The point-by-point reply to the reviewers' and editor's comments: (Our responses are marked in blue color)

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

Authors: Dandan Duan, Dainan Zhang, Yu Yang, Jingfu Wang, Jian 'an Chen, and Yong Ran*

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Dear Editor:

We'd like to appreciate you and three reviewers very much for the helpful and thoughtful comments on our manuscript. We have carefully revised the manuscript according to your suggestions and the reviewers' comments. The point-by-point responses are written in blue color. For your convenience, the annotated version of the manuscript is loaded with the final version of the manuscript. We sincerely appreciate your consideration.

With best regards,

Dr. Yong Ran

Anonymous Referee #1:

Duan et al., have collected sediment cores from three tropical reservoirs in South China and analyzed them for the neutral carbohydrates along with algal organic matter (AOM) content, carbon isotopic composition, and elemental C/N ratios. Based on these data, they investigate the source, composition and diagenesis of the neutral carbohydrates and their relationships with the history of algal productivity induced by climate change over the last 60 years. This manuscript presents interesting results and requires minor revision before it can be accepted for publication. The following comments might help authors in their revising:

1. First, the manuscript needs some cohesive discussion to emphasize more on the combination uses of carbon isotopic composition, pyrolytic organic parameters and carbohydrates composition.

Response:

We have added some cohesive discussion on the interrelationship and combination uses of the carbon isotopic composition, pyrolytic organic parameters and carbohydrates composition.

As shown in the Table S4, positive correlations between corrected $\delta^{13}C$ values, hydrogen index (HI), monosaccharide contents of algal origin, and five- year moving average temperature (T_5) were only observed in ZT core. The corrected $\delta^{13}C$ at LA and XFJ cores showed no relationship with other productivity parameter (HI) and T_5 even though the corrected $\delta^{13}C$ were enriched in the upper layers of LA core. This may result from the effects of organic matter degradation and variable terrestrial inputs, etc. on the carbon isotopic composition ($\delta^{13}C$) at mesotrophic and oligotrophic reservoirs (LA and XFJ). However, the HI parameter and algal monosaccharide contents showed the same changing trends, and were positively correlated with T_5 at each of the reservoirs. Thus, the pyrolytic organic parameter and monosaccharide contents were more reliable for reconstructing of historical productivity in subtropical reservoirs.

In general, the corrected carbon isotopic composition could reflect the history of total productivity in one of the sediment cores. However, it is also affected by natural biogeochemical processes and anthropogenic activities. The pyrolytic organic parameter was observed to be specific to the type of NOM (e.g. algal NOM) and could help to distinguish the relative contribution of algae and higher plant to the NOM. By applying the molecular proxy of monosaccharides, the sources and detailed information of sedimentary organic matter can be provided. Therefore, the combination uses of these parameters are strongly recommended, which can help us to better understand the historical changes of past aquatic productivity and environment in the subtropical regions.

2. Second, the correlation between air-temperature changes in South China over 60 years and the trend in organic parameters of the three studied lakes is interesting. This part might be worth exploring in the future. Thus, a research outlook could be given by the authors.

Response:

We have added an outlook of research on the correlation of air temperature changes and organic parameters.

Elevated air-temperature could be the main driving factor in increasing productivity in Arctic lakes and some subtropical reservoirs. Sedimentary organic matter and their biomarker proxies of historical productivity are important to investigate the relationship between historical productivity and air-temperature variation. However, sedimentary organic matter comes from a variety of sources, including planktonic algae, terrestrial higher plants, zooplankton, organic detritus, black carbon, and so on. Moreover, most of organic matter is degraded during settling and post diagenesis.

Therefore, it is challenging to find the appropriate indicators for primary production in aquatic ecosystems. More works need to be done in this field on specific organic matter proxies of productivity. Meanwhile, multiple biomarker proxies are also needed to trace the source and type of NOM and to rule out the impact of human activities. Moreover, compound-specific isotope ratios, fractionations, and biodegradation products of biomarkers (e.g. neutral sugars, lipids) can provide more information of algal organic matter in aquatic ecosystems. Furthermore, the mechanism and modeling of relationships between air-temperature and algal organic matter parameters are worth to be exploited and established.

Specific comments/questions:

Line 24: The “single neutral carbohydrate” should be replaced by “monosaccharide”, please correct it all throughout the text.

Response: We have changed “single neutral carbohydrate” to “monosaccharide” throughout the text according to your suggestion.

Line 47: The lowercase delta notation for isotopes should be italics. Please correct these all throughout the text.

Response: We have changed the lowercase delta to italics throughout the text according to your suggestion.

Line 94: The isotopic values are reported relative to the V-PDB Belemnite Standard, not just PDB.

Response: We have changed the “PDB” to “V-PDB Belemnite Standard” in the manuscript according to your suggestion.

Line 108: Is the “AC 5OW-X8” right? According to the Michael’s paper in 2015, the cation resin should be “AG 50W-X8”.

Response: We have changed the "AC 5OW-X8" to "AG 50W-X8" in the manuscript according to your suggestion.

Line 243: "Fig. 3" should be "Fig. S3".

Response: We have changed the "Fig. 3" to "Fig. S4" in the manuscript according to your suggestion.

Line 355: "Fig. S8" should be "Fig. S4".

Response: We have changed the "Fig. S8" to "Fig. S5" in the manuscript according to your suggestion.

Anonymous Referee #2:

This paper by Duan et al. compared organic matter characteristics ($\delta^{13}C$, C/N) and monosaccharide distributions in sediment cores from three lakes with different depths (3 m, 17 m, and 36 m) and trophic states (mesotrophic vs. oligotrophic).

The neutral sugar data is nicely presented and discussed in the context of source and changes in productivity and climate, making this a useful addition to the field. However, connections between the carbon isotopic data and the neutral sugars are not clear in the text though correlation between them is mentioned in the abstract and displayed in table S4. The manuscript would benefit from expanding on the utility of combining these types of measurements rather than discussing the data and their implications separately. After revising this and the minor (but numerous) issues below, I would recommend the paper for publication in Biogeosciences. In addition to these comments, the manuscript should be checked carefully for small grammatical errors such as missing or incorrect articles and singular/plural subject/verb issues.

Response:

We have added some paragraphs and cohesive discussions on the correlation analysis and utility of combining these parameters and biomarkers. The differences and similarity of the corrected carbon isotopic composition, pyrolytic organic parameters and carbohydrate compositions have been presented and discussed. Please see the response to Reviewer 1.

The corrected carbon isotopic composition is a good indicator of aquatic productivity in some of aquatic ecosystems. Pyrolytic organic parameters could differentiate algal organic matter and terrestrial organic fractions. Monosaccharides compositions and some of the monosaccharide ratios are appropriate proxies for identifying the specific sources and types of NOM, which can be used to reflect the historical change of productivity in aquatic ecosystems.

Minor comments:

- pg 2, lines 44-48: Phytoplankton is plural so the verbs should be 'remove,' 'deplete,' and 'discriminate.'

Response: We have changed the "removes", "depletes", and "discriminates" to "remove", "deplete", and "discriminate" in the manuscript according to your suggestion.

Line 48 should be values.

Response: We have changed "value" to "values" in the manuscript according to your suggestion.

- pg 2, line 52: O'Reilly et al. (2005)

Response: We have added "et al." before "(2005)" in the manuscript according to your suggestion.

- pg 2, line 53: Verburg reference should be 2007

Response: We have changed "2006" to "2007" in the manuscript according to your suggestion.

- pg 2, line 55: It is not clear what 'it' in this sentence is referring to, please revise

Response: The "it" stands for "the $\delta^{13}C$ values in the reservoir sediment in the Pearl River Delta". We have revised it in the manuscript according to your suggestion.

- pg 3, line 58: Kirk et al. (2011)

Response: We have added "et al." before "(2011)" in the manuscript according to your suggestion.

- pg 3, lines 66-67: Typo, add 'in' after 'help'; also 'Besides' is not correctly used here, please revise

Response: We have added "in" after "help" in the manuscript according to your suggestion. We have changed "Besides" to "Moreover" in the manuscript according to your suggestion.

- pg 4, line 94: is this actually V-PDB?

Response: Yes, it is "V-PDB". We have revised it in the manuscript according to your suggestion.

- pg 4, line 94: from where is 'Product ID: GBW 04408' sourced?

Response: The product was purchased from National Research Center for Certified Reference Materials (NRCRM), China. We have added the source of the product in the manuscript.

- pg 4, lines 107-113: Michael et al., 2015 is not listed in the references

Response: The "Michael et al., 2015" is incorrect. We have revised it to "Philben et al., 2015" in the citations throughout the manuscript.

- pg 6, line 192: Also not clear what 'it' refers to in this sentence, please clarify

Response: The "it" stands for "phytoplanktons". We have clarified "it" in the manuscript according to your suggestion.

- pg 7, line 243: In this section (and in a few other places throughout the manuscript) the monosaccharide names are strangely capitalized?

Response: monosaccharide names should not be capitalized. We have revised them throughout the manuscript according to your suggestion.

- pg 8, line 281: Hernes et al. (1996)

Response: We have added "et al." before "(1996)" in the manuscript according to your suggestion.

- pg 8, line 292: Keil et al. (1998)

Response: We have added "et al." before "(1998)" in the manuscript according to your suggestion.

- pg 9, line 308: Should be no 'et al.,' for Handa, 1969 reference

Response: We have deleted the "et al.," before "(1969)" in the manuscript according to your suggestion.

- pg 9, line 316: Another unclear 'it' usage, please revise

Response: The "it" stands for "the *k* values of deoxy S/C5 in ZT, LA and XFJ sediments are low". We have clarified "it" in the manuscript according to your suggestion.

- pg 9, line 329: Gasse et al. should be 1991 as listed in the references

Response: We have revised "2001" to "1991" in the citation according to your suggestion.

- pg 9, lines 331-332: The use of 'algae-dominated' and then 'usually dominated in : : : algaes' is redundant. Additionally, the wording of 'dominated in' as a verb is grammatically incorrect (perhaps 'are usually dominant in'?) and 'algaes' is plural without the 's'

Response: We have deleted the "algae-dominated". We will change "dominated" to "dominant". We will change "algaes" to "algae" in the manuscript according to your suggestion.

- pg 9, line 332: should be Haug and Myklestad, 1976

Response: We have revised "Haug et al., 1976" to "Haug and Myklestad, 1976" in the manuscript according to your suggestion.

- pg 9, line 334: typo ': : : the a: : :'; remove either 'the' or 'a'

Response: We have deleted "the" in the manuscript according to your suggestion.

- pg 10, line 340: the / between 'no/or' is not needed; alternatively the 'or' could be removed ('no/weak correlations')

Response: We have revised "no/or correlations" to "no/weak correlation" in the manuscript according to your suggestion.

- pg 10, line 367: this should be changed to 'neutral sugars : : : are'

Response: We have changed "is" to "are" in the manuscript according to your suggestion.

- pg 11, line 379: change 'are' to 'is'

Response: We have changed "are" to "is" in the manuscript according to your suggestion.

- pg 11, line 385: insert 'the' before 'last six decades'

Response: We have inserted "the" before "last six decades" in the manuscript according to your suggestion.

- Figure 1: Is it possible to use the same scale for all three isotope profiles? Perhaps with a range from -28 to -18 so that the reader can easily compare the three sites visually

Response: Yes, it is. We have changed them to same scale for all three isotope profiles in the manuscript according to your suggestion.

- Figure 2: The concentration range on the x-axis is quite large for the data, making it difficult to see variations with depth. Aside from the single outlier in the LA glucose profile, could these be changed to more appropriate ranges for the data?

Response: Yes, it is. We have changed these to more appropriate ranges for the data in the manuscript according to your suggestion.

- Borch et al. 1997, Gu et al. 2004, Kaiser and Benner 2000, Marchand et al. 2008, Philben et al. 2015, Mopper et al. 1992, Ran et al. 2007, and Wakeham et al. 1997 are listed in the references but not cited in the text.

Response: The revisions have been made according to your suggestion:

1) We have deleted "Borch et al. 1997" in the reference list.
2) "Gu and Schelske, 2004" should be "Gu et al., 2004", we have revised it in the citation throughout the manuscript.
3) Page 4, line 115: "Kaiser and Benner 2009" should be "Kaiser and Benner 2000" , we have revised it in the manuscript.
4) We have deleted the "Marchand et al. 2008" in the reference list.
5) The "Michael et al., 2015" should be "Philben et al., 2015", we have revised it in the citation throughout the manuscript.
6) We have deleted "Mopper et al. 1992" in the reference list.
7) We have deleted "Ran et al. 2007" in the reference list.
8) We have deleted "Wakeham et al. 1997" in the reference list.

Anonymous Referee #3:

Duan et al. obtained a very nice, enriched, dataset including neutral sugars and other parameters in three subtropical reservoirs. Based on the concentrations and composition of the neutral sugars, isotope values of TOC, and C/N ratios, they investigated source and diagenesis pathways of sedimentary organic matter (SOM). They concluded that the dominant source of SOM was phytoplankton in the ZT, LA and upper XFJ reservoirs, and there was not much degradation of carbohydrates downward in the sediment cores. Also, there seems to be a nice correlation between temperature and the levels of carbohydrates over the past 60 years. I think this paper would be of interest to the community and worthy of being published,

(1) but I have issues with the way they presented, too broad and without a clear focus. The authors discussed a lot of possible sources and phytoplankton among different reservoirs, but they did not even mention why different patterns, ZT and LA vs. XFJ, were observed,. In addition, some of the conclusions are very speculative. Overall, I do not feel this paper is ready without a major revision.

Reponses:

We have made some revisions on the discussion in order to refine a clear focus: The combined uses of neutral sugars, carbon isotopic composition, and pyrolytic organic parameters are recommended for reflecting the historical changes of productivity in subtropical reservoirs. They can also be used for investigating climate change effects on algal productivity in these reservoirs.

We also added detailed discussions on the causes and reasons for the possible sources among different reservoirs. They are related not only to inputs of algae and plant, and bacteria, but also to historical changes of hydrological conditions, nutrient level, anthropogenic activities, and so on.

(2) The section of Materials and Methods needs more work. They need to include the information about measuring the sedimentation rate and pyrolysis. I know they have these in the Duan et al. 2015 paper, but these should be briefly described, since they use those data in the Results section and you can't force the audience to read your other paper. It is unclear how many cores they collected. In other words, how representative are these cores to the whole

reservoirs. If these systems have been impacted by human activities, such as dredging, sediments in these reservoirs can be very heterogeneous.

Reponses:

We have added the measurements for the sedimentation rate and pyrolysis according to your suggestion.

We have sampled 2 or 3 cores for each reservoir, and each of the sediment cores were collected in the center of the reservoir. Moreover, the reservoirs are mainly supplied by rainfall, and are far away from the industrial center. The aquaculture is forbidden, and there are no dredging activities in the investigated areas.

(3) A main issue with the manuscript is the lack of focus on the discussion. They talked about a lot of difference topics, but it was written like a result section with titles like, “OM characteristics”, “Monosaccharide composition”, “Source of neutral carbohydrates”, and so on. In other words, it reads more like a data report rather than a research paper.

Reponses:

The object of this study is to validate the combined uses of the carbon isotopic composition, pyrolytic organic parameters, and neutral sugars as the potential proxies for historical changes of productivity in subtropical reservoirs and their relationships with the climate changes in the investigated areas.

The section of “OM characteristics” was written for the applicability of pyrolytic organic parameters as algal proxies. Both “Monosaccharide composition” and “Source of neutral carbohydrates” sections were compiled for the applicability of neutral sugars as algal proxies in the investigated areas. We have made some revisions to emphasize a clear focus according to your suggestion.

Specific comments:

Line 43: “offer”

Reponses: We have changed “offers” to “offer” in the manuscript according to your suggestion.

Line 49: delete “and impacted”

Reponses: We have deleted the “and impacted” in the manuscript according to your suggestion.

Line 54: any evidence about the Suess effect would be particularly stronger in the industrialized areas such as Pearl River Delta? I would assume this should be about the same worldwide considering the fast CO_2 mixing in the air.

Reponses: With rapid economic and industrial development in the Pearl River Delta, the local lakes and reservoirs is more easily affected by the Suess effect due to the high-emssion of CO_2 even though the CO_2 mixing is fast in the air. However, there is no data for the Suess effect in this area. Therefore, we have made some revisions on the description of the Suess effect in the manuscript according to your suggestion.

Line 127: awkward wording, should be “productivity significantly contributed to dissolved oxygen content”

Reponses: We have changed “the important role of oxygen content in the growth of productivity” to “productivity significantly contributed to dissolved oxygen content” in the manuscript according to your suggestion.

Line 130: nutrients levels are always higher in the deeper depth. What do you mean by “be brought” to deeper depths”?

Reponses: During winter, the top layers of the lake have relative higher levels of productivity, and the bottom layers have higher contents of nutrient. Moreover, the water column mixes from top to bottom in the lake due to the decrease in temperature (so-called autumn overturn). Therefore, the relative high contents of nutrients can be transported by the water flow to the upper depths, resulting in the increase of nutrients and productivity in the entire water column. We have made some revisions in the manuscript according to your suggestion.

Line 136: again, describe the pyrolysis

Reponses: We have added the instruction and description of pyrolysis in the manuscript according to your suggestion.

Line 193-196: have to be careful about the C/N ratios. Decomposition of terrestrial organic matter can decrease C/N ratios, not necessarily source related. This has been well documented in composting studies. Also, the C/N ratios of 3 in the XFJ upper layers should be interpreted in a more careful way. I don't think you can simply say "algal origin", because C/N ratios fresh algae are typically about 6-7, and even pure bacterial biomass typically have C/N ratios of 4. It is not very clear how you would get SOM with such low C/N ratios

Reponses: The very low C/N ratios are likely to be related to inorganic N in minerals. As the TOC contents are quite low in XFJ, their inorganic N contents will affect the C/N ratios. We have discussed this effect in the revised manuscript.

Line 200: the removal of CH_4 (^{13}C light) should lead to the accumulation of ^{13}C heavy SOM

Reponses: We have changed "The removal of $^{12}CH_4$ by intensive methanogenesis also leads to the accumulation of ^{13}C-depleted OM" to "the removal of CH_4 (^{13}C light) should lead to the accumulation of ^{13}C heavy SOM" in the manuscript according to your suggestion.

Line 214-216: too speculative. The DO level you mentioned refers to the water, not sediment. I think the major OM decomposition in these OM-enriched sediments is through anaerobic pathway, unless you have DO profile data in sediment cores.

Reponses: We have deleted the speculative part and rewrite the paragraph in the manuscript according to your suggestion.

Line 270: it's interesting to note the correlations between Zn and Cu and carbohydrates. I think more data analysis is needed, such as the contents of Zn and Cu in algae and how they trace metal got preserved, etc. It's not enough to simply have a correlation and then argue they were from phytoplankton. For example, it could have been sourced from industry contamination.

Reponses: We don't have Zn and Cu data in algae from the investigated areas. However, the Pb contents in the sediments of these reservoirs are very low, suggesting that there is no or little industry contamination in investigated areas.

Section 4.4. When the individual carbohydrates are normalized to TOC, I don't think there is much a decreasing trend at all (Table S2). In other words, carbohydrates simply are not good indicators of digenesis. This section should be strongly condensed.

Reponses: We have condensed the section 4.4 in the manuscript according to your suggestion. More investigations are needed to understand the fractions and degradation products of neutral carbohydrates.

Section 4.5. This section is interesting, but still at a speculative stage. Issues why we would expect carbohydrate increase, such as increased phytoplankton production or decomposition of SOM under warmer climate?

Reponses: We have observed significant correlations among T_5 temperature and a few of algal monosaccharides in the investigated reservoirs. Moreover, each of these monosaccharides is positively and significantly related to algal parameters (e.g. HI and S2). However, the diagenesis processes of neutral sugars and OM are estimated to be quite slow in the bottom sediments. Some fractions could be selectively preserved and remained unchanged during the post deposition. Therefore, the productivity proxies derived from some of the neutral sugars could be significantly related to the climate warming.

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 monosaccharide ~~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~~ offer an important tool for reconstructing the history of nutrient loading and eutrophication in lacustrine sediments (Schelske and Hodell, 1991; 1995). Phytoplankton preferentially ~~removes~~remove dissolved $^{12}CO_2$ from epilimnetic water and ~~depletes~~ depleted ^{12}C in the remaining dissolved inorganic carbon (Hodell and Schelske, 1998). As supplies of $^{12}CO_2$ become diminished, phytoplankton ~~discriminates~~ discriminate 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~~ values 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 et al. (2005) had not corrected for the Suess effect in the heterotrophic Lake Tanganyika in Africa, Verburg (~~2006~~2007) found that the corrected $\delta^{13}C$ values were used as a productivity proxy. In the Pearl River Delta (PRD), the development of

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industrialization and urbanization could enhance the high-emssion of CO_2Suess effect _during recent years. Hence, the $\delta^{13}C$ values of reservoir sediments in the PRD it needs to correct for the Suess effect.

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

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

2 Materials and Methods

2.1 Study area and sample collection

Zengtang reservoir (ZT), Lian'an reservoir (LA), and Xinfengjiang reservoir (XFJ) with different depths and trophic states were chosen for this investigation. The reservoirs are mainly supplied by rainfall and are far away from the industrial center. AThe aquaculture is forbidden and there is no dredging activities are forbidden in the investigated reservoiresareas. The detailed description of the study sites are shown in the previous literature (Duan et al., 2015). In brief, ZT is a shallow, polymictic reservoir with a mesotrophic level, whereas LA is a deep and mesotrophic reservoir. XFJ is a deep and oligotrophic reservoir. Both LA and XFJ are monomictic reservoirs. The most abundant algal species in the ZT, LA, and XFJ reservoirs are green algae, cyanophyta, and diatoms.

Undisturbed sediment cores were collected from the central part of the studied lakes using a 6 cm diameter gravity corer 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 m, and 36 m, respectively. The core liners were put down slowly in order to avoid disturbance. The sediment cores were sliced into 2 cm thick intervals using extrusion equipment. It is noted that the top four slices of the ZT core were merged into two intervals (0–4 cm and 5–8 cm) due to the insufficient amount of sample for neutral sugar analysis. All subsamples were immediately placed in plastic bags, sealed, and stored at low temperature (0–10 °C), and then were quickly transported to the laboratory, where they were freeze-dried and stored until further analysis.

2.2 Physicochemical properties in water

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

2.3 Rate of sedimentation

Each sliced sample was analyzed for ^{210}Pb and ^{137}Cs radiometric dating (Duan et al., 2015). Briefly, the activities of ^{210}Pb and ^{137}Cs were measured by S-100 Multi Channel Spectrometer (Canberra, USA) with a PIPS Si detector and a GCW3022 H-P Ge coaxial detector, respectively. Excess ^{210}Pb activities were measured by subtracting the average ^{210}Pb activities of deeper layers in sediment cores and the constant rate of supply dating model (CRS) were used for the calculation of chronology and sedimentation rates.

2.4 Rock-Eval analysis

All of the samples were analyzed by Rock-Eval 6 (Vinci Technologies, France). The detailed procedures were reported in the previous literature (Duan et al., 2014; Duan et al., 2015). Briefly, bulk sediment was firstly pyrolyzed in an inert, O_2-free oven (100–650 °C) and secondly combusted in an oxidation oven (400–850°C). Several parameters such as S1, S2, S3, residue carbon (RC) and total organic carbon (TOC) can be generated by flame ionization detector (FID) and infrared spectroscopy (IR). S1 and S2 represent the fractions of hydrocarbons (HC) released during the pyrolysis step, where S3 was derived from the fractions of CO and CO_2 released during the two procedures. The residue carbon after combustion defined as RC and the sum of the generated organic fractions is TOC. The hydrogen index (HI) and oxygen index (OI) are calculated by normalizing the contents of S2 and S3 to TOC

2.5 Stable carbon isotopic analysis

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

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

where R is the $^{13}C/^{12}C$ ratio and the standard is the V-Pee Dee Belemnite. Black carbon (Product ID: GBW04408, National Research Center for Certified Reference Materials, China) was used as the reference standard for the determination of accuracy and precision. The precision of $\delta^{13}C$ for the replicates was < 0.19‰±0.12 (n = 40).

Measured values of $\delta^{13}C$ were corrected for the Suess effect with the following polynomial equation (Schelske and Hodell, 1995), where t is time (in yr):

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

The calculated time-dependent depletion in $\delta^{13}C$ induced by fossil fuel combustion since 1840 was subtracted from the measured $\delta^{13}C$ for each dated sediment section.

2.6 Neutral sugar analysis

Sediment samples (about 5 mg) from the three reservoirs were weighted and hydrolyzed in glass ampules with 12 M 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 of acid), the ampules were flame-sealed and the samples were stirred and hydrolyzed in a 100 °C water bath for 3 h. The hydrolysis was terminated by placing the ampules in an ice bath for 5 min. Then, the deoxyribose was added as the internal standard (Philben~~Michael~~ et al., 2015). Before instrumental analysis, the samples were run through a mixed bed of anion (AG 2-X8, 20–50 mesh, Bio-Rad) and cation (~~AC~~ AG 50~~5O~~W-X8, 100–200 mesh, Bio-Rad) exchange resins (Philben~~Michael~~ et al., 2015). Self-absorbed AG11 A8 resin was utilized to remove the acid. The volume of resin needed for complete neutralization depended on the amount of acid used for hydrolysis (Philben~~Michael~~ et al., 2015). After purification ~~and desalting~~ with a mixture of cation and anion exchange resins, neutral sugars were isocratically separated with 25 mM NaOH on a PA 1 column in a Dionex 500 ion chromatography system, which was equipped with a pulsed amperiometric detector (PAD) detector (model ED40) (Philben~~Michael~~ et al., 2015). The detector setting was based on Skoog and Benner

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(1997). Chromatographic data were recorded with a personal computer equipped with Hewlett Packard Chemstation software (Skoog and Benner, 1997; Kaiser and Benner, ~~2009~~2000).

For every ten analyses, a blank sample and a duplicate sample were analyzed to check accuracy and precision. No neutral sugars were detected in the blanks. Only glucose, galactose, mannose, rhamnose, fucose, and xylose were detected and analyzed in samples due to the loss of ribose in the process of acid hydrolysis. The recovery of the monosaccharides in the sediments ranged from 73% to 95%. The analytical precision of duplicate samples performed on different days was within ±3% for glucose and ±5% for other sugars. In this study, the total neutral carbohydrates (TCHO) are defined as the sum of all identified monosaccharides.

3 Results

3.1 Physicochemical properties of water

As shown in Fig~~.~~ure S1 in the supporting data, chlorophyll a concentrations in the water column of LA are higher in spring and summer than in fall and winter, which is consistent with the seasonal distribution of the content of dissolved oxygen. The vertical profiles of chlorophyll a and dissolved oxygen also show similar patterns; depleted dissolved oxygen in the hypolimnion accompanies low content of chlorophyll a throughout the year, suggesting the productivity significantly contributed to dissolved oxygen content~~important role of oxygen content in the growth of productivity~~. In general, the bottom sediments in LA are mostly under anaerobic conditions. Water temperature is higher in summer and fall, resulting in thermal stratification in the water column. During winter, the lake mixes from top to bottom due to the decrease in temperature (so-called autumn overturn). Therefore, the relative high contents of nutrient can be transported by the water flow to the upper depths, resulting in the increase of nutrient and productivity in the entire water colume~~The nutrient can be brought to deeper depths and may increase the productivity in the entire water column~~.

The concentration of chlorophyll a (average: 0.94 μg/L) in the water column of XFJ is much lower than that in LA. The 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~~.~~ure S1 in the supporting data), suggesting the bottom sediments are under aerobic conditions.

3.2 Characteristics of OM

The data from Rock-Eval pyrolysis are listed in Table S1 in the supporting data, which were reported previously (Duan et al., 2015). As shown in Table S1, pyrolytic parameter S1 and S2 represent the fractions of hydrocarbons (HC) released during the pyrolysis step, where S3 was derived from the fractions of CO and CO_2 released during the pyrolysis and oxidation procedures. The hydrogen index (HI) is calculated by normalizing the contents of S2 to TOC (Duan et al., 2015). 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 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 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 sediment cores.

$\delta^{13}C$ values (‰) range from −22.2‰ to −21.6‰ in the ZT core, from −26.4‰ to −24.1‰ in the LA core, and from −27.2‰ to −23.1‰ in the XFJ core, with the average values of −21.9‰, −25.4‰, and −24.9‰, respectively (Fig~~.~~ure 1). After 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 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‰, respectively (Fig~~.~~ure 1).

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

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The detailed results from ^{210}Pb and ^{137}Cs radiometric dating was reported previously (Duan et al., 2015). The mass accumulation rates (MAR) were cited and displayed in the Table S1 in the supporting data. As the ZT, LA, and XFJ reservoirs had been small lakes before the dam construction, the chronological records for the ZT, LA, and XFJ cores are longer than the time scales of the dam construction.

3.3 Neutral sugar data

The concentrations of seven monosaccharides (glucose, galactose, mannose, arabinose, rhamnose, fucose, and xylose) are presented in Figure 2~~,~~ and Figure S2, and/or listed in Table S2 in the supporting data. Glucose (0.2–2.34 mg/g) is the most abundant sugar in all the reservoir sediments, followed by galactose (0.09–1.2 mg/g), mannose (0.03–0.92 mg/g), and xylose (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) are relatively low in the reservoir sediments. The TCHO concentrations at the ZT, LA, and XFJ reservoirs range from 1.94 to 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 sediment cores. Carbohydrate yield (%) is the molar concentration of monosaccharide carbon normalized by TOC. 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 12.52% in the XFJ core, with average values of 8.68%, 7.79%, and 7.33%, respectively (Fig~~.~~ure 3).

Compositions of neutral sugars in the three sediment cores are calculated based on their concentrations. Glucose (21.1–27.6 mol%) is the most abundant monosaccharide, followed by mannose (14–21.5 mol%), galactose (14.7–18.7 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 ZT sediments. Glucose (22.2–37.4 mol%) is also the most abundant monosaccharide, followed by galactose (12–20 mol%), 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 fucose (3.3–7.74 mol%) in the LA sediments. For the XFJ core, glucose (18.5–48 mol%) is still the most abundant monosaccharide, followed by galactose (12.3–3.7 mol%), mannose (3.8–23 mol%), arabinose (8.3–14.5 mol%), rhamnose (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 °C since 1960, and the mean air temperature in the Heyuan area has increased by about 1.52 °C 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~~.~~ure ~~S5~~S6).

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~~ phytoplankton 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~~.~~ure 1), suggesting the predominant contribution of phytoplankton in the OM of reservoirs. It is noted that the very low C/N ratios in XFJ core are likely to be related to inorganic N in minerals. As the TOC contents are quite low in XFJ, their inorganic N contents will affect the C/N ratios. 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~~et al., 2004). High phytoplankton can enhance isotopic fractionation and result in enrichment of ^{13}C in dissolved inorganic carbon. The removal of ~~^{12}~~CH_4 (^{13}C light) by intensive methanogenesis also leads to the accumulation of ^{13}C heavy ~~depleted~~ OM in sediments (Gu ~~and Schelske~~et al., 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~~.~~ure 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~~.~~ure 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 contribution of algal origin in the sediments (Fig~~.~~ure 1). Therefore, the decrease of corrected $\delta^{13}C$ at XFJ is mainly due to the biodegradation of OM under aerobic conditions. ~~The dissolved oxygen content is 8.54 mg/L at a depth of 36 m, which can provide sufficient oxygen for microbial metabolism (Fig. ure S2 S1 in the supporting data)~~. The preferential degradation of more ^{13}C-enriched organic compounds (e.g., carbohydrates and proteins) would lead to a decrease in the $\delta^{13}C$ values in the residue OM (Lehmann et al., 2002).

4.2 Monosaccharide compositions in sediment cores

As shown in Table. S2, the TCHO concentrations in the ZT and LA cores show significant decrease in the downcore sediments, which are similar to the vertical profiles of S2, TOC, C/N, corrected $\delta^{13}C$, and HI (Table S1 and S2 in the supporting data). For the XFJ core, the TCHO and HI still decline in the downcore sediments as do those in the ZT and LA 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 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 enriched with neutral sugars at the surface layers of the sediment core.

Monosaccharide compositions were calculated for investigating the applicability of netrual sugars as productivity proxies. The compositions of neutral sugars in ZT and LA cores show that glucose is the most abundant sugar in these two reservoir sediments while galactose, mannose, and arabinose are relatively more abundant than rhamnose, xylose, and fucose (Fig~~.~~ure 2 and Figure S2), which is similar to the monosaccharide composition in phytoplankton (Hamilton and Hedges,

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1988). Moreover, the relative abundances of monosaccharides do not vary much in the ZT and LA cores except for the apparent changes of glucose and xylose at depths of 10, 16, 32, and 34 cm in the LA core. For the XFJ reservoir, the monosaccharide composition in the upper layers (0–16 cm) of the sediment core also indicates a dominant origin of algal carbohydrates. However, xylose significantly increases at a few depths (XFJ core: at 18, 24, and 32 cm depths) (Fig~~.~~ure 2). Moreover, glucose shows an increasing trend correlated with the abundant xylose, especially between the depths of 18 cm and 34 cm. The pattern of carbohydrate composition in these samples (18–34 cm) is not in agreement with the post-depositional process of diagenesis as observed in previous studies (Hamilton and Hedges, 1988; Hedges et al., 1994). They found that the diagenesis process often led to a decrease in glucose along with a corresponding increase in bacteria-derived deoxy sugars (rhamnose and fucose) in sediment cores. Therefore, these outliers (18–34 cm) might be related to increasing vascular plant input or hydrological variation at XFJ, as discussed in the following paragraph.

4.3 Source of neutral carbohydrates

Molecular-level diagnostic parameters have often been used to differentiate microbial, planktonic, and terrestrial sources (Cowie and Hedges, 1984; Guggenberger et al., 1994). T~~Thus, t~~hey ~~could be used as~~are potential proxies for productivity in lakes and reservoirs. Diagnostic carbohydrate parameters and their results are presented in Fig~~.~~ure ~~S2~~ S3 and ~~S3~~ S4 in the supporting data.

The ratios of mannose to xylose could indicate the OM sources derived from phytoplankton, bacteria, gymnosperm, and angiosperm tissues (Cowie and Hedges, 1984). As shown in Fig~~.~~ure ~~S3~~ S4 in the supporting data, the values of the ~~Mannose~~mannose/~~Xylose~~ xylose 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 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) in the LA core. Thus, most of the samples can be identified as a phytoplankton source (1.5–3.5), suggesting the important contribution of AOM in these two areas. However, most of the ~~Mannose~~mannose/~~Xylose~~ xylose ratios are in the range of 0.23–0.87 for gymnosperm tissues (< 1) at depths deeper than 16 cm in the XFJ sediments, which indicates the presence of terrestrial OM derived from angiosperm leaves and grasses~~. (Fig. S7)~~

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The above conclusion is also confirmed by the %~~Xylose$_b$~~ xylose$_b$ parameters ('b' represents a value on glucose-free base) plotted in Fig~~.~~ure 2 and Fig~~.~~ure ~~S3~~ S4 in the supporting data. %~~Xylose$_b$~~ xylose$_b$ is a useful biomarker to differentiate the type of terrestrial input (Cowie and Hedges, 1984). In most of the samples at ZT and LA, %~~Xylose$_b$~~ xylose$_b$ is in the ranges of 9.34–11.8 and 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 low %~~Xylose$_b$~~ xylose$_b$ values (6.2–17.0) indicate the primary phytoplankton origin of neutral sugars at ZT and LA. The high values at the depths of 10 cm and 32 cm in the LA core might indicate important terrestrial input. Further evidence is also obtained from %(~~Arabinose~~ arabinose + ~~Galactose~~galactose)$_b$ plotted in Fig~~.~~ure ~~S3~~ S4 in the supporting data and from %(~~Fucose~~ fucose + ~~Rhamnose~~rhamnose)$_b$ plotted in Fig~~.~~ure ~~S2~~ S3 in the supporting data. The results from the %~~Xylose$_b$~~ xylose$_b$ versus %(~~Fucose~~ fucose + ~~Rhamnose~~rhamnose)$_b$ plots suggest a phytoplankton origin in reservoir sediments, which is consistent with that reported in the literature (Boschker et al., 1995). As for the %(~~Arabinose~~ arabinose + ~~Galactose~~galactose)$_b$ ratios, their values are mostly in the range of 30.7–44.4 in the sediment cores at ZT, LA, and XFJ, indicating that the sedimentary OM samples are largely derived from phytoplankton with the ratios of 22–47. Only a 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 likely to indicate an additional origin from non-woody angiosperm tissues and grasses, as demonstrated by Cowie and Hedges (1994). The above result also implies a different origin for neutral sugars in the upper layers of the XFJ core (0–16 cm) than in the lower layers (> 18 cm), which have been increasingly affected by terrestrial input.

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In order to support the above conclusions of the sources of OM by neutral sugars in the reservoirs, monosaccharide concentrations and heavy metal data are compared~~ to each other~~ (Table S3 and S4 in the supporting data). It is found that almost all of the monosaccharides (except ~~Xylose~~ xylose at LA and XFJ) are significantly related to heavy metals (e.g., Zn and Cu) in the sediment cores of ZT and LA, and the upper layers of the XFJ core (0–16 cm) (Table S4 in the supporting data). However, only galactose, mannose, and fucose are positively correlated with Zn and Cu in the core of XFJ (0–34 cm), although the lower layers are increasingly affected by allochthonous input, as discussed in the above paragraphs. As Zn and Cu are essential nutrients for phytoplankton growth, these relationships provide additional~~more~~ evidence for the important contribution of AOM to carbohydrates in the investigated sediments. However, the Pb contents in the sediments of these reservoirs are very low, suggesting that there is no or little industry contamination in the investigated areas~~this area~~.

ZT reservoir is a shallow reservior~~lake~~ and has relative higher trophic level. ~~For~~ LA reservoirs~~, it~~ is deeper and has longer water residence time and~~with~~ a medium trophic level~~state~~. Both ZT and LA reservoirs are dominated by autochthonous green algae and diatom, which ~~may~~ contribute to majority of carbohydrates in their sediments. However, XFJ reservoir ~~may~~ receive relatively high input of higher plants from the surrounding runoff. Therefore, the different ~~possible~~ sources of carbohydrates are~~is~~ related ~~to~~ not only to input~~native species~~ of algae~~,~~ and plant~~, and bacteria~~, but also to historical changes of hydrological conditions~~,~~ and nutrient level, etc.

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4.4 Diagenesis of neutral carbohydrates

Carbohydrates are not only useful in identifying the sources of OM but also in evaluating early diagenetic processes occurring in the post-depositional environment. The four parameters, deoxysugars/pentoses (deoxy S/C5) ratio, glucose content (mol% or wt%), %(~~Fucose~~ fucose + ~~Rhamnose~~rhamnose)$_b$, and carbohydrate yield (%) in the sediment cores are often used to evaluate diagenetic changes of OM (Cowie and Hedges, 1984; Ittekkot and Arain, 1986; Opsahl and Benner, 1999; Benner and Opsahl, 2001; Kaiser and Benner, 2009).

Glucose content is an important factor used to assess the degradation state of OM. Glucose accounts for 58 to 90% of the carbohydrates in fresh plankton and terrestrial tissues (Cowie and Hedges, 1984; Opsahl and Benner, 1999; da Cunha et al., 2002). Hernes et al. (1996) proposed that relative mol% glucose in particulate OM could be used as a diagenetic indicator for organic material in the equatorial Pacific region. In this investigation, wt% glucose in the sediments ranges from 22 to 29.1% at ZT, from 23.3 to 39.2% at LA, and from 19.6 to 50.3% at XFJ (Fig~~.~~ure 3), suggesting that neutral sugars are biodegraded in the sedimentary OM. This conclusion is also confirmed by the carbohydrate yield (%), which usually represent 30–40% of TOC in fresh tissues of plant and phytoplankton but less than 9% in sediments (Cowie and Hedges, 1984; Opsahl and Benner, 1999). Carbohydrate yields range from 1.93 to 13.53% in the sediments of the three reservoirs (Fig~~.~~ure 3). It is also suggested that neutral sugars degrade significantly in the investigated sediments. These results are consistent with the general observation from previous studies (Ogier et al., 2001). In general, the carbohydrates in the reservoir sediments are extensively transformed and degraded. However, the stability of their compositions was observed~~found~~ in the downcore sediments. Whether the carbohydrate compounds are degraded mainly in the water column or in the sediment core will be discussed below (Fig~~.~~ure 3).

Keil et al. (1998) found that the %wt (~~Fucose~~ fucose + ~~Rhamnose~~rhamnose)$_b$ values could reflect the diagenesis process of neutral carbohydrates. This index was elevated as the sediment particle sizes decreased, suggesting that smaller size fractions showed a higher degree of degradation. Their observation was also consistent with other diagenetic indices such as lignin and non-protein biomarkers (Keil et al., 1998). In this study, the values of %wt (~~Fucose~~ fucose + ~~Rhamnose~~rhamnose)$_b$ at three reservoirs do not vary significantly with the sediment core, and there is no decline in wt% glucose with a corresponding increase of %wt (~~Fucose~~ fucose + ~~Rhamnose~~rhamnose)$_b$ in each of the ZT, LA, and XFJ sediment cores (Fig~~.~~ure 3), suggesting that the process of degradation occurs mainly during the settling period rather than after deposition. Further evidence in support of this conclusion can be obtained from the ratio of deoxy sugars (e.g., rhamnose and fucose) to C5 (e.g., arabinose and xylose) (deoxy S/C5). The deoxy S/C5 ratios also remain almost unchanged throughout the sediment cores of ZT, LA, and XFJ (Fig~~.~~ure 3). Therefore, although sinking organic matter-rich particles and their carbohydrates in these reservoirs suffer from intensive oxidation and degradation in the water column during their transit to bottom sediments, some fractions are selectively preserved in the sediment cores, and remained almost unchanged during post-deposition, as observed before (Cowie and Hedges, 1984; Moers et al., 1990; Hicks et al., 1994).

Carbohydrates ~~are derived not only from~~consist of storage polymer b~~ut also from the~~and cell membrane of phytoplankton. ~~The monosaccharide residues in both kinds of polymers are bound to each other via glycosidic bonds (Cowie et al., 1992; Cowie and Hedges, 1994; Hernes et al., 1996).~~ In general, glucose is bound mainly in an unbranched, starchlike β-1,3-glucan storage polymer (Handa~~ et al~~, 1969), whereas mannose, galactose, xylose, fucose, and rhamnose are characteristically more abundant in the cell walls (Cowie et al, 1992). ~~The cell-wall aldoses are bound primarily in branched and often heterogeneous structural polymers. On the contrary, glucose, arabinose, and ribose are relatively concentrated in intracellular polysaccharides.~~ Part of carbonhydrates are highly likely to be preserved by sedimentary clay minerals. ~~In the present study, concentrations of mannose, galactose, arabinose, and xylose on a glucose free base are dominant in the sediment cores, and the carbohydrate compositions are mostly unchanged.~~ Hence, the neutral carbohydrates in the sediment cores ~~are largely related to structural polysaccharides, which is~~could be ~~more~~ resistant to microbial degradation~~ than storage polysaccharides~~.

In support of the above conclusion, the *k* values of deoxy S/C5 were calculated using a "multi-G" model (Wang et al., 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. Thus, ~~It is found~~ the *k* values of deoxy S/C5 indicate that the decomposition of 95% neutral sugar in reservoir sediments will take thousands of years, which is similar to the results of TCHO in the ocean sediments (Wang et al., 1998) and the degradation of OM in the lacustrine sediments (Li et al., 2013).

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~~The increasing downcore trends of glucose and OM in the XFJ core are different from those in the ZT and LA cores, suggesting that t~~As delineated abive, the variations of OM and neutral sugars~~ sugars are site independent and~~ are~~ismay be~~ related to the different trophic states, the various sources of OM, and the hydrological changes in different depositional environments. Moreover, the downcore OM profiles in some of the sediment cores investigated in other aquatic environments have not exhibited decreasing trends (Kirk et al., 2011, Meyer, 1997), which are not consistent with the traditional degradation model and mechanism. Hence, more works are~~would be~~ needed for investigating the sources, ~~compositions~~fractionations, and biodegradation products~~early diagenesis~~ of carbohydrates in different aquatic environments.

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4.5 Effects of climate change on primary productivity and carbohydrates

Carbohydrates are important organic components from aquatic algae and have undergone extensive degradation during settling. However, large amounts of resistant structural carbohydrates (e.g., cell walls) containing source information can be preserved in the sinking particles and sediments. Moreover, HI has been widely utilized as a useful indicator of primary productivity during recent years (Gasse et al., ~~2001~~1991; Stein et al., 2006; Bechtel and Schubert, 2009). As shown in Fig. 4 and Table S4 in the supporting data, HI values in the ZT and LA cores are positively correlated with concentrations of monosaccharides, especially the ~~algae-dominated,~~ galactose, mannose, fucose, and arabinose~~ (Ittekkot and Arain, 1986; Hamilton and Hedges, 1988; D'souza et al., 2003)~~, which are usually ~~dominated~~ dominant in structral cell walls of planktonic ~~algaes~~ algae ((Ittekkot and Arain, 1986; Hamilton and Hedges, 1988; D'souza et al., 2003; Hecky et al., 1973; Haug and Myklestad~~et al.~~, 1976). For the XFJ core, significant correlations are also found between ~~the~~ some of the concentrations of monosaccharides and the HI values, except for 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 depths of 18–34 cm in the XFJ core are excluded due to the inputs of allochthonous OM to the sediment cores. Therefore, monosaccharides (e.g., galactose and mannose) can be used for the reconstruction of historical productivity in the subtropical reservoirs.

As shown in Table S4 in the supporting information, the contents of glucose, galactose, arabinose, mannose, fucose, and rhamnose are also positively correlated with S2 and HI values in the ZT, LA, and XFJ sediment cores. However, each of them shows no~~/or~~ weak correlations with the diagenetic parameters of neutral sugars and OM (e.g., %(~~Fucose~~ fucose + ~~Rhamnose~~rhamnose)[b], ~~Deoxy~~ deoxy S/C5). Moreover, the xylose concentrations representing terrestrial inputs do not show significant correlations with the productivity proxies (e.g., S2 and HI) or any of the other monosaccharide concentrations at LA and XFJ. Thus, the above evidence supports that the increasing neutral sugars in the reservoir sediments are mainly attributed to algal productivity rather than the degradation of neutral sugars during post-diagenesis.

In order to understand the effects of climate change on the historical variations of primary productivity, the T_5 values over 60 years are compared with the each ~~profiles~~ of carbohydrate profiles~~s~~ in the three reservoirs (Fig~~.~~ure 5 and Table S4). The monosaccharide profiles at ZT and LA show good correlation with T_5 during the past 60 years (for ZT, ~~Galactose~~galactose:T_5, $R^2 = 0.824$, $p < 0.01$; ~~Mannose~~mannose:T_5, $R^2 = 0.824$, $p < 0.01$; ~~Fucose~~fucose:T_5, $R^2 = 0.805$, $p < 0.01$; for LA, ~~Galactose~~galactose:T_5, $R^2 = 0.885$, $p < 0.01$; ~~Mannose~~mannose:T_5, $R^2 = 0.699$, $p < 0.01$; ~~Fucose~~fucose:T_5, $R^2 = 0.883$, $p < 0.01$;), suggesting that an increase in temperature likely enhances the deposition of carbohydrates in sediments (Fig~~.~~ure 5 and Table S4). Moreover, total nitrogen (TN) and total phosphorus (TP) concentrations show~~ed~~ weaker correlations with T_5 than carbohydrates for the sediment cores of ZT and LA (Table S5; Duan et al., 2015). The TN and TP concentrations can be used to reflect the historical inputs of nutrients in the ZT and LA reservoirs. Furthermore, the TP and TN concentrations at ZT and LA remained at a low level (mostly TP < 0.1 mg/g, TN < 0.4%) during the past six decades and are far lower than those in sediments of other eutrophic reservoirs (Duan et al., 2015). Further evidence can be found in the results from principal component analyses (PCA) in the Fig~~.~~ ure ~~S8~~ S45 in the supporting data. The T_5, HI, and monosaccharides are in the first principal component and account for 76.5% and 67.3% of the total variance in the LA and XFJ reservoirs, whereas the second principal component of TP and TN accounts for 8.36% and 11.7% of the total variance, respectively. Hence, the nutrient input is not the key factor affecting carbohydrates in the three reservoirs. In addition, the factor of light can also be excluded by the records of the annual hours of daylight, which show progressively decreasing trends from 1950 to 2010 at Guangzhou and Heyuan (Fig~~.~~ ure ~~S5~~S6). In conclusion, the increase in deposition of carbohydrates in sediments at ZT and LA corroborates very well with the increase in temperature (Fig~~.~~ure 5). For the XFJ reservoir, the profiles of monosaccharides also show a positive correlation with the temperature variations (for XFJ, ~~Galactose~~galactose:T_5, $R^2 = 0.702$, $p < 0.01$; ~~Fucose~~fucose:T_5, $R^2 = 0.744$ $p < 0.01$;), but show no relationship with TN or TP concentrations (Fig~~.~~ure 5, Table S4). Although the primary productivity is lower in the XFJ reservoir than in the ZT or LA reservoirs, it is still significantly affected by the increasing temperature. Although the TOC and S2 values have declined with increasing temperature in the XFJ core profile due to the phosphorus-limited trophic level, the neutral sugar contents still increase (Fig~~.~~ure 5). Therefore, the above results suggest that neutral sugar in the ZT, LA, and XFJ reservoirs ~~is~~ are strongly associated with climate warming in the subtropical area.

As shown in the Table S4, positive correlations between corrected $\delta^{13}C$ values, HI, monosaccharide contents, and T_5 are significant~~were only observed~~ in ZT core. But t~~T~~he corrected $\delta^{13}C$ in~~at~~ LA and XFJ cores ~~have no relations~~are not correlated with other production parameters and T_5~~, even the corrected $\delta^{13}C$ were enriched in the upper layers of LA core~~. This may related to~~result from~~ the impacts of organic matter degradation, terrestrial inputs, and human activities on the carbon isotopic composition ($\delta^{13}C$) in~~at~~ mesotrophic LA and oligotrophic XFJ reservoirs~~ (LA and XFJ)~~. Moreover, ~~For t~~the ~~pyrolytic organic parameters (e.g. HI)~~ values and ~~molecular biomarkers (e.g.~~ neutral sugar data~~s), they~~ ~~have~~show the same changing trends and are~~were~~ ~~both~~ positively correlated with five T_5 in~~at~~ each of the three~~all~~ reservoirs. Thus, the ~~pyrolytic organic~~HI parameters and monosaccharide contents are more reliable for reconstructing ~~of~~ historical productivity in subtropical reservoirs. Therefore, the combined~~nation~~ use of these parameters and biomarkers are strongly recommended, which can help us to better understand the historical change of productivity and environments in the subtropical reservoirs.

It is challenging to find the appropriate indicators for primary production in aquatic ecosystems. More works need~~s~~ to be done ~~in theoretical and applied research~~ on specific organic matter for~~of~~ productivity proxy. Meanwhile, multiple biomarker proxies are also need in order to trace the source and type of biological productivity, and to rule out the impact of other human activities. Moreover, compound-specific isotope ratios, fractionation, and biodegradation products of biomarkers such as~~(e.g.~~ neutral sugars, lipids~~)~~ can provide more ~~accurate and detailed~~ information onf algal organic matter in aquatic ecosystems. Furthermore, the mechanism and modeling of relationships between air-temperature and algal organic matter parameters are worth to be exploited and established.

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5 Conclusions

The sources, composition, and diagenesis of carbohydrates in the sediment cores of three subtropical reservoirs were investigated by conducting acid hydrolysis coupling with high-performance liquid chromatography (HPLC) with pulsed amperometric detection (PAD). Glucose, mannose, and galactose are the most abundant monosaccharides. Monosaccharide composition and diagnostic parameters (mannose/xylose ratio, arabinose plus galactose, xylose) indicate a predominant contribution of phytoplankton in the whole sediment cores of the ZT and LA reservoirs and in the upper layers of the XFJ core (0–16 cm). The carbohydrates are partially degraded during the settling. It is found that the degradation proxies (S2/RC, %wt (fucose + rhamnose)$_b$, and deoxy S/C5) have not varied much in all of the whole sediment cores.

The corrected $\delta^{13}C$ and C/N ratios in sedimentary OM can be used to reflect the historical changes of productivity in the subtropical reservoirs. Based on the higher corrected $\delta^{13}C$ values and the lower C/N ratios, increased productivity was observed in the upper layers of ZT and LA reservoirs, which ~~are~~ is consistent with the increase of monosaccharides (e.g., galactose, mannose, fucose, and arabinose) and HI. As for XFJ reservoir, the corrected $\delta^{13}C$ values abruptly decrease with very low C/N ratios, which may indicate different sources and biodegradation in the underlying sediments. Moreover, strong positive correlation between TCHO and HI is found both in the mesotrophic reservoirs (ZT and LA) and in the oligotrophic reservoir (XFJ) in this investigation, suggesting that TCHO is related to primary productivity in the studied subtropical reservoirs. Furthermore, increasing levels of carbohydrates in the three reservoir cores show significant relationships with T_5 during the last 60 years. Elevated temperatures lead to increasing levels of carbohydrates in the sediment profiles during the last six decades. Therefore, this investigation provides important evidence for the effect of climate change on the aquatic ecosystems in the low latitude region. To further develop the productivity indicator of carbohydrates, more works are~~is~~ needed to understand the fractionation and biodegradation products, and to improve~~improve~~ the detection of ~~all~~ the sedimentary monosaccharides (e.g., ribose) during acid pyrolysis.

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Author contribution

Jing'an Chen and Yong Ran designed the experiments and Dandan. Duan, Dainan Zhang, Jingfu Wang, and Yu Yang carried them out. Dandan Duan prepared the manuscript with contributions from all co-authors.

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgments

Data supporting Figures S1–S5 are available as Tables S1, S2, S3, and S4 in Supporting Information. The annual average air temperature and five-year moving averages of the air temperature on the time scale of 60 years in the Guangzhou area and Heyuan area were obtained from the China Meteorological Data Sharing Service System (CMDSSS).

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Figure captions

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

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

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

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

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

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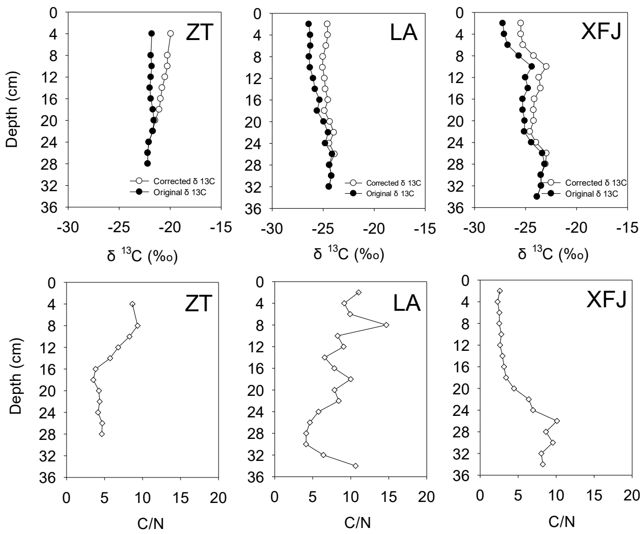

Figure 1. Vertical variations of original $\delta^{13}C$, corrected $\delta^{13}C$, and C/N in sediment cores of three reservoirs

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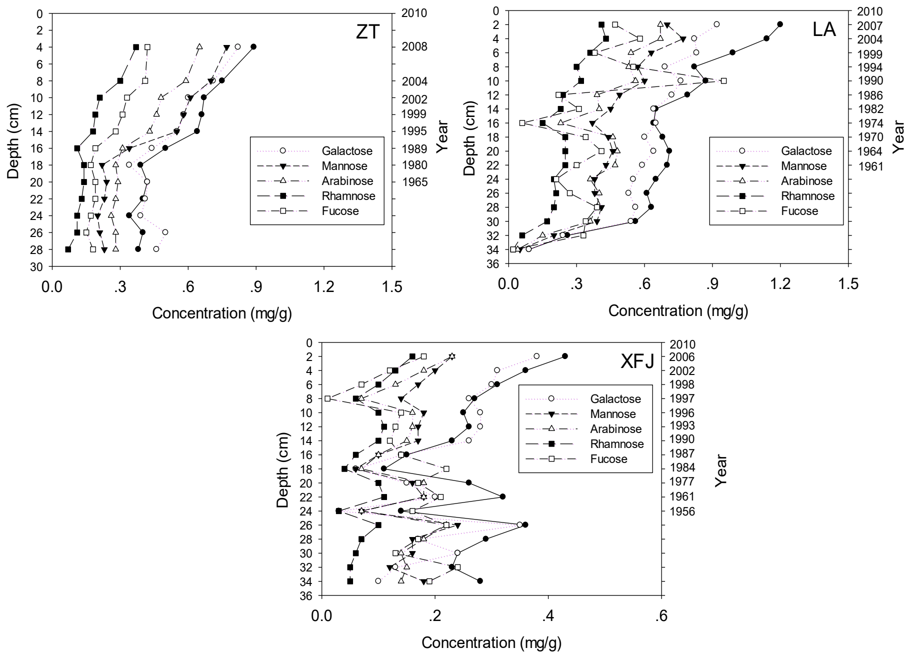

Figure 2. Profiles of neutral carbohydrates (glucose was not inexcluded) in the sediment cores of the reservoirs. Glucose contents in the sediment cores were included in Supplemental Figure S2.

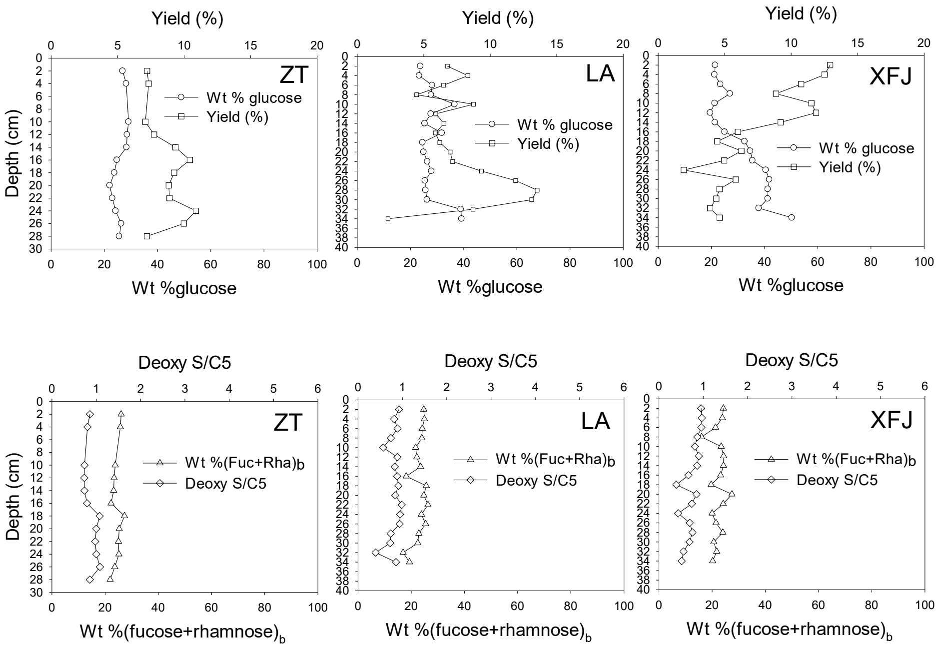

Figure 3. Vertical profiles of yield (%), wt% glucose, deoxy S/C5, and wt% (~~Fucose~~fucose+~~Rhamnose~~rhamnose)$_b$ at the ZT, LA, and XFJ reservoirs

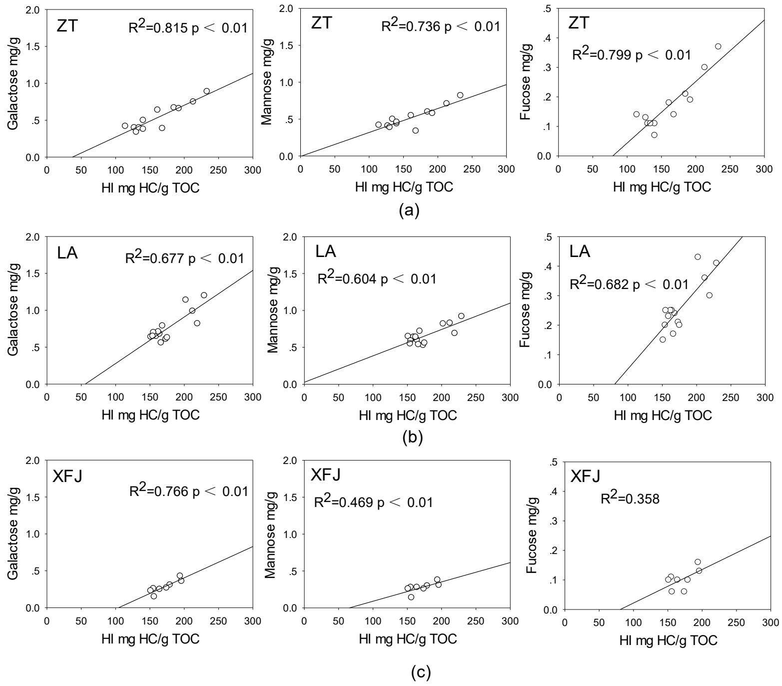

Figure 4. Relationship of HI with galactose, mannose, and fucose in the ZT, LA, and XFJ reservoirs (For LA, the sample at 8-10 cm depths and at 30-34 cm depths were excluded; For XFJ, samples below 16 cm were excluded). The HI data were cited from Duan et al. (2015).

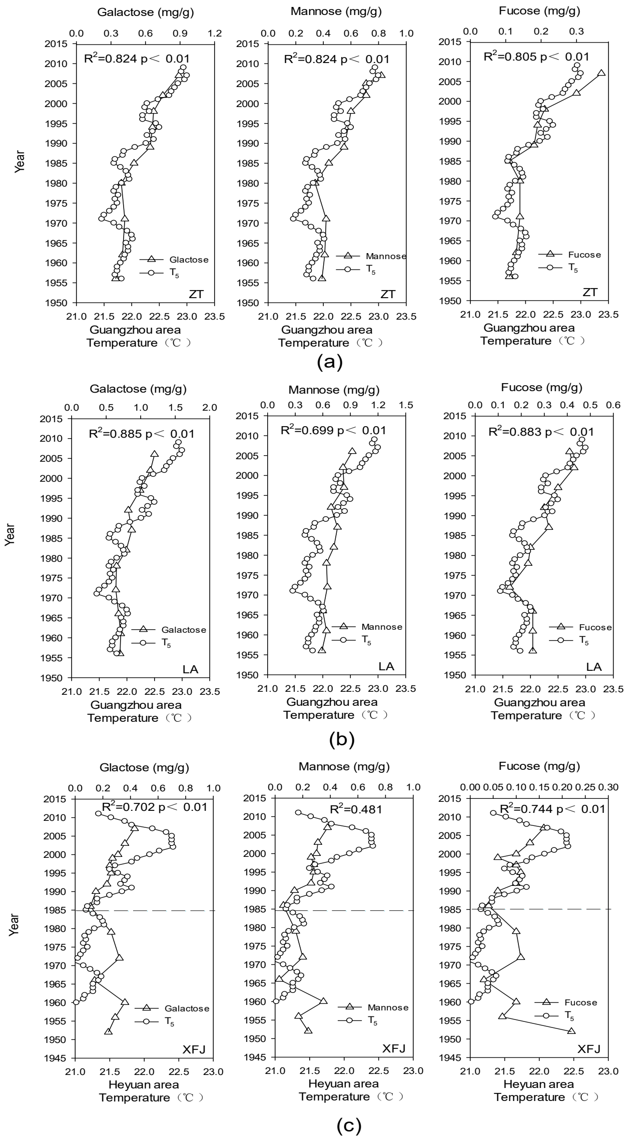

Figure 5. Temporal profiles of five-year moving temperature (T_5) and ~~single neutral sugars~~monosacchrides in sediment cores from the three reservoirs.