

Quantitative and qualitative characteristics of dissolved organic matter from eight dominant aquatic macrophytes in Lake Dianchi, China

Xiaoxia Qu · Li Xie · Ying Lin · Yingchen Bai · Yuanrong Zhu · Fazhi Xie · John P. Giesy · Fengchang Wu

Received: 13 December 2012 / Accepted: 22 April 2013 / Published online: 11 May 2013
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Abstract The aim of this research was to determine and compare the quantitative and qualitative characteristics of dissolved organic matters (DOM) from eight aquatic macrophytes in a eutrophic lake. C, H, N, and P in ground dry leaves and C, N, and P in DOM of the species were determined, and C/N, C/P, C/H, DOC/C, TDN/N, TDP/P, DOC/TDN, and DOC/TDP were calculated. Chemical structures of the DOM were characterized by the use of multiple techniques including UV-visible, FT-IR, and ^{13}C CP/MAS spectra. The results showed subtle differences in quantity and quality of DOM among species and life-forms. Except oriental pepper which had a C/H of 0.7, C/H of all the other species was 0.6. C/N and C/P of ground leaves was 10.5–17.3 and 79.4–225.3, respectively, which were greater in floating and submerged species than in the others. Parrot feather also had a small C/P (102.8). DOC/C, TDN/N, and

TDP/P were 7.6–16.8, 5.5–22.6, and 22.9–45.6 %, respectively. Except C/N in emergent and riparian species, C/N in the other species and C/P in all the species were lower in their DOM than in the ground leaves. DOM of the macrophytes had a SUVA_{254} value of 0.83–1.80. The FT-IR and ^{13}C NMR spectra indicated that the DOM mainly contained polysaccharides and/or amino acids/proteins. Percent of carbohydrates in the DOM was 37.3–66.5 % and was highest in parrot feather (66.5 %) and crofton weed (61.5 %). DOM of water hyacinth, water lettuce, and sago pondweed may have the greatest content of proteins. Aromaticity of the DOM was from 6.9 % in water lettuce to 17.8 % in oriental pepper. DOM of the macrophytes was also different in polarity and percent of Ar–OH. Distinguished characteristics in quantity and quality of the macrophyte-derived DOM may induce unique environmental consequences in the lake systems.

Responsible editor: Hailong Wang

X. Qu

Institute of Water Science, Beijing Normal University,
Beijing 100875, People's Republic of China

X. Qu · L. Xie · Y. Lin · Y. Bai · Y. Zhu · F. Xie · F. Wu (✉)
State Key Laboratory of Environmental Criteria and Risk
Assessment, Chinese Research Academy of Environmental
Science, Beijing 100012, People's Republic of China
e-mail: wufengchang@vip.skleg.cn

L. Xie

Institute of Geology, Nanjing Normal University,
Nanjing 210000, People's Republic of China

J. P. Giesy

Department of Veterinary Biomedical Sciences and Toxicology
Center, University of Saskatchewan, Saskatoon, SK, Canada

J. P. Giesy

Zoology Department and Center for Integrative Toxicology,
Michigan State University, East Lansing, MI 48824, USA

Keywords Aquatic macrophytes · Leaves · Dissolved organic matters · Quantitative characteristics · Qualitative characteristics · Lake Dianchi

Introduction

Dissolved organic matter (DOM) is a complex mixture of soluble organic compounds derived from soil, water, sediment, or biological residues. It plays important roles on the physical, chemical, and biological processes in the terrestrial or aquatic systems (Fellman et al. 2008; Wang et al. 2009). DOM is the key component in the global carbon cycle, the storage pool of carbon (C), nitrogen (N), and phosphorous (P), the important supplier for heterotrophic microbes, an important contributor of COD and BOD in aquatic systems, a regulator of pH of the lake water, and the complexant and sorbent of the inorganic and organic pollutants, affecting their transfer, transformation, and toxicity (Wu et al. 2008).

In aquatic systems, DOM is mainly from two sources: (1) allochthonous organic matter from terrestrial DOM through rainwater or groundwater or suspension of sediments; (2) autochthonous release from macrophytes, phytoplankton, macroalgae, or the zooplankton during growth or decomposition stages (Zhang et al. 2013).

Sources and compositions of DOM are key topics in DOM research (Wu et al. 2008). Chemical properties of DOM determine their fates and roles in environments, such as reactivity, degradation rates, and photochemical behavior. Chemical characteristics and environmental behavior of DOM from environments (water and soil) have been widely and thoroughly studied (Kögel-Knabner 1997; Senesi et al. 2003; Leenheer and Croué 2003; He et al. 2006; Wang et al. 2009). However, fewer studies have been conducted on DOM derived from other sources, especially the autochthonous materials. There have been some researches on chemical characteristics of DOM derived from phytoplankton or macroalgae (Baines and Pace 1991; Carlson and Carlson 1984; Nguyen et al. 2005; Wada et al. 2007; Henderson et al. 2008; Zhang et al. 2009, 2013). However, few studies have been conducted on DOM from macrophytes; and until now, its composition and behavior in the aquatic systems were still quite unclear (Zhang et al. 2013). As one of the primary producers in the aquatic systems, actively growing macrophytes release 1–10 % of their photosynthetic products as DOM to the water (Carpenter and Lodge 1986), which is an important contributor to the DOM pools of lakes. Systematic research on both the quantity and quality of macrophyte-derived DOM was of great need to fill this gap in DOM research.

Take eight macrophytes with four different life-forms (riparian, emergent, floating, and submerged) in Lake Dianchi, a eutrophic lake located in southwest China, as examples, C, H, N, P contents in their ground dry leaves and C, N, and P in DOM were determined. The element composition in the ground samples and DOM were compared among species and life-forms. By using the multiple spectroscopy including UV-visible, Fourier transform infrared, and ^{13}C CP/MAS spectra, chemical structures of the macrophyte DOM were identified. This study was to present a whole view of the quantitative and qualitative properties of DOM released by several representative macrophytes in the freshwater systems worldwide. It will be of great significance in the studies on degradation and humification process of the macrophyte-derived DOM, on their fate and roles in the environment, on differences in composition, degradation, and environmental behavior of DOM from different sources, on the composition, temporal, and spatial distribution of DOM in the whole lakes, and eventually on the global carbon cycle.

Materials and methods

Study site and plant material collection

Lake Dianchi with a volume of approximately $1.2 \times 10^{11} \text{ m}^3$ at an elevation of 1,886 m is located in the southwestern plateau of China ($24^\circ 48' \text{N}$; $102^\circ 40' \text{E}$). The mean depth of the lake is 4.4 m, and the maximum is 15.1 m. The climate is subtropical plateau monsoon, with a long, warm and humid summer (mean temperature = 25°C) and a short, cool and dry winter (mean temperature = 14°C). The lake is divided into two sections, the northwestern part is called Caohai and the southern part called Waihai. The two sections are separated by a dike with a sluice. Although Caohai section occupies only 4 % of the whole lake, it is the major part which receives wastewater from industry, agriculture, and domestic sewage from adjacent cities, and plant diversity in this section is the greatest in the whole lake (Wang and Chen 2009). Leaves of seven dominant perennials and an annual (oriental pepper) occurred in Caohai part of the lake were collected in late Oct. 2010. They were distributed around or inside the lake as circles, i.e., the crofton weed (*Eupatorium adenophorum* Spreng., Asteraceae) grows on the lakeside, water oats (*Zizania caduciflora* Turcz., Gramineae), common reed (*Phragmites australis* Trin., Gramineae), and oriental pepper (*Polygonum orientale* L., Polygonaceae) are emergent plants living in the shallow area, parrot feather (*Myriophyllum aquaticum* (Vell.) Verdc., Haloragidaceae) is an emergent or submerged species growing in the shallow area or center of the lake (Barko and Smart 1983), water hyacinth (*Eichhornia crassipes* (Mart.) Solms, Pontederiaceae) and water lettuce (*Pistia stratiotes* L., Araceae) are floating plants in the center of the lake, sago pondweed (*Potamogeton pectinatus* L., Potamogetonaceae) is the submerged species distributed beneath the water surface (Fig. 1)

Preparation of dissolved organic matter

Plant materials were killed at 90°C for 1–2 h and then completely dried at 60°C for 12–24 h. After drying, they were ground to pass through a 1-mm sieve. DOM was obtained by extraction with 35:1 (v/w) water (ultrapure, Milli-Q) to sample ratio, and the mixtures were then shaken at 4°C for 18 h. Suspensions were centrifuged ($7560 \times g$) for 20 min and then filtered by vacuum through $0.45\text{-}\mu\text{m}$ pore size polycarbonate filters (He et al. 2009). Part of the DOM was used directly for quantification of C, N, and P and UV-visible spectroscopy. The remaining portion was freeze-dried and kept in a desiccator at room temperature for FT-IR and ^{13}C NMR scanning.

C, H, N, and P concentration determination

C, N, and H in ground dry leaves were determined by an elemental analyzer (Elementar vario macro EL, Germany).

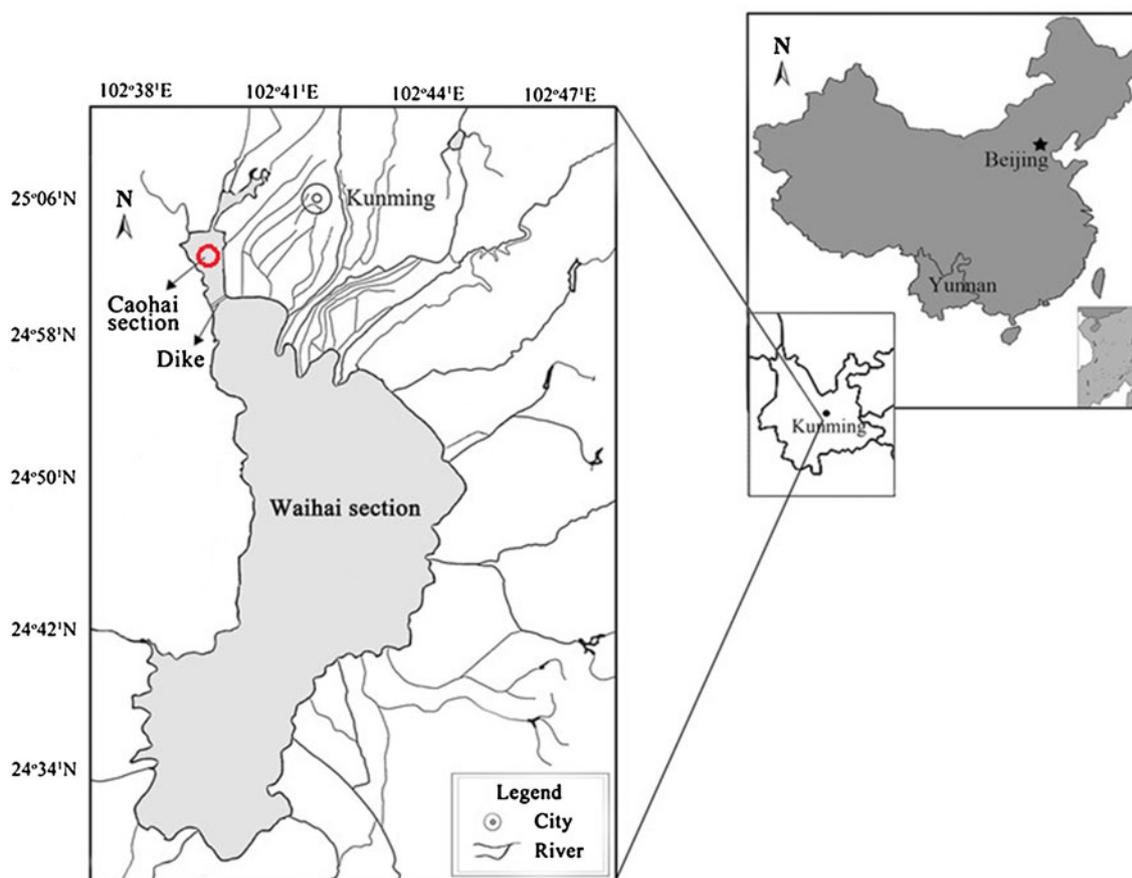


Fig. 1 Map of the sampling site

The pressures were 0.2 MPa for He and 0.25 MPa for O₂. The temperature in the oxidation furnace was 1,150 °C and that in the reduction furnace was 850 °C. P was determined by methods described in Pardo et al. (2003). Briefly, P was obtained by calcinating 0.2 g solid sample at 450 °C for 3 h before being shaken with 20 ml 3.5 M HCl for 16 h and then being tested by the molybdenum blue method proposed by Murphy and Riley (1962). Concentrations of dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were determined by use of a multi N/C 3100 analyzer (Analytic Jena, German), with detection limits of 0.45 mg C L⁻¹ for DOC and 0.1 mg N L⁻¹ for TDN. TDP was also determined by the molybdenum blue method (Murphy and Riley 1962). For all of the tests, three parallel samples of every species were prepared.

Spectroscopy

DOM was characterized by use of UV-visible, FT-IR, and solid-state ¹³C-NMR spectroscopies. UV-visible spectra in the range of 200–700 nm were measured by the use of an UV-Vis 8453 DAA UV-visible spectrophotometer (Agilent Technologies, Wilmington, DE, USA) in a 1.0 cm quartz

cuvette. Ultrapure (Milli-Q) water was used as a blank. Specific UV absorbencies at 254 and 280 nm (SUVA₂₅₄, SUVA₂₈₀, L·mg⁻¹C·m⁻¹) were calculated by the UV₂₅₄ and UV₂₈₀ divided by DOC, respectively. FT-IR spectra were recorded in the range of 650–4000 cm⁻¹ by use of a PerkinElmer Spectrum 100N FT-IR spectrophotometer from disk containing about 1 mg freeze-dried DOM sample. The spectral resolution was 2 cm⁻¹, and 100 scans were averaged. Solid-state CP/MAS ¹³C NMR spectra of freeze-dried DOM samples were performed on a Bruker AV-300 spectrometer at 12.5 kHz by using a standard 4 mm double-bearing probe head. The recycle delay was 1 s, the pulse width was 2.4 μs, and the contact time was set as 2,000 μs.

Statistical analysis

The C, H, N, P, DOC, TDN, and TDP contents were compared among the macrophyte species by using one-way repeated measures ANOVA with Origin 8.0 software (OriginLab, Inc., USA). If an ANOVA showed significant effects (*p*<0.05), a post hoc Tukey’s test was conducted to test differences among species (*p*<0.05) (Sokal and Rohlf 1995).

Results

C, H, N, and P contents

Element composition in the ground dry leaves and DOM of the macrophytes was shown in Table 1. Except oriental pepper which had a C/H ratio of 0.7, C/H ratios of all the other macrophytes were approximately 0.6. Both C/N and C/P were greater in the emergent and riparian macrophytes (14.2–17.3 and 152.4–225.3, respectively) than in the floating or submerged species (10.5–12.3 and 79.4–92.2, respectively). Parrot feather, which is a special species with both submerged and emergent life-forms, had a C/N (16.6) similar to those of the emergent plants (15.5–17.3) and a C/P (102.8) comparable to that of submerged species (92.2).

DOC, TDN, and TDP represent the portion of DOM which can be dissolved in water, and thus easily released to surface waters of lakes where it can influence cycling of N and P and other biogeochemical processes. The macrophytes released 7.6–16.8 % of their total C as DOC. DOC released by the emergent oriental pepper and floating species was similar (1,094.7–1,112.0 mg/L) ($p < 0.05$) (Table 1). And DOC of all the other species (945.8–1,983.0 mg/L) was significantly greater than that produced by the submerged sago pondweed (772.1 mg/L) ($p < 0.05$). The percent of TDN in N had a wider range with 5.5 % in oriental pepper to 22.6 % in water lettuce when compared to the ratio of DOC to C (7.6–16.8 %). Among C, N, and P, the percent released was greatest for TDP/P (22.9–45.6 %), which might be due to the greatest solubility of the P compounds. Both TDN and TDP were greater in floating species (219.6–232.6 and 109.5–133.6 mg/L, respectively) than in the other macrophytes (57.9–135.0 and 54.1–99.2 mg/L, respectively). Although concentrations of TDN and TDP in the DOM were not strongly correlated with content of N and P in the ground leaves, which is probably due to different solubilities of compounds containing N and P, DOC/TDN, and DOC/TDP exhibited similar trends to those of C/N and C/P, where they were lesser in DOM of floating and submerged species (5.5–7.1 and 21.2–30.5, respectively) than in emergent and riparian plants (13.0–22.4 and 44.5–94.7, respectively). Although parrot feather exhibited a similar C/N (16.6) with the emergent species (15.5–17.3), its DOC/TDN (8.2) and DOC/TDP (24.6) was as low as those in the floating and submerged species (5.5–7.1 and 21.2–30.5, respectively). Furthermore, except the emergent and riparian species whose DOC/TDN (13.0–22.4) were similar to their C/N (14.2–17.5), DOC/TDN of the other species (5.5–8.2) and DOC/TDP of all the species (21.2–94.7) were lower than C/N (10.5–16.6) and C/P (79.4–225.3) in the ground dry leaves.

Table 1 Element composition in the ground dry leaves and DOMs of the eight macrophytes in Lake Dianchi

Leaves	C* (%)	H* (%)	H* (%)	N* (%)	P* (%)	C/H [#]	C/N [#]	C/P [#]	DOC (mg/L)	TDN (mg/L)	TDP (mg/L)	DOC/C (%)	TDN/N (%)	TDP/P (%)	DOC/TDN [#]	DOC/TDP [#]
Crofton weed	41.3±0.05 ^{8a}	5.6±0.05 ^a	6.3±0.06 ^b	3.4±0.01 ^a	0.7±0.02 ^a	0.6	14.2	152.4	1,983.0±36.58 ^a	107.4±0.98 ^a	54.1±1.0 ^a	16.8	11.1	27.1	21.5	94.7
Oriental pepper	49.2±0.15 ^b	6.3±0.06 ^b	5.6±0.02 ^a	3.7±0.01 ^b	0.7±0.00 ^{ab}	0.7	15.5	181.6	1,112.0±28.60 ^b	57.9±2.05 ^b	64.6±0.18 ^b	7.9	5.5	32.3	22.4	44.5
Water oats	40.0±0.16 ^c	5.6±0.02 ^a	6.0±0.03 ^b	2.7±0.03 ^c	0.5±0.05 ^{bc}	0.6	17.3	206.7	1,375.2±38.12 ^c	116.1±1.65 ^{ad}	65.2±1.69 ^b	12.0	15.1	45.6	13.8	54.5
Common reed	43.6±0.46 ^d	6.0±0.03 ^b	5.3±0.03 ^c	3.2±0.04 ^d	0.5±0.00 ^c	0.6	15.9	225.3	969.9±40.67 ^d	87.3±0.70 ^c	39.9±0.28 ^c	7.8	9.5	27.9	13.0	62.8
Parrot feather	39.8±0.05 ^e	4.9±0.06 ^d	5.0±0.01 ^e	2.8±0.01 ^e	1.0±0.04 ^d	0.6	16.6	102.8	945.8±14.93 ^d	135.0±2.19 ^d	99.2±1.90 ^d	8.3	16.9	34.7	8.2	24.6
Sago pondweed	35.7±0.01 ^e	5.0±0.01 ^e	5.1±0.03 ^e	3.9±0.01 ^f	1.0±0.01 ^{ef}	0.6	10.7	92.2	772.1±3.71 ^e	126.6±2.93 ^{ad}	65.3±0.94 ^b	7.6	11.4	22.9	7.1	30.5
Water hyacinth	36.9±0.05 ^f	5.1±0.03 ^e	5.1±0.03 ^e	4.1±0.03 ^f	1.2±0.00 ^e	0.6	10.5	79.4	1,094.7±15.88 ^e	232.6±4.30 ^e	133.6±0.74 ^e	10.4	19.9	39.0	5.5	21.2
Water lettuce	35.8±0.14 ^e	5.1±0.03 ^e	5.1±0.03 ^e	3.4±0.04 ^f	1.1±0.03 ^{ef}	0.6	12.3	84.1	1,107.0±42.85 ^e	219.6±8.23 ^e	109.5±2.11 ^f	10.8	22.6	34.8	5.9	26.1

Superscript lower-case letters are not connected with same alphabetical letter indicate significant differences ($p < 0.05$). The values were obtained on dry mass basis (*asterisk*); (number sign) atomic ratio, (section sign) data are presented as the mean±SE

UV-visible spectra

Absorbencies in UV-Vis spectra of DOM of the eight species were inversely proportional to wavelength (Fig. 2). UV-Vis spectra of DOM of all macrophytes exhibited absorbance shoulders in the near UV (200–380 nm) region, which indicated the presence of conjugated double bonds or delocalized bonds in constituents of DOM, such as conjugated alkenes, unsaturated carbonyl compounds, or aromatic substances (Damji and Green 2001). Except for water hyacinth, which had only a mild absorption peak at 324 nm, spectra of the other seven plants exhibited a shoulder between 250 and 280 nm, which is due to π - π^* electron transition in unsaturated structures, such as those in aniline derivatives, phenolic arenes, polyenes, and polycyclic aromatic hydrocarbons with two or more rings (Chin et al. 1994; Duarte et al. 2003; He et al. 2009). A second smaller shoulder between 300 and 350 nm in the spectra of crofton weed, oriental pepper, water oats, sago pondweed, and the absorption peak at 324 nm in water hyacinth might be due to the red shift induced by elongation of the conjugated systems or by substituted chromophores or auxochromes on the conjugated systems and/or benzene rings (Damji and Green 2001). $SUVA_{254}$ was ranged from 0.83 in common reed to 1.80 in crofton weed, and $SUVA_{280}$ was from 0.54 in common reed to 1.51 in parrot feather.

FT-IR spectra

FT-IR spectra of the eight species were quite similar (Fig. 3). The profile of every spectrum was dominated by four prominent bands at 3,300, 1,600, 1,400, and 1,000 cm^{-1} . The broad band around 3,300 cm^{-1} was attributed to N–H or H bonded O–H stretching of phenols, alcohols, carboxylic acids, and/or other substances which contains hydroxyl groups (Francioso

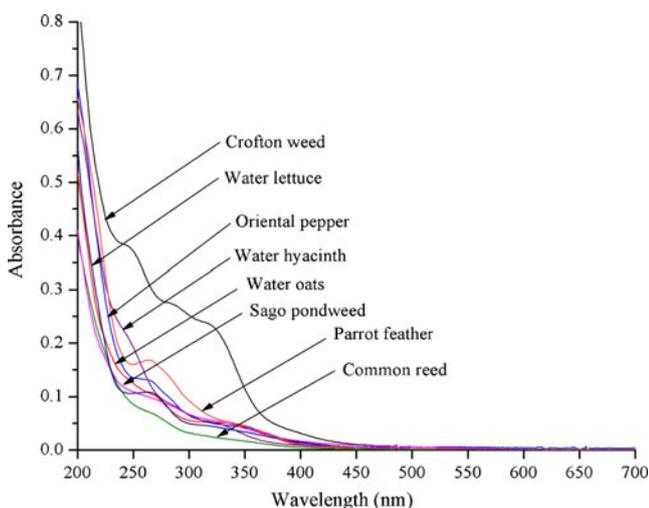
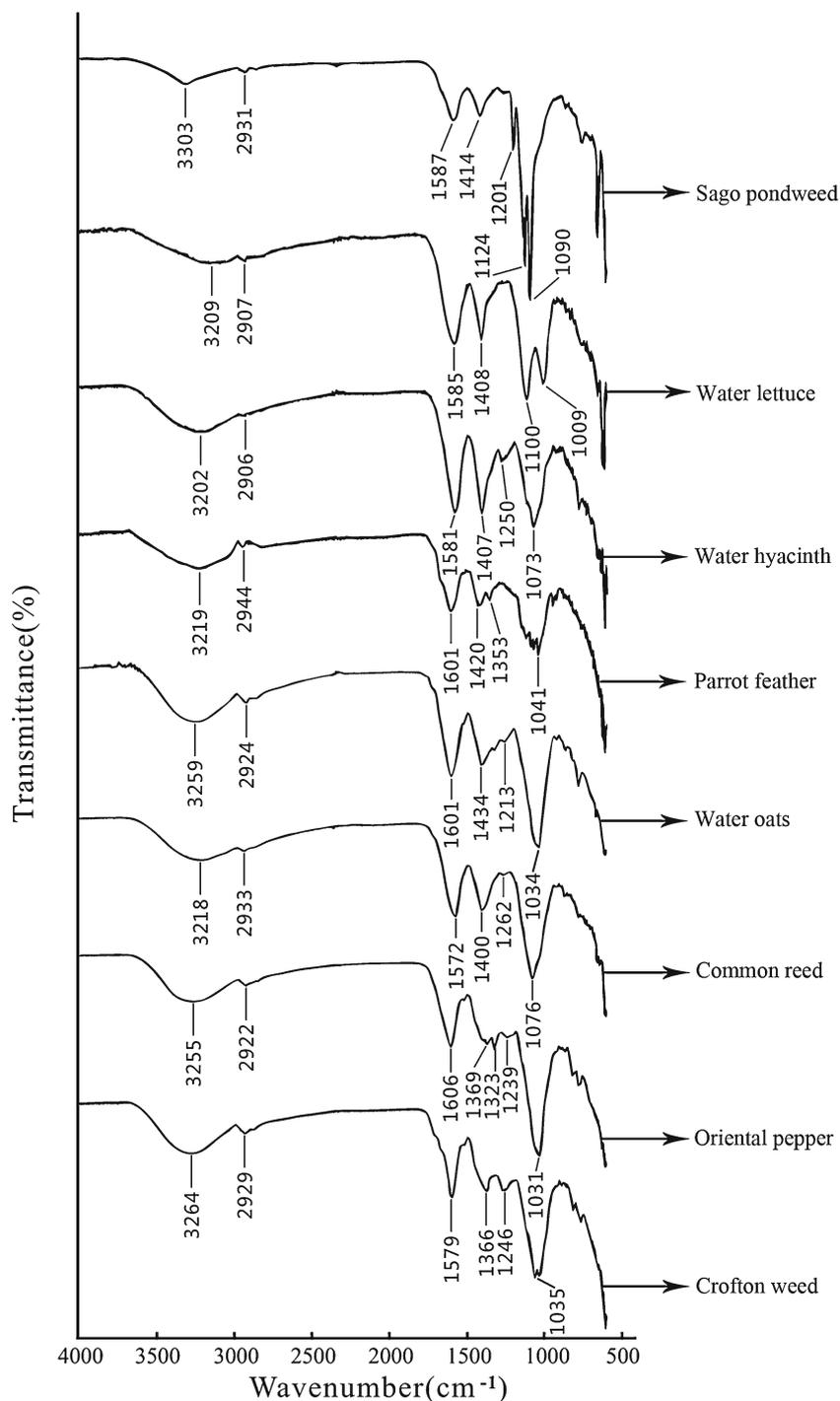


Fig. 2 UV-Vis spectra of the leaf DOM from the eight macrophytes in Lake Dianchi

et al. 1996). The sharp band at about 1,600 cm^{-1} corresponds to aromatic C = C vibration, olefinic carbon–carbon bonds, symmetric stretching of COO^- groups, and H-bonded C = O of conjugated ketones (Francioso et al. 1996; Olk et al. 2000; Senesi et al. 2003). The band at 1,353–1,434 cm^{-1} was assigned to phenolic O–H and symmetric bending vibrations of aliphatic C–H groups (Francioso et al. 1996; Agnelli et al. 2000; Duarte et al. 2005; He et al. 2009). The sharp peak near 1,000 cm^{-1} can be attributed to alcoholic, polysaccharide, polysaccharide-like C–O stretching, and/or Si–O of silicate impurities (Olk et al. 2000; He et al. 2009). P-containing compounds have also been reported to contribute to this peak (He et al. 2006). In spectra of all the macrophytes studied, there was also a minor peak at 2,906–2,940 cm^{-1} , which was attributed to C–H stretching of methyl and methylene groups of aliphatic chains (Agnelli et al. 2000; Olk et al. 2000; Duarte et al. 2005; He et al. 2006). The weaker band at 1,519 cm^{-1} in the spectrum of oriental pepper was ascribed to stretching vibrations of aromatic C = C bond or C = O vibrations of amide groups (Duarte et al. 2005). The peaks at 1,201 cm^{-1} in sago pondweed, 1,213 cm^{-1} in water oats, 1,239 cm^{-1} in oriental pepper, 1,246 cm^{-1} in crofton weed, 1,250 cm^{-1} in water hyacinth, and at 1,262 cm^{-1} in common reed were contributed by C–O stretching of ethers, esters, phenols and carboxylic acids, or O–H deformation in COOH groups (Senesi et al. 2003; Chang Chien et al. 2007). O–H and N–H at ca. 3,300 cm^{-1} , the possible COO^- at 1,600 cm^{-1} , peaks for COOH at 1,239–1,262 cm^{-1} , and C–H stretching around 2,900 and at 1,353–1,434 cm^{-1} were diagnostic for amino acids. Sharp peaks of C–O stretching at 1,000 cm^{-1} plus C–H stretching around 1,400 and 2,900 cm^{-1} indicated the presence of polysaccharides. The C–O signals, C–H peaks, O–H stretching, and P signals around 1,000 cm^{-1} were indicative of the sugar–phosphate backbone of the nucleotides. The N–H, C = C, and C = O vibrations indicated existence of the nitrogenous bases pyrimidine and purines. By combing the sugar–phosphate backbones with nitrogenous bases by hydrogen bonding between O and H and N and H, the double helix of DNA and/or RNA can be inferred. Combining the peaks of C–H groups and phenolic O–H at around 1,400 cm^{-1} , peaks due to C–H stretching vibration at 2,906–2,940 cm^{-1} , and absence of peaks for COO^- groups at 1,630–1,660 and 1,710–1,725 cm^{-1} in the FT-IR spectra, the DOM fractions seemed to be mainly composed of aliphatic and/or phenolic groups, with a smaller proportion of humic substances.

The FT-IR spectra also showed differences among the macrophytes. In the FT-IR spectra of the macrophytes, the transmittance peak around 1,000 cm^{-1} was strongest in sago pondweed, which may be due to a large content of carbohydrate, Si–O substances or P-containing compounds. The strongest peak around 1,400 cm^{-1} was shown in water hyacinth and water lettuce, which illustrated a greater percentages of C–H or phenolic O–H in extracts of these plants. The

Fig. 3 FT-IR spectra of the leaf DOM from the eight macrophytes in Lake Dianchi



shallowest peaks around $1,600\text{ cm}^{-1}$ in extracts of parrot feather and sago pondweed reflected a small proportion of substances with conjugated systems/benzene rings. The deepest C–H peak around $2,900$ and $1,366\text{ cm}^{-1}$ in the FT-IR spectrum of crofton weed suggest the larger proportion of aliphatic carbon in its DOM. The strongest peaks around $3,300\text{ cm}^{-1}$ in water oats and oriental pepper were indicative of a greater proportion of substances containing O–H or N–H, such as alcohols, phenolic acids, amino acids, or anilines.

Solid-state CP/MAS ^{13}C NMR

The solid-state ^{13}C NMR spectra and distribution of the different C-types were shown in Fig. 4 and Table 3. The NMR spectra for the eight aquatic macrophytes were generally similar. The predominant bands were found around 174, 104, 72, and 25 ppm. In the ^{13}C NMR spectrum, shifts of 0–50 ppm is attributed to alkyl, 50–60 ppm indicates NCH and/or OCH_3 , 60–96 ppm is for carbohydrate C, 96–

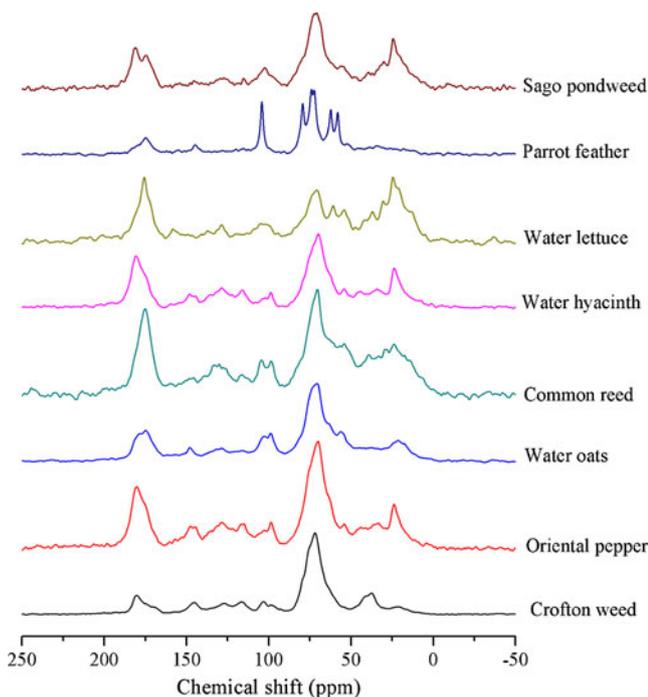


Fig. 4 CP/MAS ¹³C NMR spectra of the leaf DOM from the eight macrophytes in Lake Dianchi

110 ppm indicates O–C–O anomers, 110–145 indicates aromatic C, 145–162 ppm indicates aromatic C–O, 162–190 ppm indicates COO and N–C = O, and 190–220 ppm indicates ketone, quinone, and/or aldehyde carbons (Kögel-Knabner 1997; Mao et al. 2007; He et al. 2009). Bands at ~174 ppm for the eight species were from COO and/or N–C = O. The signals at about 104 ppm were from O–C–O anomers. The peaks at 72 and 60 ppm were assigned to OC, OCH, and OCH₂, respectively. The apparent peaks below 50 ppm were from nonpolar alkyls of CCH, CCH₂, and CCH₃. The COO peak at approximately 174 ppm and the NCH at 50–60 ppm, plus the apparent band below 50 ppm suggested the presence of amino acids, peptides, or proteins. The O–C–O anomers at approximately 104 ppm associated with the dominant OCH at approximately 72 ppm and/or the OCH₂ peak at 60 ppm indicated the existence of sugar chains of starch/cellulose/lignin. The existence of sugar rings and the N–C = O and C–H located below 50 ppm were likely due to the presence of nucleic acids (DNA and RNA). Alkyl groups and COO were also indicative of the presence of phenolic or carboxylic acids. Since these samples were plant materials, which were mainly composed of DNA and RNA, amino acids, proteins, starch, lignin, and/or lipids, the ¹³C NMR results were related to their natural properties.

There were some differences in distribution of the major C-types among the species. For example, peaks at approximately 25 ppm, the location of C indicating long-chain polymethylene material, (CH₂)_n-type structures, such as fatty acids, waxes, and resins (Chen et al. 2005) were greatest in water lettuce and

sago pondweed among the species. The percent of carbohydrate C (50–110 ppm) were greatest in parrot feather (66.5 %) and crofton weed (61.5%). Aromatic C (110–160 ppm) was greatest in oriental pepper (17.8 %) and lowest in water lettuce (6.9 %). DOM of water lettuce and water hyacinth contained the highest percent of COO and/or N–C = O (160–190 ppm) (18.5 and 18.3 %, respectively). Distribution of the protonated and alkyl-substituted aromatic carbon (110–145 ppm) (Kögel-Knabner 1997) were higher in crofton weed (12.1 %), oriental pepper (13.9 %), water hyacinth (13.4 %), and common reed (10.8 %) than in the other species (4.9–8.7 %). In the same grass family, water oats had more carbohydrates, greater polarity but less COOH–C than common reed do. The greatest proportions of Ar–OH (145–162 ppm) were found in oriental pepper (3.9 %), water hyacinth (3.4 %), water oats (3.3 %), and parrot feather (3.2 %), while the least were in water lettuce (1.9 %) and sago pondweed (1.9 %). Aromaticity of DOM (110–160 ppm) in the eight aquatic macrophytes decreased in the order: oriental pepper > water hyacinth > crofton weed > common reed > water oats > parrot feather > sago pondweed > water lettuce; and the polarity decreased in the order of parrot feather > water oats > crofton weed > oriental pepper > sago pondweed > water hyacinth > common reed > water lettuce.

Discussion

Except the annual oriental pepper, leaves of all the other aquatic macrophytes are the major contributors of organic matters to the lake based on their large biomass. The riparian plant crofton weed mainly contributes its OMs to the lake by its leaves through dispersal by wind. Thus, OMs from leaves of these species can affect biogeochemical process of the lakes. As one of the important indicators of the organic matter, C/N was reported to be greater than 20 in terrestrial vascular plants and 4–10 in cyanobacteria (Meyers 1994). C/N ratios in the macrophytes studied here was 10.5–17.3, which is greater than that of the algae, but less than that of terrestrial vascular plants. Among the macrophytes studied, water hyacinth, water lettuce, and sago pondweed exhibited lesser C/N and C/P than the others. This is due to the greater concentrations of N and P in these plants. It has been found by Polomki et al. (2009) that among water hyacinth, water lettuce, and parrot feather, the first two exhibited the greatest concentrations of N. It has also been reported that an addition of P can increase tolerance of water lettuce to heavy metals (Mufarrege et al. 2010), and there is enrichment of N and P by sago pondweed (Howard-Williams 1981). Parrot feather had a preference of P rather than N, as showed by the greater C/N and lesser C/P. As reported by Sytsma and Anderson (1993), parrot feather forms a pool of N but not P in its rhizome, and the emergent tissue contains 80 % of P but only 10–30 % of N in the whole body. The greater C/N and C/P in water hyacinth, water lettuce, sago

pondweed, and the greater C/P in parrot feather suggest a mechanism to remove excess N and P from the lakes by these aquatic macrophytes.

DOC, TDN, and TDP in the DOM exhibited different distributions when compared to that of C, N, and P in the ground leaves, which could be due to solubility of the compounds in different species. DOC of the macrophytes (772.1–1,983.0 mg/L) was greater than those of cyanobacteria (12 to 25 mg/L) (Nguyen et al. 2005). Since the amount of DOM is always evaluated by concentrations of DOC, this result indicated that DOM released by the macrophytes is greater than that by cyanobacteria. It has also been reported that the amount of CDOM released by the macrophyte *Potamogeton malaianus* was at least twice more than that produced by the *Microcystis* algae (Zhang et al. 2013). In Wada et al. (2007), DOC released by phytoplankton was 5–15 % of their NPP and that by macroalgae was 18–62 %. Compared with the DOC/C of 7.6–16.8 % observed in our study, macroalgae seem to have a greater ability to produce dissolved carbon, while phytoplankton exhibits lesser ability to release soluble C. As shown by the greater concentration of TDN in water hyacinth, water lettuce, and sago pondweed, a relatively great release of bioavailable N, such as amino acids/peptides/proteins by these species to the lake, was expected. As indicated by the high TDP/TP, P compounds seemed to be the most soluble species when compared with C compounds and N compounds, which indicated that P in the macrophytes is more easily to be returned to the lake through DOM than N. Except for emergent and riparian species whose DOC/TDN was similar to their C/N, DOC/TDN of the other species and DOC/TDP of all the species were less than C/N and C/P in the ground dry leaves, which indicates that in the DOM released by macrophytes to lake Dianchi, there should be more N and P per unit C than those in the organic matter they accumulated. Furthermore, DOC/TDN and DOC/TDP in the submerged plant, the floating species, and parrot feather were even lower, which illustrated their greater potential to release dissolved N and P to the lake. Therefore, to avoid the large release of the nutrients back to the lake, an appropriate timing of harvest for these species should be paid attention to.

The ratio of C/H is a function of the degree of saturation of hydrocarbons. Greater magnitudes of C/H indicate a greater degree of unsaturation. Compared with C/H of IHSS HA and FA (0.97–1.43) (IHSS, <http://www.humicsubstances.org/elements.html>) and of the soil humic substances (0.81–0.94) (Ding et al. 2002), the macrophytes with a C/H or 0.6–0.7 are likely to have a lower aromaticity. Oriental pepper with the highest C/H (0.7) may have a higher aromaticity than the other species. SUVA₂₅₄ and SUVA₂₈₀ which are positively correlated with molecular weight, aromaticity, and humification of organic molecules have been suggested as indicators of chemical composition in DOM from water and soil (Weishaar et al. 2003; Fellman et al. 2008). Based on the linear model between

SUVA₂₅₄ and aromaticity of the humic substances constructed by Weishaar et al. (2003), the SUVA₂₅₄ values of 0.83–1.80 in the DOM extracted from the macrophytes (Table 2) should indicate an aromatic C content of about 7–15 %. When comparing with the SUVA₂₅₄ values in soil samples (4.2) (Chen et al. 2003), ground water (2.3–3.9) (Swietlik et al. 2004), IHSS FA (3.6) (Weishaar et al. 2003), and DOM from the allochthonous material (3.7–4.2) (Nguyen et al. 2005), DOM of the macrophytes, seemed to have a lower aromaticity. However, aromaticity of DOM from macrophytes may be similar to or higher than that in the phytoplankton (SUVA₂₅₄=0.48–0.8) (Nguyen et al. 2005; Henderson et al. 2008).

The FT-IR and ¹³C NMR spectra showed more detailed information on chemical composition of the DOM (Figs. 3 and 4; Table 3). DOM of the eight macrophytes was mainly composed of polysaccharides and amino acids/peptides/proteins. Phenolic acids, carboxylic acids, long-chain fatty acids, aniline, alcohols, esters, ethers, terpenes, and ketones also present in the DOM. Content of carbohydrates in the DOM of the macrophytes (37.3–66.5 %) was very high when compared with 15 % in the macroalgae and 15–49 % in the phytoplankton (Wada et al. 2007). Besides the common composition of DOM from the macrophytes, there were also specialties among them. The strongest transmittance peak around 1,400 cm⁻¹ in the FT-IR spectrum and the greatest percent of carbon around 25 ppm in the ¹³C NMR of water lettuce indicated a large proportion of longer-chain n-alkanes in DOM of this species, which is consistent with what was found by Xiong et al. (2010) that the enhanced long-chain n-alkanes in sediments of Lake Dianchi might be mainly from submerged/floating aquatic

Table 2 UV-Vis indexes of the leaf DOM from the eight macrophytes in Lake Dianchi

Samples	SUVA ₂₅₄ (L·mg ⁻¹ C·m ⁻¹)	SUVA ₂₈₀ (L·mg ⁻¹ C·m ⁻¹)
Crofton weed	1.80	1.39
Oriental pepper	1.20	0.92
Water oats	0.86	0.59
Common reed	0.83	0.54
Water hyacinth	1.59	0.82
Water lettuce	0.96	0.74
Parrot feather	1.72	1.51
Sago pondweed	1.37	1.12
Blue/green algae ^{a, b}	0.48–0.8	–
IHSS FA ^c	3.6	
Autochthonous DOC ^b	1.9	
Allochthonous DOC ^b	3.7–4.2	

– means data not available;

^a Cited from Henderson et al. (2008)

^b Cited from Nguyen et al. (2005)

^c Cited from Weishaar et al. (2003)

Table 3 Percent distribution of characteristic carbons in the solid-state ¹³C NMR spectra of the leaf DOM from macrophytes in Lake Dianchi

Samples	Percent of different types of Carbon by ¹³ C NMR								Al-C ^a (%)	Ar-C ^b (%)	Polar C ^c (%)	Carbohydrate (50–110 ppm)
	0–50	50–60	60–96	96–110	110–145	145–162	162–190	190–220				
Crofton weed	14.8	3.6	52.9	5.0	12.1	2.6	9.0	0.0	77.0	14.8	73.1	61.5
Oriental pepper	18.6	4.6	36.4	5.1	13.9	3.9	16.8	0.6	64.6	17.8	67.5	46.1
Water oats	16.5	7.9	41.8	8.5	8.7	3.3	13.3	0.0	75.7	11.9	74.8	58.2
Common reed	26.9	8.2	28.6	5.8	10.8	2.7	17.0	0.0	70.1	13.4	62.3	42.6
Water hyacinth	22.4	4.8	31.9	3.5	13.4	3.4	18.3	2.4	62.6	16.6	64.2	40.1
Water lettuce	37.4	7.5	24.1	5.7	4.9	1.9	18.5	0.0	75.2	6.9	57.7	37.3
Parrot feather	12.3	10.0	45.5	10.9	7.7	3.2	10.3	0.0	79.1	10.7	80.0	66.5
Sago pondweed	26.7	5.9	34.4	6.0	6.9	1.9	16.8	1.4	73.0	8.7	66.4	46.3
Blue-green algae ^d									64.0	12.0		
IHSS (http://www.humicsubstances.org/thornnmr.html) HA ^e	–	–	–	–	–	–	–	–	14–29	31–58	–	–
IHSS (http://www.humicsubstances.org/thornnmr.html) FA ^e	–	–	–	–	–	–	–	–	22–33	22–30	–	–
Sediment in the five main rivers of China ^f	–	–	–	–	–	–	–	–	–	17–33	–	–

– means data not available or not used;

^a Al-C% was calculated by the Al-C region (0–110 ppm)/C in the whole region (0–220 ppm)

^b Ar-C% was calculated by the Ar-C region (110–160 ppm)/C in the whole region (0–220 ppm)

^c Polar C region (50–110 and 145–220 ppm)

^d Cited from Nguyen et al. (2005)

^e Cited from <http://www.humicsubstances.org>

^f Cited from He et al. (2008)

macrophytes. The shallowest peak around 1,600 cm⁻¹ in the FT-IR spectra of parrot feather, the deepest C-H peak around 2,900 cm⁻¹ and the peak at 1,366 cm⁻¹ in crofton weed, and the greatest percent of carbons in the range of 50–110 ppm in ¹³C NMR of these two species were signs for the greatest percent of carbohydrates (66.5 and 61.5 %, respectively) in their DOM. The combination of the greatest N and TDN in water lettuce and water hyacinth and their greatest percent C in the range of 162–190 ppm (18.5 and 18.3 %, respectively) in the ¹³C NMR spectra indicated a possible existence of a great amount of amino acids/peptides/proteins in DOM of these two species. Since carbohydrates and amino acids/protein are the organic substances with the greatest bioavailability, DOM of water lettuce, water hyacinth, parrot feather, and crofton weed should be most easily used by the epiphytes or microbes in the lake. Common reed and oriental pepper also have a larger carbon contents in 162–190 ppm (17.0 and 16.8 %, respectively) in the ¹³C NMR; but based on their relatively small TDN contents and the peaks for phenols or carboxylic acids at 1,246 and 1,262 cm⁻¹ in the FT-IR spectrum, the great percent of C in this range might be due to a great percent of carboxylic acids. The greatest proportions of Ar-OH in DOM of oriental pepper (3.9 %), water hyacinth (3.4 %), water oats (3.3 %), and

parrot feather (3.2 %) hints their greater binding potential with metals (Croué et al. 2003).

Aromatic carbon content is an important indicator of DOC reactivity. It was reported that aromaticity of DOC or humic substances can influence their reactivity with many substances, such as with oxidants (chlorine or ozone), the inorganic species (e.g., mercury), and the hydrophobic organic carbons (e.g., PAHs) (Peuravuori 2001; Weishaar et al. 2003). As shown in Table 3, aromaticity in the macrophyte DOM was less than those in IHSS HA (31–58 %), IHSS FA (22–30 %), and the sediment samples (17–33 %) but was similar to that in the phytoplankton (12 %) (Nguyen et al. 2005; He et al. 2008; IHSS 2008b, <http://www.humicsubstances.org/thornnmr.html>). These results also indicated that aliphatic C (0–110 ppm) is the major C species in DOM of the macrophytes, and the content of aromatic C (110–160 ppm) was not much, which may be due to the absence of decomposition and humification in the freshly-extracted samples. The differences in aromaticity in DOM of different species also indicated their different reactivity with other chemicals in the lake system, such as the inorganic or organic pollutants. It was reported that the greatest sorption of nonpolar hydrophobic organic pollutants occurred on sorbents with the least polarity, while the

most polar organic pollutants appeared with the sorbent containing accessible and polar aromatic cores (Chen et al. 2005). Thus, DOM of parrot feather with the greatest polarity (80.0 %) would be most favored by the polar organic pollutants, and water lettuce with the least polarity (57.7 %) should absorb more nonpolar organic pollutants. After years of pollution control in Lake Dianchi, inflow of pollutants is now mostly from domestic sewage, which is mainly composed of nonpolar substances, such as detergents. Therefore, the plants with lesser polarity, such as water lettuce, water hyacinth, and common reed in their DOM should have a greater influence on the currently prevalent hydrophobic pollutants in the lake than the other species do.

Conclusion

Quantitative and qualitative properties of DOM derived from eight typical macrophytes in Lake Dianchi were characterized. C/N in macrophytes was greater than that of phytoplankton but lesser than that in the terrestrial vascular plants. Floating and submerged species exhibited lesser C/N and C/P than did emergent and riparian species. Leaves of parrot feather have a preference of P rather than N. Release of P through the macrophyte-derived DOM was greater than that of N. Except N in the emergent and riparian species, N and P seems to be more concentrated in the DOM than in the ground leaves of the macrophytes. C/H, SUVA₂₅₄ and SUVA₂₈₀, FT-IR, and ¹³C NMR spectra all showed high content of aliphatic carbons, but less aromatic C in DOM of the macrophytes. Aromaticity in the macrophyte-derived DOM was lower than that in DOM from the allochthonous sources, sediment, or the humic substances but similar to or higher than that in the phytoplankton-derived DOM. Oriental pepper is the species with the greatest aromaticity in its DOM among the macrophytes studied. The macrophyte DOM is primarily composed of polysaccharides, nucleic acids, amino acids, proteins, and there are existence of the small molecular acids such as phenolic acids and carboxylic acids. Content of carbohydrate in the macrophyte-derived DOM was higher than those in phytoplankton and macroalgae. Among the macrophytes, parrot feather and crofton weed contained the greatest percent of carbohydrates in their DOM, and DOM of water hyacinth, water lettuce, and sago pondweed may have the greatest content of amino acids/proteins. Special quantitative and qualitative characteristic of the macrophyte-derived DOM will induce unique environment consequences in aquatic system, and the different chemical properties of DOM from different species or life-forms reflected their particular roles.

Acknowledgments This work was jointly supported by National Natural Science Foundation of China (40973090, 41261140337) and National Basic Research program of China (2008CB418200).

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