
$R^2 = 0.4515, \ P \leqslant 0.05$

$y = -0.006x + 1.3461$
$R^2 = 0.4388, P \leqslant 0.05$

Fig. 3 Correlation of For$^-$ and Ace$^-$, SO$_4{}^{2-}$ and Py$^-$, NO$_3{}^-$ and Lac$^-$ in porewaters of Bosten Lake.

acid was a product and substrate of marine bacteria in porewaters. Dicarboxylic acid was considered as an important intermediate product in circulation of tricarboxylic acid and glyoxylic acid, also an important intermediate between the synthesis and catabolism of amino acid (Steinberg and Bada, 1982, 1984). The minimum concentration of oxalic acid in porewaters (0.6 μmol/L) appeared at the sediment/water interface, and the maximum concentration of 16.84 μmol/L appeared at 6 cm depth (Fig. 3). These results were inconsistent with the results obtained by Smith and Oremland (1983), who reported that the content of oxalic acid reached maximum at 2 cm depth below the sediment/water interface and decreased rapidly with increasing sediment depth. Our results in porewaters of Bosten Lake indicated that oxalic acid content tended to increase above the 6 cm sediment depth, but tended to decrease below the 6 cm depth with degradation of oxalic acid. The bioavailable oxalic acid was exhausted below the 9 cm depth and its concentration generally kept constant downwards. The content profile of oxalic acid could be described as increasing-decreasing-stabilization trend. Although the vertical concentration of oxalic acid was similar to the other four organic acids (lactic, acetic,

formic, sorbic acid), its accumulation and degradation were characterized as being intermittent.

In the current study, the five content profiles, as lactic, acetic, formic, sorbic and oxalic acid out of the above-mentioned six organic acids, can be described by a three-stage model: (1) in case the rate of consumption was lower than the rate of accumulation, the contents of organic acids tended to increase with depth, (2) in case the rate of consumption was higher than the rate of accumulation, the contents of organic acids tended to decrease with depth, and (3) at the non-bioavailable stage organic acids possessed dual nature, i.e., production and consumption coexisted and both arrived at a biological balance. This model of those organic acids can be described as Fig. 4.

Pyruvic acid which demonstrated the only increasing trend in all profiles is considered to be the precursor of some diacids and its life period is very short. Nevertheless, there did exist an important life chemical substance during the circulating path of tricarboxylic acid where amino acids and saccharides can be produced (Patel and Roche, 1990). In addition, according to Stevenson (1994), pyruvic acid, as the terminal material produced through microbial fermentation of DOM, could be further degradated by special organisms, such as denitrifying bacteria, sulfate-reducing bacteria and methanobacteria. At the same time, pyruvic acid was just the most important organic acid and living matter in pore waters. These findings are important
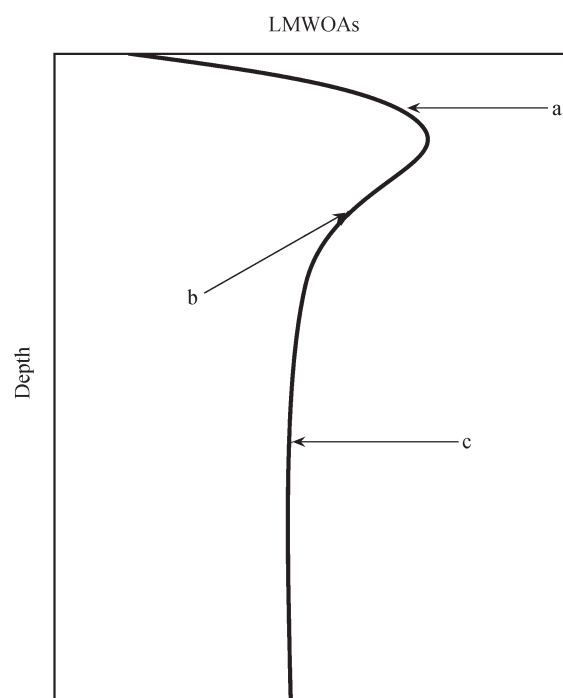

Fig. 4 Explanation model for the profile LMWOAs commonly observed in porewaters of Bosten Lake. a: Production rate of organic acids was higher than the degradation rate by microorganisms, leading to an accumulation of organic acids and increasing trend; b: production rate of organic acids was lower than degradation rate by microorganisms, leading to a consumption of organic acids and decreasing trend; c: reach to the balance between production and degradation of organic acids, content does not change with depth. However, content of pyruvic acid still increased in bottom sediment due to the frequent activity of pyruvic acid-producing bacteria.

in the biochemical and molecular biological studies. As illustrated correlation between sulfate and pyruvic acid in Fig. 2, the content profile of pyruvic acid was just opposite to that of sulfate. The sulfate concentration tended to gradually decrease with increasing sediment depth while pyruvic acid content tended to increase. There was a strong and negative linear correlation existing between two concentrations ($R^2 = 0.57$, $P < 0.05$). Fortin et al. (1996) detected the production of formate and acetate in the oxidation zone from tailings and inferred the local sulfate-reducing bacteria community used acetate and formate as electron sources. Although the content magnitude between pyruvic acid and sulfate differentiated largely in Bosten Lake, there was still a close relationship between them with respect to sulfate reducing reaction. It was reported that organic acids as a kind of enzyme could constrain sulfate reaction in sediments (Albert et al., 1995). Similarly, sulfate as an electronic acceptor might control the production of organic acids to some extent. The concentration of pyruvic acid in Bosten Lake had two important turning points at 17 and 38 cm depths through the entire profile. The formation of pyruvic acid depended on the reducing reaction of sulfate as an electronic acceptor above the 15 cm depth, but the sulfate concentrations showed a slight variation against a continuous increase of pyruvic acid content below the 15 cm depth. From the inference of Patel and Roche (1990) and Stevenson (1994), it could be deduced that pyruvic acid in our study was neither synthesized to amino acids and saccharides nor degradated to lower molecular organic acids. Put it another way, the production of pyruvic acid preponderated over its consumption during the dynamic balance of synthesis and degradation in the profile. The higher concentration in bottom reflected that the microbial resistance of pyruvic acid. Meanwhile, the production of pyruvic acid and consumption of large quantity of DOM in pore waters should be closely related to the sulfate reducing reaction. In summer and autumn seasons, the warming up sediment environment and the sulfate reducing reaction intensified the bacteria activity which made the sulfate changed gradiently and rapidly in porewaters. Sulfate was exhausted at 15 cm depth, this was because the diffusive rate of sulfate from overlying water to sediment was lower than the rate of sulfate reduction. However, pyruvic acid was strongly accumulated at 15 cm depth with the help of the sulfate-reducing bacteria and gradually increased with depth. As viewed from the whole profile, pyruvic acid seemed to continuously produce and accumulate as the special bio-degradation product of organic matter or a refractory organic product.

Microbiological and biogeochemical evidence indicates that microorganisms can produce and consume LMWOAs in the biochemical processes. It is the mineralization of organic matter in which microorganisms can survive for long time in the anaerobic environment in bottom sediment (Miller et al., 1979; Kristensen et al., 1994; Ho et al., 2002; Liang et al., 2003; Renella et al., 2004; Rusch et al., 2005).

3 Conclusions

The concentrations of LMWOAs and their contributions relative to total dissolved organic carbon in Bosten Lake are highly variable in vertical profiles in the sediment porewater, although they both showed increasing trend with increasing depth. The phenomenon indicates that with early diagenesis intensifying, organic matter was continuously oxidized and decomposed into small molecular-weight organic components. The results also indicate that organic acids can be described by a multi-stage behavior model during the early diagenesis.

Unlike organic components in other surface environments, organic acids in the sediment porewaters were dominated by pyruvic and acetic acid, with formic acid and TFA being the least components. LMWOAs were the important chemical components in DOM in sediment porewaters, they may have an obvious influence on the organic carbon cycling in the eco-environment, and may also provide important driving force during the early diagenesis. The results imply that low molecular-weight organic acids should be considered when investigating the chemical and biological characteristics of porewaters.

As viewed from the vertical profiles of LMWOAs, except pyruvic acid and TFA, the concentrations of other five organic acids were relatively high in the surface sediments. Although various organic acids had their own characteristics with respect to vertical profiles, they may be related to the strong activity of microbes in the surface sediments. Besides, another possibility could not be excluded that labile DOM fraction decomposable to lactic, acetic, formic, sorbic and oxalic acid, which were deficient in the bottom sediment and the source of relevant organic acids was inhibited. Those five organic acids were mainly controlled by three stages, i.e., accumulation, consumption and non-bioavailability. TFA, whose concentration was a diffusive modality from surface layer to understratum, was degradation product of allochthonous fluorocarbons.

Seven organic acids studies may possess unique environmental behaviors during the early diagenesis: TFA was mainly dependent on the anthrogenic sources. The initial accumulation of pyruvic acid was closely related to the degradation of DOM by sulfate-reducing bacteria, and the accumulation in bottom also accounted for its bioinert characteristics and special generation in the anaerobic bottom. The content profile of lactic acid was closely related to the denitrification in which nitrate acted as electronic acceptor to decompose lactic acid anaerobically. There was a strong and positive correlation in the vertical concentrations between formic and acetic acid. The results indicate that different organic acids in sediment porewaters were different in their origins and sources.

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