Source, composition, and environmental implication of neutral carbohydrates in sediment cores of subtropical reservoirs, South China

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Abstract.

Neutral carbohydrates along with algal organic matter (AOM) content, carbon isotopic composition, and elemental C/N ratios were investigated in three sediment cores of various trophic reservoirs in South China. Neutral monosaccharides, AOM, and carbon stable isotope ratios were determined by high-performance anion-exchange chromatography, Rock-Eval pyrolysis, and Finnigan Delta Plus XL mass spectrometry, respectively. The carbon isotopic compositions were corrected via the Suess effect. The concentrations of total neutral carbohydrates (TCHO) range from 0.51 to 6.4 mg/g at mesotrophic reservoirs, and from 0.83 to 2.56 mg/g at an oligotrophic reservoir. Monosaccharide compositions and diagnostic parameters indicate a predominant contribution of phytoplankton in each of the three cores, which is consistent with the results inferred by the corrected carbon isotopic composition and C/N ratios. The sedimentary neutral carbohydrates are largely structural polysaccharides and, thus, are resistant to degradation in the sediments. Moreover, the single neutral carbohydrate content is highly related with the carbon isotopic composition, algal productivity (hydrogen index), and increasing mean air temperature during the past 60 years. The nutrient input, however, is not a key factor affecting the primary productivity in the three reservoirs. The above evidence shows that neutral carbohydrates have been significantly elevated by climate change even at low latitude regions.

1 Introduction

Carbohydrates are the most abundant compounds in the biosphere, and they are present in the natural environment as both structural and storage compounds of aquatic and terrestrial organisms, comprising about 20–40 wt% of plankton (Parsons et al., 1984), more than 40 wt% of bacteria (Moers et al., 1993), and more than 75 wt% of vascular plants (Moers et al., 1993). Due to their high biological reactivity and availability, carbohydrates are preferentially utilized by heterotrophic organisms (e.g., bacteria and fungi) during transport of organic matter from water columns to underlying sediments (Hernes et al., 1996; Khodse et al., 2007), resulting in the preservation of more refractory structural carbohydrates in sedimenting particles (Cowie and Hedges, 1994; Burdige et al., 2000; Jensen et al., 2005; He et al., 2010). Moreover, the compositional signature of structural carbohydrates depends more on planktonic sources than the diagenetic pathway (Hernes et al., 1996). Thus, although carbohydrates exhibit different degrees of degradation, some structural fractions are selectively preserved and their compositions are mostly unchanged, which can be used as a powerful tool for elucidating sources, deposition processes, and diagenetic fates of organic matter (OM) in aquatic environments (Cowie and Hedges, 1984; Moers et al., 1990; Hicks et al., 1994, Meyers, 1997; Unger et al., 2005; Aufdenkampe et al., 2007; Skoog et al., 2008; Khodse and Bhosle, 2012; Panagiotopoulos et al., 2012).

Carbon isotope analyses in sedimentary OM offers an important tool for reconstructing the history of nutrient loading and eutrophication in lacustrine sediments (Schelske and Hodell, 1991; 1995). Phytoplankton preferentially removes dissolved $^{12}CO_2$ from epilimnetic water and depletes ^{12}C in the remaining dissolved inorganic carbon (Hodell and Schelske, 1998). As supplies of $^{12}CO_2$ become diminished, phytoplankton discriminates less against ^{13}C and sinking OM, incorporating more $^{13}CO_2$. Therefore, increased or decreased productivity can be reflected by enriched or depleted values of $\delta^{13}C$ in OM from the underlying sediments. However, during recent years, the $\delta^{13}C$ value in atmospheric CO_2, water column, and sedimentary OM have been significantly diminished and impacted by the Suess effect (Schelske and Hodell, 1995), which is defined as the change in the abundance of carbon isotopes (^{14}C, ^{13}C, ^{12}C) in natural OM reservoirs due to anthropogenic activities (e.g., fossil fuel combustion) (Keeling, 1979). Thus, the Suess effect needs to be considered when applying $\delta^{13}C$ in lacustrine sediments as a proxy for aquatic productivity. Although O'Reilly (2005) had not corrected for the Suess effect in the heterotrophic Lake Tanganyika in Africa, Verburg (2006) found that the corrected $\delta^{13}C$ values were used as a productivity proxy. In the Pearl River Delta, the development of industrialization and urbanization could enhance the Suess effect during recent years. Hence, it needs to correct for the Suess effect.

56   Several studies have shown that climate warming plays a significant role to algal productivity by using the S2 proxy in
57   the Arctic lakes during recent decades (Outridge et al., 2005; Outridge et al., 2007; Stern et al., 2009; Carrie et al., 2010).
58   However, Kirk (2011) investigated 14 Canadian Arctic and sub-Arctic lakes and found that the relationship between the S2
59   proxy and climate warming was irrelevant. In addition, only limited investigations have focused on the impact of global
60   change on aquatic productivity in subtropical lakes (Hambright et al., 1994; Smol et al., 2005). Therefore, the above
61   observations call for more investigations on the effects of trophic levels, early diagenesis, and sources of organic matter on
62   the relationship between algal productivity and climate warming.

63   For this investigation, subtropical reservoirs in rural areas having different trophic states were chosen. Our purpose is to
64   assess the source and diagenetic state of the carbohydrates, and their relationship with algal productivity in sediment cores
65   by using carbohydrate compositions combined with Rock-Eval parameters, carbon isotopic composition, and elemental C/N
66   ratios. In addition, trace metals data (Cu and Zn) cited from our previous paper (Duan et al., 2014) are used to help
67   understanding the source of carbohydrates. Besides, neutral carbohydrates and recorded temperature data were statistically
68   analyzed to explore the effects of climate warming on the historical variations of neutral carbohydrates in subtropical regions
69   over the last four decades.

70   ## 2   Materials and Methods

71   ### 2.1   Study area and sample collection

72   Zengtang reservoir (ZT), Lian'an reservoir (LA), and Xinfengjiang reservoir (XFJ) with different depths and trophic
73   states were chosen for this investigation. The detailed description of the study sites are shown in the previous literature
74   (Duan et al., 2015). In brief, ZT is a shallow, polymictic reservoir with a mesotrophic level, whereas LA is a deep and
75   mesotrophic reservoir. XFJ is a deep and oligotrophic reservoir. Both LA and XFJ are monomictic reservoirs. The most
76   abundant algal species in the ZT, LA, and XFJ reservoirs are green algae, cyanophyta, and diatoms.

77   Undisturbed sediment cores were collected from the central part of the studied lakes using a 6 cm diameter gravity corer
78   with a Plexiglass liner in 2010 and 2011. The water depths for the sampling sites at ZT, LA, and XFJ reservoirs are 3 m, 17
79   m, and 36 m, respectively. The core liners were put down slowly in order to avoid disturbance. The sediment cores were
80   sliced into 2 cm thick intervals using extrusion equipment. It is noted that the top four slices of the ZT core were merged into
81   two intervals (0–4 cm and 5–8 cm) due to the insufficient amount of sample for neutral sugar analysis. All subsamples were
82   immediately placed in plastic bags, sealed, and stored at low temperature (0–10 ℃), and then were quickly transported to the
83   laboratory, where they were freeze-dried and stored until further analysis.

84   ### 2.2   Physicochemical properties in water

85   Vertical and temporal variation of chlorophyll a, dissolved oxygen, and temperature in the water column of the LA
86   reservoir were recorded by a CTD-90M probe (Sea & Sun Technology, Germany) in increment mode, which enables us to
87   carry out a great number of profile records in the field (Fig. S1 in the supporting data). For the XFJ reservoir, the
88   physicochemical record was conducted only in March 2014. The lack of data from the ZT reservoir is due to its
89   reconstruction after the sediment core sampling.

90   ### 2.3   Stable carbon isotopic analysis

91   Samples were initially decarbonated by the moderate HCl solution, and then the stable carbon isotopic composition was
92   measured by a Finnigan Delta Plus XL mass spectrometry. The $\delta^{13}C$ values (‰) were given by the equation below：

93   $$\delta^{13}C\ (‰) = (R_{sample}/R_{standard} - 1) \times 1000$$

94 where R is the ^{13}C/^{12}C ratio and the standard is the Pee Dee Belemnite. Black carbon (Product ID: GBW 04408) was used as

95 the reference standard for the determination of accuracy and precision. The precision of δ^{13}C for the replicates was <

96 0.19‰ ± 0.12 (n = 40).

97   Measured values of δ^{13}C were corrected for the Suess effect with the following polynomial equation (Schelske and

98 Hodell, 1995), where t is time (in yr):

99      $\delta^{13}\text{C (‰)} = -4577.8 + 7.3430t - 3.9213 \times 10^{-3}t^2 + 6.9812 \times 10^{-7}t^3$

100   The calculated time-dependent depletion in δ^{13}C induced by fossil fuel combustion since 1840 was subtracted from the

101 measured δ^{13}C for each dated sediment section.

2.4 Neutral sugar analysis

103   Sediment samples (about 5 mg) from the three reservoirs were weighted and hydrolyzed in glass ampules with 12 M

104 H_2SO_4 for 2 h at room temperature. After nine milliliters of Milli-UV + water were added (1.2 M H_2SO_4, final concentration

105 of acid), the ampules were flame-sealed and the samples were stirred and hydrolyzed in a 100 °C water bath for 3 h. The

106 hydrolysis was terminated by placing the ampules in an ice bath for 5 min. Then, the deoxyribose was added as the internal

107 standard (Michael et al., 2015). Before instrumental analysis, the samples were run through a mixed bed of anion (AG 2-X8,

108 20–50 mesh, Bio-Rad) and cation (AC 5OW-X8, 100–200 mesh, Bio-Rad) exchange resins (Michael et al., 2015).

109 Self-absorbed AG11 A8 resin was utilized to remove the acid. The volume of resin needed for complete neutralization

110 depended on the amount of acid used for hydrolysis (Michael et al., 2015). After purification and desalting with a mixture of

111 cation and anion exchange resins, neutral sugars were isocratically separated with 25 mM NaOH on a PA 1 column in a

112 Dionex 500 ion chromatography system, which was equipped with a pulsed amperiometric detector (PAD) detector (model

113 ED40) (Michael et al., 2015). The detector setting was based on Skoog and Benner (1997). Chromatographic data were

114 recorded with a personal computer equipped with Hewlett Packard Chemstation software (Skoog and Benner, 1997; Kaiser

115 and Benner, 2009).

116   For every ten analyses, a blank sample and a duplicate sample were analyzed to check accuracy and precision. No

117 neutral sugars were detected in the blanks. Only glucose, galactose, mannose, rhamnose, fucose, and xylose were detected

118 and analyzed in samples due to the loss of ribose in the process of acid hydrolysis. The recovery of the monosaccharides in

119 the sediments ranged from 73% to 95%. The analytical precision of duplicate samples performed on different days was

120 within ±3% for glucose and ±5% for other sugars. In this study, the total neutral carbohydrates (TCHO) are defined as the

121 sum of all identified monosaccharides.

3 Results

3.1 Physicochemical properties of water

124   As shown in Fig. S1 in the supporting data, chlorophyll a concentrations in the water column of LA are higher in spring

125 and summer than in fall and winter, which is consistent with the seasonal distribution of the content of dissolved oxygen.

126 The vertical profiles of chlorophyll a and dissolved oxygen also show similar patterns; depleted dissolved oxygen in the

127 hypolimnion accompanies low content of chlorophyll a throughout the year, suggesting the important role of oxygen content

128 in the growth of productivity. In general, the bottom sediments in LA are mostly under anaerobic conditions. Water

129 temperature is higher in summer and fall, resulting in thermal stratification in the water column. During winter, the lake

130 mixes from top to bottom due to the decrease in temperature. The nutrient can be brought to deeper depths and may increase

131 the productivity in the entire water column.

132   The concentration of chlorophyll a (average: 0.94 μg/L) in the water column of XFJ is much lower than that in LA. The

133   oxygen content varies from 9 mg/L at a depth of 1 m to 8.54 mg/L at a depth of 36 m (Fig. S1 in the supporting data),

134   suggesting the bottom sediments are under aerobic conditions.

3.2   Characteristics of OM

136   The data from Rock-Eval pyrolysis are listed in Table S1 in the supporting data, which were reported previously (Duan

137   et al., 2015). As shown in Table S1, pyrolytic parameter S1 and S2 represent the fractions of hydrocarbons (HC) released

138   during the pyrolysis step, where S3 was derived from the fractions of CO and CO_2 released during the pyrolysis and

139   oxidation procedures. The hydrogen index (HI) is calculated by normalizing the contents of S2 to TOC (Duan et al., 2015).

140   TOC and hydrogen index (HI) are in the ranges of 0.78–2.98 and 114–231 mg HC/g TOC, respectively, in the ZT core; in

141   the ranges of 0.88–4.31 and 151–229 mg HC/g TOC, respectively, in the LA core; and in the ranges of 0.47–1.76 and

142   141–196 mg HC/g TOC, respectively, in the XFJ core. In general, the HI values are enriched in the surface layers of all the

143   sediment cores.

144   $\delta^{13}C$ values (‰) range from −22.2‰ to −21.6‰ in the ZT core, from −26.4‰ to −24.1‰ in the LA core, and from

145   −27.2‰ to −23.1‰ in the XFJ core, with the average values of −21.9‰, −25.4‰, and −24.9‰, respectively (Fig. 1). After

146   the correction for the Suess effect, $\delta^{13}C$ values (‰) vary from −21.7‰ to −19.9‰ in the ZT core, from −5.1‰ to −23.9‰ in

147   the LA core, and from −25.5‰ to −22.9‰ in the XFJ core, with the average values of −20.8‰, −24.6‰, and −24.1‰,

148   respectively (Fig. 1).

149   Elemental C/N ratios vary from 3.51 to 9.34 in the ZT core, from 4.12 to 14.7 in the LA core, and from 2.3 to 10.1 in

150   the XFJ core, with the mean values of 5.56, 8.15 and 5.14, respectively (Fig. 1).

151   The detailed results from ^{210}Pb and ^{137}Cs radiometric dating was reported previously (Duan et al., 2015). The mass

152   accumulation rates (MAR) were cited and displayed in the Table S1 in the supporting data. As the ZT, LA, and XFJ

153   reservoirs had been small lakes before the dam construction, the chronological records for the ZT, LA, and XFJ cores are

154   longer than the time scales of the dam construction.

3.3   Neutral sugar data

156   The concentrations of seven monosaccharides (glucose, galactose, mannose, arabinose, rhamnose, fucose, and xylose)

157   are presented in Figure 2, and/or listed in Table S2 in the supporting data. Glucose (0.2–2.34 mg/g) is the most abundant

158   sugar in all the reservoir sediments, followed by galactose (0.09–1.2 mg/g), mannose (0.03–0.92 mg/g), and xylose

159   (0.01–0.95 mg/g). Concentrations of arabinose (0.05–0.77 mg/g) , rhamnose (0.04–0.67 mg/g), and fucose (0.02–0.43 mg/g)

160   are relatively low in the reservoir sediments. The TCHO concentrations at the ZT, LA, and XFJ reservoirs range from 1.94 to

161   5.36 mg/g, from 0.51 to 6.4 mg/g, and from 0.83 to 2.56 mg/g, respectively, and show decreasing downcore trends in all the

162   sediment cores. Carbohydrate yield (%) is the molar concentration of monosaccharide carbon normalized by TOC.

163   Carbohydrate yield (%) ranges from 7.08 to 10.9% in the ZT core, from 2.31 to 13.53% in the LA core, and from 1.93 to

164   12.52% in the XFJ core, with average values of 8.68%, 7.79%, and 7.33%, respectively (Fig. 3).

165   Compositions of neutral sugars in the three sediment cores are calculated based on their concentrations. Glucose

166   (21.1–27.6 mol%) is the most abundant monosaccharide, followed by mannose (14–21.5 mol%), galactose (14.7–18.7

167   mol%), arabinose (10.7–17.1 mol%), rhamnose (11–12.9 mol%), xylose (8.8–10.1 mol%), and fucose (3.2–7.2 mol%) in the

168   ZT sediments. Glucose (22.2–37.4 mol%) is also the most abundant monosaccharide, followed by galactose (12–20 mol%),

169   mannose (11.1–20.5 mol%), arabinose (10.7–14.4 mol%), rhamnose (6.9–11.9 mol%), xylose (5.09–18.32 mol%), and

170   fucose (3.3–7.74 mol%) in the LA sediments. For the XFJ core, glucose (18.5–48 mol%) is still the most abundant

171   monosaccharide, followed by galactose (12.3–3.7 mol%), mannose (3.8–23 mol%), arabinose (8.3–14.5 mol%), rhamnose

172   (6–11.2 mol%), xylose (0.75–21.6 mol%), and fucose (2.9–8.2 mol%) in the sediment core.

3.4 Meteorological records of the studied areas

The five-year moving average temperature (T_5) was calculated from the reported database (Duan et al., 2015). The mean air temperature in the Guangzhou area has increased by about 1.5 ℃ since 1960, and the mean air temperature in the Heyuan area has increased by about 1.52 ℃ between 1957 and 2004. Therefore, the above data suggests a significant trend in climate warming in the investigated areas during the last six decades (Duan et al., 2015). The annual hours of daylight in Guangzhou and Heyuan on the time scale of 60 years have been obtained from the China Meteorological Data Sharing Service System (CMDSSS). The annual hours of daylight in both areas are somehow variable and show a progressively decreasing trend from 1950 to 2010 (Fig. S5).

4 Discussion

4.1 OM characteristics in sediment cores

The content and composition of sedimentary OM derived from the Rock-Eval analysis could provide the source and early diagenetic information of OM in the reservoir cores. The S1, S2, S3, TOC, and HI show significant decreasing trends with increasing profile depths in the ZT and LA cores, suggesting that the sedimentary OM has either been affected by autochthonous inputs or by extensive degradation (Duan et al., 2015). For the XFJ core, the TOC as well as the other pyrolytic parameters (except HI proxy) show increasing trends with depth, suggesting the degradation and oxidation of OM and/or terrestrial inputs of the OM are the primary factors affecting the variation of OM.

Carbon isotope analyses offer an important tool for identifying the sources of OM in lacustrine sediments. Different primary producers have distinctive carbon isotope compositions. The average $\delta^{13}C$ values of C3 plants is around −27‰ to −26‰, whereas the C4 plants have average $\delta^{13}C$ values of −14‰ to −13‰. Although the $\delta^{13}C$ values in phytoplankton are in a broad range of −17‰ to −45‰ (Boschker et al., 1995), it can be identified by the combination of other proxies (e.g., elemental C/N ratios). All the corrected $\delta^{13}C$ values of sedimentary OM in the three reservoirs vary from −25.5‰ to −19.9‰ (Fig. 1), which are in the range of phytoplankton and C3 plants. However, their corresponding C/N ratios are relatively low than those for higher plants (> 12) (Fig. 1), suggesting the predominant contribution of phytoplankton in the OM of reservoirs. The $\delta^{13}C$ values in ZT sediments are more enriched (average: −20.8‰) than those in LA (average: −24.6‰) or XFJ (average: −24.1‰) sediments, which may be attributed to high phytoplankton productivity (chlorophyll a = 90.7 µg/L), anaerobic sediments with high rates of methanogenesis, and lack of terrestrial carbon inputs in shallow water bodies (Gu and Schelske, 2004). High phytoplankton can enhance isotopic fractionation and result in enrichment of ^{13}C in dissolved inorganic carbon. The removal of $^{12}CH_4$ by intensive methanogenesis also leads to the accumulation of ^{13}C-depleted OM in sediments (Gu and Schelske, 2004).

After correcting for the Suess effect, the OM in sediments becomes more enriched in ^{13}C from the bottom to the top of the ZT core (Fig. 1), reflecting a progressive increase in historical productivity, which is consistent with the vertical variations of TOC, C/N, and HI. Similar observations were also found in the LA core from a depth of 16 cm to the surface layer. Therefore, both ZT and LA reservoirs undergo significant increases in primary productivity during the recent years. As shown in Fig. 1, the correction for the Suess effect can result in opposite conclusions regarding the aquatic productivity, based on uncorrected $\delta^{13}C$ values for ZT and LA. Similar results are also observed in Lake Brunnsviken (Routh et al., 2004), Lake Eric (Schelske and Hodell 1995), and deep Lake Tahoe (Chandra et al., 2005), suggesting the importance, in terms of productivity, of the correction for the Suess effect in the recent $\delta^{13}C$ values for lacustrine sediment cores.

For the XFJ reservoir, the corrected $\delta^{13}C$ values increase from depths of 22 to 10 cm and then decrease abruptly to the surface layers, which may result from the biodegradation of OM in aerobic sediments or from a great number of recent terrestrial loading. However, values of C/N ratios in the upper layers of the XFJ core are very low (C/N ≈ 3) and indicate a

213 contribution of algal origin in the sediments (Fig. 1). Therefore, the decrease of corrected δ^{13}C at XFJ is mainly due to the

214 biodegradation of OM under aerobic conditions. The dissolved oxygen content is 8.54 mg/L at a depth of 36 m, which can

215 provide sufficient oxygen for microbial metabolism (Fig. S2 in the supporting data). The preferential degradation of more

216 ^{13}C-enriched organic compounds (e.g., carbohydrates and proteins) would lead to a decrease in the δ^{13}C values in the residue

217 OM (Lehmann et al., 2002).

4.2   Monosaccharide compositions in sediment cores

219   As shown in Table. S2, the TCHO concentrations in the ZT and LA cores show significant decrease in the downcore

220 sediments, which are similar to the vertical profiles of S2, TOC, C/N, corrected δ^{13}C, and HI (Table S1 and S2 in the

221 supporting data). For the XFJ core, the TCHO and HI still decline in the downcore sediments as do those in the ZT and LA

222 cores (Table S1 and S2 in the supporting data). In general, the content of TCHO (0.51–6.4 mg/g) in the three reservoirs is

223 similar to that of a sediment core in the eutrophic French Aydat lake (1.19–4.58 mg/g) (Ogier et al., 2001), which was also

224 enriched with neutral sugars at the surface layers of the sediment core.

225   The compositions of neutral sugars in ZT and LA cores show that glucose is the most abundant sugar in these two

226 reservoir sediments while galactose, mannose, and arabinose are relatively more abundant than rhamnose, xylose, and fucose

227 (Fig. 2), which is similar to the monosaccharide composition in phytoplankton (Hamilton and Hedges, 1988). Moreover, the

228 relative abundances of monosaccharides do not vary much in the ZT and LA cores except for the apparent changes of

229 glucose and xylose at depths of 10, 16, 32, and 34 cm in the LA core. For the XFJ reservoir, the monosaccharide

230 composition in the upper layers (0–16 cm) of the sediment core also indicates a dominant origin of algal carbohydrates.

231 However, xylose significantly increases at a few depths (XFJ core: at 18, 24, and 32 cm depths) (Fig. 2). Moreover, glucose

232 shows an increasing trend correlated with the abundant xylose, especially between the depths of 18 cm and 34 cm. The

233 pattern of carbohydrate composition in these samples (18–34 cm) is not in agreement with the post-depositional process of

234 diagenesis as observed in previous studies (Hamilton and Hedges, 1988; Hedges et al., 1994). They found that the diagenesis

235 process often led to a decrease in glucose along with a corresponding increase in bacteria-derived deoxy sugars (rhamnose

236 and fucose) in sediment cores. Therefore, these outliers (18–34 cm) might be related to increasing vascular plant input or

237 hydrological variation at XFJ, as discussed in the following paragraph. .

4.3   Source of neutral carbohydrates

239   Molecular-level diagnostic parameters have often been used to differentiate microbial, planktonic, and terrestrial

240 sources (Cowie and Hedges, 1984; Guggenberger et al., 1994). Diagnostic carbohydrate parameters and their results are

241 presented in Fig. S2 and S3 in the supporting data.

242   The ratios of mannose to xylose could indicate the OM sources derived from phytoplankton, bacteria, gymnosperm, and

243 angiosperm tissues (Cowie and Hedges, 1984). As shown in Fig. 3 in the supporting data, the values of the Mannose/Xylose

244 ratios in most of the sediments at ZT and LA range from 1.51 to 2.70 and 1.49 to 3.50, respectively, except at a depth of 8

245 cm (1.46) in the ZT core and at the depths of 4 cm (1.18), 8 cm (1.05), 10 cm (0.67), 16 cm (8.60), and 28–32 cm (0.6–1.33)

246 in the LA core. Thus, most of the samples can be identified as a phytoplankton source (1.5–3.5), suggesting the important

247 contribution of AOM in these two areas. However, most of the Mannose/Xylose ratios are in the range of 0.23–0.87 for

248 gymnosperm tissues (< 1) at depths deeper than 16 cm in the XFJ sediments, which indicates the presence of terrestrial OM

249 derived from angiosperm leaves and grasses (Fig. S7)

250   The above conclusion is also confirmed by the %Xylose$_b$ parameters ('b' represents a value on glucose-free base)

251 plotted in Fig. 2 and Fig. S3 in the supporting data. %Xylose$_b$ is a useful biomarker to differentiate the type of terrestrial

252 input (Cowie and Hedges, 1984). In most of the samples at ZT and LA, %Xylose$_b$ is in the ranges of 9.34–11.8 and

253 7.10–15.8, respectively, except at the depths of 10 cm (23.5), 16 cm (3.02), and 32 cm (26.4) in the LA core. The

254 low %Xylose$_b$ values (6.2–17.0) indicate the primary phytoplankton origin of neutral sugars at ZT and LA. The high values

255 at the depths of 10 cm and 32 cm in the LA core might indicate important terrestrial input. Further evidence is also obtained

256 from %(Arabinose + Galactose)$_b$ plotted in Fig. S3 in the supporting data and from %(Fucose + Rhamnose)$_b$ plotted in Fig.

257 S2 in the supporting data. The results from the %Xylose$_b$ versus %(Fucose + Rhamnose)$_b$ plots suggest a phytoplankton

258 origin in reservoir sediments, which is consistent with that reported in the literature (Boschker et al., 1995). As for

259 the %(Arabinose + Galactose)$_b$ ratios, their values are mostly in the range of 30.7–44.4 in the sediment cores at ZT, LA, and

260 XFJ, indicating that the sedimentary OM samples are largely derived from phytoplankton with the ratios of 22–47. Only a

261 few high values at a depth of 16 cm (48) in the LA core and at depths of 8 cm (50.6) and 34 cm (48.9) in the XFJ core are

262 likely to indicate an additional origin from non-woody angiosperm tissues and grasses, as demonstrated by Cowie and

263 Hedges (1994). The above result also implies a different origin for neutral sugars in the upper layers of the XFJ core (0–16

264 cm) than in the lower layers (> 18 cm), which have been increasingly affected by terrestrial input.

265   In order to support the above conclusions of the sources of OM by neutral sugars in the reservoirs, monosaccharide

266 concentrations and heavy metal data are compared to each other (Table S3 and S4 in the supporting data). It is found that

267 almost all monosaccharides (except Xylose at LA and XFJ) are significantly related to heavy metals (e.g., Zn and Cu) in the

268 sediment cores of ZT and LA, and the upper layers of the XFJ core (0–16 cm) (Table S4 in the supporting data). However,

269 only galactose, mannose, and fucose are positively correlated with Zn and Cu in the core of XFJ (0–34 cm), although the

270 lower layers are increasingly affected by allochtonous input, as discussed in the above paragraphs. As Zn and Cu are

271 essential nutrients for phytoplankton growth, these relationships provide more evidence for the important contribution of

272 AOM to carbohydrates in the investigated sediments.

273 **4.4   Diagenesis of neutral carbohydrates**

274   Carbohydrates are not only useful in identifying the sources of OM but also in evaluating early diagenetic processes

275 occurring in the post-depositional environment. The four parameters, deoxysugars/pentoses (deoxy S/C5) ratio, glucose

276 content (mol% or wt%), %(Fucose + Rhamnose)$_b$, and carbohydrate yield (%) in the sediment cores are often used to

277 evaluate diagenetic changes of OM (Cowie and Hedges, 1984; Ittekkot and Arain, 1986; Opsahl and Benner, 1999; Benner

278 and Opsahl, 2001; Kaiser and Benner, 2009).

279   Glucose content is an important factor used to assess the degradation state of OM. Glucose accounts for 58 to 90% of

280 the carbohydrates in fresh plankton and terrestrial tissues (Cowie and Hedges, 1984; Opsahl and Benner, 1999; da Cunha et

281 al., 2002). Hernes (1996) proposed that relative mol% glucose in particulate OM could be used as a diagenetic indicator for

282 organic material in the equatorial Pacific region. In this investigation, wt% glucose in the sediments ranges from 22 to 29.1%

283 at ZT, from 23.3 to 39.2% at LA, and from 19.6 to 50.3% at XFJ (Fig. 3), suggesting that neutral sugars are biodegraded in

284 the sedimentary OM. This conclusion is also confirmed by the carbohydrate yield (%), which usually represent 30–40% of

285 TOC in fresh tissues of plant and phytoplankton but less than 9% in sediments (Cowie and Hedges, 1984; Opsahl and

286 Benner, 1999). Carbohydrate yields range from 1.93 to 13.53% in the sediments of the three reservoirs (Fig. 3). It is also

287 suggested that neutral sugars degrade significantly in the investigated sediments. These results are consistent with the

288 general observation from previous studies (Ogier et al., 2001). In general, the carbohydrates in the reservoir sediments are

289 extensively transformed and degraded. However, the stability of their compositions was found in the downcore sediments.

290 Whether the carbohydrate compounds are degraded mainly in the water column or in the sediment core will be discussed

291 below (Fig. 3).

292   Keil (1998) found that the %wt (Fucose + Rhamnose)$_b$ values could reflect the diagenesis process of neutral

293 carbohydrates. This index was elevated as the sediment particle sizes decreased, suggesting that smaller size fractions

294 showed a higher degree of degradation. Their observation was also consistent with other diagenetic indices such as lignin

295 and non-protein biomarkers (Keil et al., 1998). In this study, the values of %wt (Fucose + Rhamnose)$_b$ at three reservoirs do

296 not vary significantly with the sediment core, and there is no decline in wt% glucose with a corresponding increase of %wt

297 (Fucose + Rhamnose)$_b$ in each of the ZT, LA, and XFJ sediment cores (Fig. 3), suggesting that the process of degradation

298 occurs mainly during the settling period rather than after deposition. Further evidence in support of this conclusion can be

299 obtained from the ratio of deoxy sugars (e.g., rhamnose and fucose) to C5 (e.g., arabinose and xylose) (deoxy S/C5). The

300 deoxy S/C5 ratios also remain almost unchanged throughout the sediment cores of ZT, LA, and XFJ (Fig. 3). Therefore,

301 although sinking organic matter-rich particles and their carbohydrates in these reservoirs suffer from intensive oxidation and

302 degradation in the water column during their transit to bottom sediments, some fractions are selectively preserved in the

303 sediment cores and remain almost unchanged during post-deposition, as observed before (Cowie and Hedges, 1984; Moers et

304 al., 1990; Hicks et al., 1994).

305 Carbohydrates are derived not only from storage polymer but also from the cell membrane of phytoplankton. The

306 monosaccharide residues in both kinds of polymers are bound to each other via glycosidic bonds (Cowie et al., 1992; Cowie

307 and Hedges, 1994; Hernes et al., 1996). In general, glucose is bound mainly in an unbranched, starchlike β-1,3-glucan

308 storage polymer (Handa et al, 1969), whereas mannose, galactose, xylose, fucose, and rhamnose are characteristically more

309 abundant in the cell walls (Cowie et al, 1992). The cell-wall aldoses are bound primarily in branched and often

310 heterogeneous structural polymers. On the contrary, glucose, arabinose, and ribose are relatively concentrated in intracellular

311 polysaccharides. In the present study, concentrations of mannose, galactose, arabinose, and xylose on a glucose-free base are

312 dominant in the sediment cores, and the carbohydrate compositions are mostly unchanged. Hence, the neutral carbohydrates

313 in the sediment cores are largely related to structural polysaccharides, which is more resistant to microbial degradation than

314 storage polysaccharides.

315 In support of the above conclusion, the *k* values of deoxy S/C5 were calculated using a "multi-G" model (Wang et al.,

316 1998) to evaluate neutral sugar degradation. The k value is 0.0025 yr^{-1} for ZT, 0.0021 yr^{-1} for LA, and 0.0025 yr^{-1} for XFJ. It

317 is found that the decomposition of 95% neutral sugar in sediments will take thousands of years, which is similar to the results

318 of TCHO in the ocean sediments (Wang et al., 1998) and the degradation of OM in the lacustrine sediments (Li et al., 2013).

319 The increasing downcore trends of glucose and OM in the XFJ core are different from those in the ZT and LA cores,

320 suggesting that the variation of OM and neutral sugars are site-independent and may be related to the different trophic states,

321 the various sources of OM, and the hydrological changes in different depositional environments. Moreover, the downcore

322 OM profiles in some of the sediment cores have not exhibited decreasing trends (Kirk et al., 2011, Meyer, 1997), which are

323 not consistent with the traditional degradation model and mechanism. Hence, more work would be needed for investigating

324 the sources, compositions, and early diagenesis of carbohydrates in different aquatic environments.

4.5 Effects of climate change on primary productivity and carbohydrates

326 Carbohydrates are important organic components from aquatic algae and have undergone extensive degradation during

327 settling. However, large amounts of resistant structural carbohydrates (e.g., cell walls) containing source information can be

328 preserved in the sinking particles and sediments. Moreover, HI has been widely utilized as a useful indicator of primary

329 productivity during recent years (Gasse et al., 2001; Stein et al., 2006; Bechtel and Schubert, 2009). As shown in Fig. 4 and

330 Table S4 in the supporting data, HI values in the ZT and LA cores are positively correlated with monosaccharides, especially

331 the algae-dominated, galactose, mannose, fucose, and arabinose (Ittekkot and Arain, 1986; Hamilton and Hedges, 1988;

332 D'souza et al., 2003), which are usually dominated in structral cell walls of planktonic algaes (Hecky et al., 1973; Haug et al.,

333 1976). For the XFJ core, significant correlations are also found between the monosaccharides and the HI values, except for

334 rhamnose, fucose, and xylose. It is noted that the a few samples at depths of 8–10 cm and 30–34 cm in the LA core and at

335 depths of 18–34 cm in the XFJ core are excluded due to the inputs of allochthonous OM to the sediment cores. Therefore,

336 monosaccharides (e.g., galactose and mannose) can be used for the reconstruction of historical productivity in the subtropical

337 reservoirs.

338   As shown in Table S4 in the supporting information, the contents of glucose, galactose, arabinose, mannose, fucose,

339   and rhamnose are also positively correlated with S2 and HI values in the ZT, LA, and XFJ sediment cores. However, each of

340   them shows no/or weak correlations with the diagenetic parameters of neutral sugars and OM (e.g., % (Fucose + Rhamnose)[b],

341   Deoxy S/C5). Moreover, the xylose concentrations representing terrestrial inputs do not show significant correlations with

342   the productivity proxies (e.g., S2 and HI) or any of the other monosaccharide concentrations at LA and XFJ. Thus, the above

343   evidence supports that the increasing neutral sugars in the reservoir sediments are mainly attributed to algal productivity

344   rather than the degradation of neutral sugars during post-diagenesis.

345   In order to understand the effects of climate change on the historical variations of primary productivity, the T_5 values

346   over 60 years are compared with the profiles of carbohydrates in the three reservoirs (Fig. 5 and Table S4). The

347   monosaccharide profiles at ZT and LA show good correlation with T_5 during the past 60 years (for ZT, Galactose:T_5, R^2 =

348   0.824, $p < 0.01$; Mannose:T_5, $R^2 = 0.824$, $p < 0.01$; Fucose:T_5, $R^2 = 0.805$, $p < 0.01$; for LA, Galactose:T_5, $R^2 = 0.885$, $p <$

349   0.01; Mannose:T_5, $R^2 = 0.699$, $p < 0.01$; Fucose:T_5, $R^2 = 0.883$, $p < 0.01$;), suggesting that an increase in temperature likely

350   enhances the deposition of carbohydrates in sediments (Fig. 5 and Table S4). Moreover, total nitrogen (TN) and total

351   phosphorus (TP) showed weaker correlations with T_5 than carbohydrates for the sediment cores of ZT and LA (Table S5;

352   Duan et al., 2015). The TN and TP concentrations can be used to reflect the historical inputs of nutrients in the ZT and LA

353   reservoirs. Furthermore, the TP and TN concentrations at ZT and LA remained at a low level (mostly TP < 0.1 mg/g, TN <

354   0.4%) during the past six decades and are far lower than those in sediments of other eutrophic reservoirs (Duan et al., 2015).

355   Further evidence can be found in the results from principal component analyses (PCA) in the Fig. S8 in the supporting data.

356   The T_5, HI, and monosaccharides are in the first principal component and account for 76.5% and 67.3% of the total variance

357   in the LA and XFJ reservoirs, whereas the second principal component of TP and TN accounts for 8.36% and 11.7% of the

358   total variance, respectively. Hence, the nutrient input is not the key factor affecting carbohydrates in the three reservoirs. In

359   addition, the factor of light can also be excluded by the records of the annual hours of daylight, which show progressively

360   decreasing trends from 1950 to 2010 at Guangzhou and Heyuan (Fig. S5). In conclusion, the increase in deposition of

361   carbohydrates in sediments at ZT and LA corroborates very well with the increase in temperature (Fig. 5). For the XFJ

362   reservoir, the profiles of monosaccharides also show a positive correlation with the temperature variations (for XFJ,

363   Galactose:T_5, $R^2 = 0.702$, $p < 0.01$; Fucose:T_5, $R^2 = 0.744$ $p < 0.01$;), but show no relationship with TN or TP concentrations

364   (Fig. 5, Table S4). Although the primary productivity is lower in the XFJ reservoir than in the ZT or LA reservoirs, it is still

365   significantly affected by the increasing temperature. Although the TOC and S2 values have declined with increasing

366   temperature in the XFJ core profile due to the phosphorus-limited trophic level, the neutral sugar contents still increase (Fig.

367   5). Therefore, the above results suggest that neutral sugar in the ZT, LA, and XFJ reservoirs is strongly associated with

368   climate warming in the subtropical area.

369   **5   Conclusions**

370   The sources, composition, and diagenesis of carbohydrates in the sediment cores of three subtropical reservoirs were

371   investigated by conducting acid hydrolysis coupling with high-performance liquid chromatography (HPLC) with pulsed

372   amperometric detection (PAD). Glucose, mannose, and galactose are the most abundant monosaccharides. Monosaccharide

373   composition and diagnostic parameters (mannose/xylose ratio, arabinose plus galactose, xylose) indicate a predominant

374   contribution of phytoplankton in the whole sediment cores of the ZT and LA reservoirs and in the upper layers of the XFJ

375   core (0–16 cm). The carbohydrates are partially degraded during the settling. It is found that the degradation proxies

376   (S2/RC, %wt (fucose + rhamnose)$_b$, and deoxy S/C5) have not varied much in all of the whole sediment cores.

377   The corrected δ^{13}C and C/N ratios in sedimentary OM can be used to reflect the historical changes of productivity in the

378   subtropical reservoirs. Based on the higher corrected δ^{13}C values and the lower C/N ratios, increased productivity was

379 observed in the upper layers of ZT and LA reservoirs, which are consistent with the increase of monosaccharides (e.g.,

380 galactose, mannose, fucose, and arabinose) and HI. As for XFJ reservoir, the corrected $\delta^{13}C$ values abruptly decrease with very

381 low C/N ratios, which may indicate different sources and biodegradation in the underlying sediments. Moreover, strong

382 positive correlation between TCHO and HI is found both in the mesotrophic reservoirs (ZT and LA) and in the oligotrophic

383 reservoir (XFJ) in this investigation, suggesting that TCHO is related to primary productivity in the studied subtropical

384 reservoirs. Furthermore, increasing levels of carbohydrates in the three reservoir cores show significant relationships with T_5

385 during the last 60 years. Elevated temperatures lead to increasing levels of carbohydrates in the sediment profiles during last

386 six decades. Therefore, this investigation provides important evidence for the effect of climate change on the aquatic

387 ecosystems in the low latitude region. To further develop the productivity indicator of carbohydrates, more work is needed to

388 improve the detection of all the sedimentary monosaccharides (e.g., ribose) during acid pyrolysis.

389 **Author contribution**

390 Jing'an Chen and Yong Ran designed the experiments and Dandan. Duan, Dainan Zhang, Jingfu Wang, and Yu Yang carried

391 them out. Dandan Duan prepared the manuscript with contributions from all co-authors.

392 **Competing interests**

393 The authors declare that they have no conflict of interest.

394 **Acknowledgments**

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562 **Figure captions**

563 **Figure 1**. Vertical variations of original $\delta^{13}C$, corrected $\delta^{13}C$, and C/N in sediment cores of three reservoirs

564 **Figure 2.** Profiles of neutral carbohydrates in sediment cores of the reservoirs

565 **Figure 3.** Vertical profiles of yield (%), Deoxy S/C5, wt% Glucose and wt % (Fucose+Rhamnose)$_b$ in the ZT, LA, and
566 XFJ reservoirs

567 **Figure 4.** Relationship of HI with single sugar compounds in the ZT, LA, and XFJ reservoirs (For LA, the sample at 8-10 cm
568 depths and at 30-34 cm depths were excluded; For XFJ, samples below 16 cm were excluded). The HI data are coted from
569 Duan et al. (2015).

570 **Figure 5.** Temporal profiles of five-year moving temperature (T_5), hydrogen index(HI) and single neutral sugars in sediment
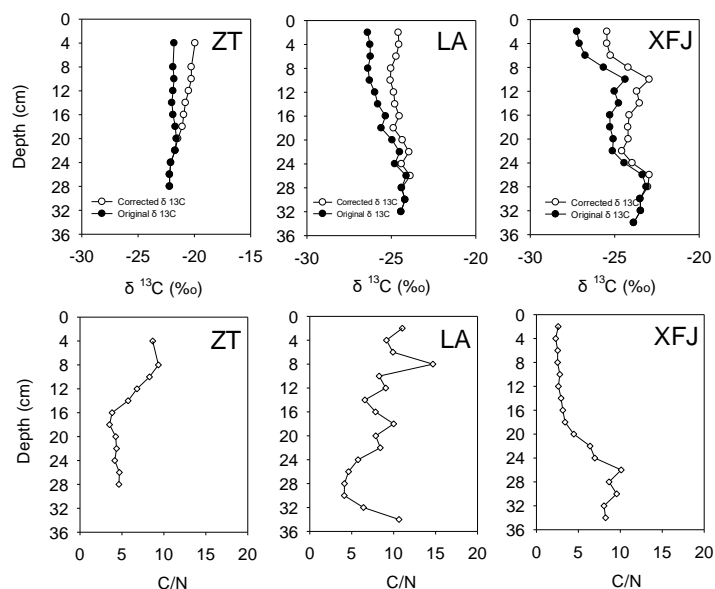571 cores from the three reservoirs.

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Figure 1. Vertical variations of original δ^{13}C, corrected δ^{13}C, and C/N in sediment cores of three reservoirs

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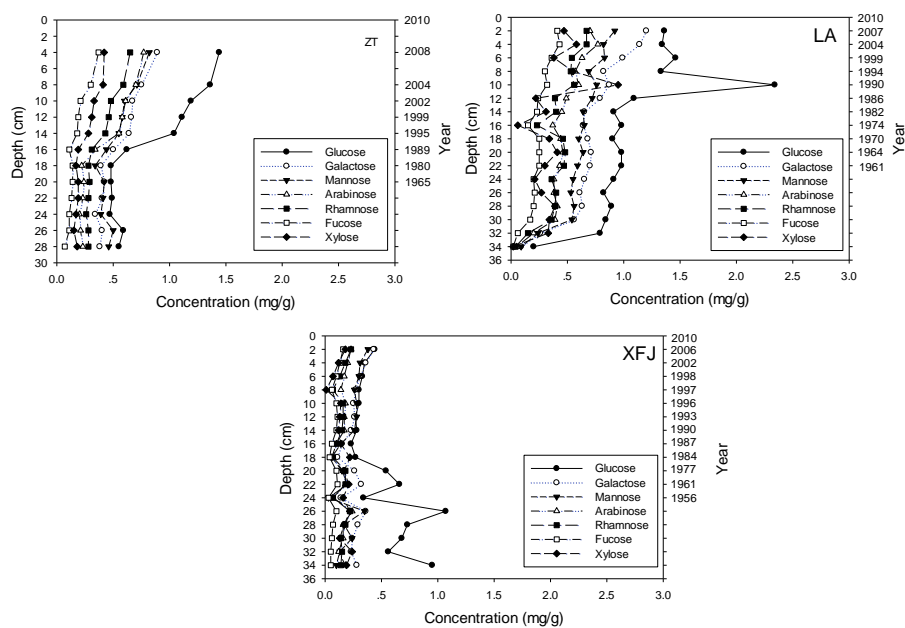578

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Figure 2. Profiles of neutral carbohydrates in the sediment cores of the reservoirs

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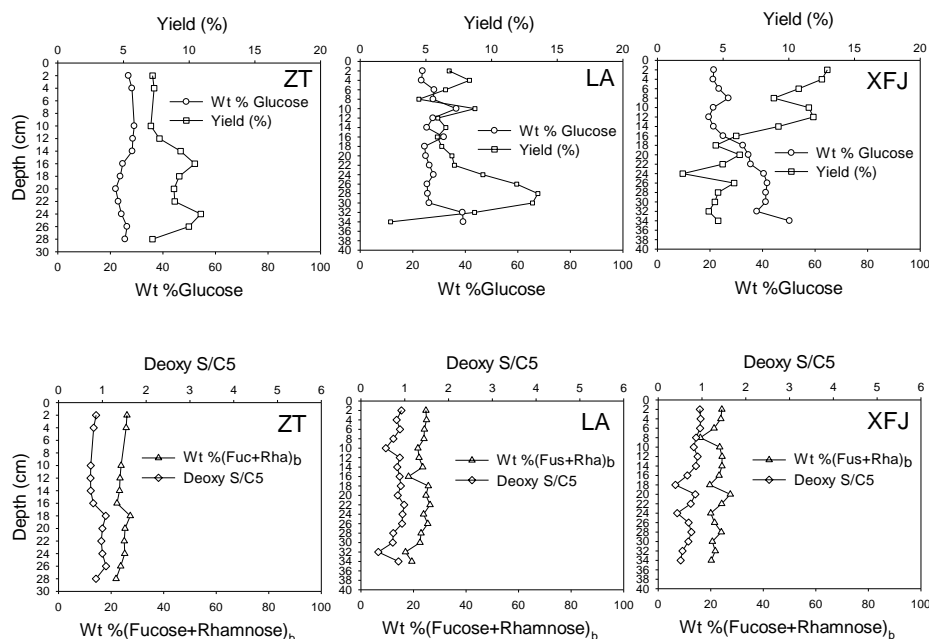**Figure 3.** Vertical profiles of yield (%), wt% glucose, deoxy S/C5, and wt% (Fucose+Rhamnose)$_b$ at the ZT, LA, and XFJ

reservoirs

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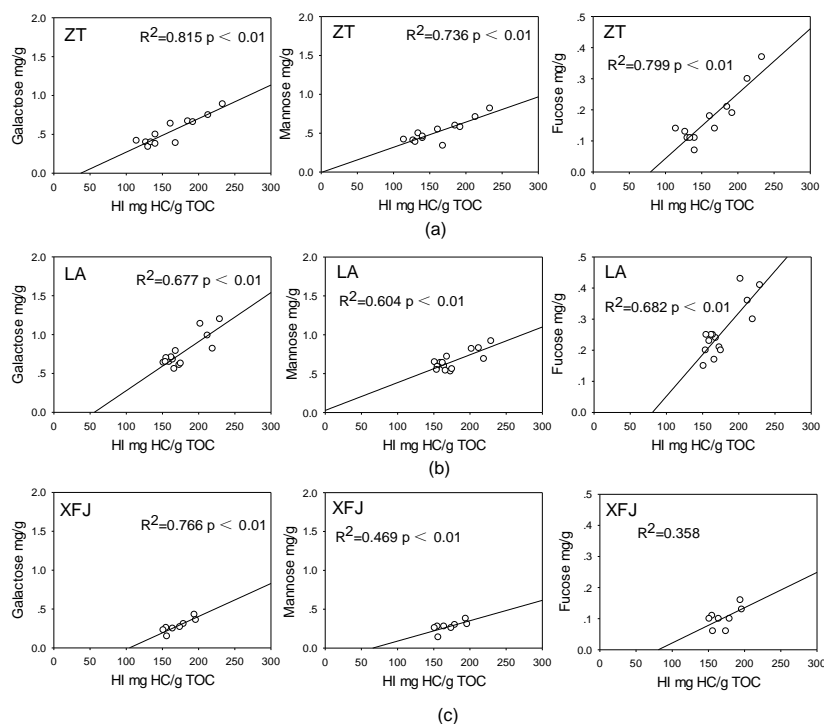631
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639 **Figure 4**. Relationship of HI with galactose, mannose, and fucose in the ZT, LA, and XFJ reservoirs (For LA, the sample
640 at 8-10 cm depths and at 30-34 cm depths were excluded; For XFJ, samples below 16 cm were excluded). The HI data
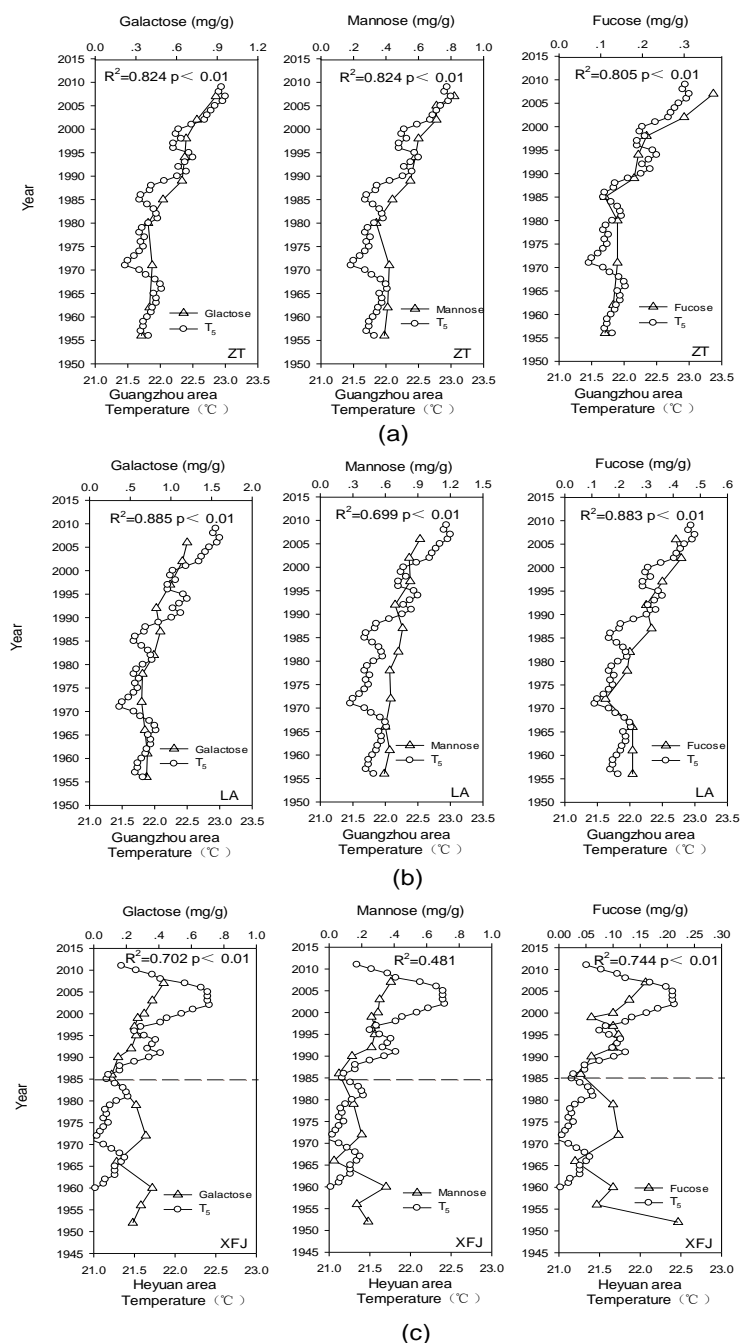641 were cited from Duan et al. (2015).

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Figure 5. Temporal profiles of five-year moving temperature (T_5) and single neutral sugars in sediment cores from the three reservoirs.