Variations in $\delta^{13}C_{DIC}$ and influencing factors in a shallow macrophytic lake on the Qinghai-Tibetan Plateau: implications for the lake carbon cycle

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Abstract

The primary sources of dissolved inorganic carbon (DIC) in water are carbonate materials and CO_2 produced during the biological processing of organic matter. The application of carbon isotope techniques to terrestrial and aquatic ecosystems can accurately elucidate carbon fluxes and other carbon cycle processes in these systems. Lake ecosystems on the Qinghai-Tibetan Plateau are fragile and sensitive to changes in climate and environment. This study explored the relationship between the carbon isotopic composition ($\delta^{13}C$) of the DIC ($\delta^{13}C_{DIC}$) in the Genggahai Lake, the lake environment, and the climate of the watershed based on the observed physicochemical parameters of water in areas with different types of submerged macrophyte communities, combined with changes in the temperature and precipitation during the same period. Overall, the $\delta^{13}C_{DIC}$ of the Genggahai Basin exhibited a large range of values, with an average $\delta^{13}C_{DIC}$ for inflowing spring water ($\delta^{13}C_{DIC\text{-}I}$) of –11.1 most negative, followed by an average $\delta^{13}C_{DIC}$ value of –10.8 from the Shazhuyu River ($\delta^{13}C_{DIC\text{-}R}$) and an average$\delta^{13}C_{DIC}$ value of –6.91 Variations in the photosynthetic activity intensity of different aquatic plants yield significantly changing $\delta^{13}C_{DIC\text{-}L}$ values in areas with varied aquatic plant communities. Hydrochemical observations revealed that $\delta^{13}C_{DIC\text{-}I}$ and aquatic plant photosynthesis primarily affected the differences in the $\delta^{13}C_{DIC\text{-}L}$ values of the Genggahai Lake, thereby identifying them as the key components of the lake carbon cycle.

Hydrological Processes

1. INTRODUCTION

Carbon cycles have become one of the most extensively researched topics with regard to global climate change (Yang et al., 2021). Lakes, accounting for 3.7% of the global land area, are an important component of the inland water system, which regulate the carbon cycle by storing, transporting, and transforming carbon (Tranvik et al., 2009; Holgerson and Raymond, 2016; Cole et al., 1994; Holgerson & Raymond, 2016; Ran et al., 2017; Yan et al., 2018). For example, lake sediments can contain 0.03–0.07 Pg C a^{-1} (Molot & Dillon, 1996; Dean & Gorham 1998; Kortelainen et al., 2006), which is roughly equal to or higher than the carbon buried in marine sediments (Cole et al., 2007). The annual CO_2 emissions from lakes has been estimated at 0.11–0.57 Pg C a^{-1} (Sobek et al., 2005; Holgerson and Raymond, 2016). Additionally, the CO_2 and CH_4 released by organic matter mineralization play a major role in and significantly affect the terrestrial carbon cycle (Kortelainen et al., 2006; Tranvik et al., 2009; Holgerson & Raymond, 2016; Martinsen et al., 2020). Knowledge of the lake carbon cycle can therefore contribute to a comprehensive understanding of the terrestrial carbon cycle (Hanson et al., 2004; Balmer & Downing, 2011).

Dissolved inorganic carbon (DIC) occurs in water in the form of CO_2, ${CO_3}^{2-}$, ${HCO_3}^{-}$, and H_2CO_3. The primary sources of DIC in lake water are external inflowing water, atmospheric CO_2, organic matter decomposition, and CO_2 produced during metabolism of aquatic organisms. Carbon isotopes ($\delta^{13}C$) can record the cycling of carbon cycling during each of these links, which involve equilibrium and kinetic fractionation (Zhang et al., 1995; Myrbo & Shapely, 2006). Thus, $\delta^{13}C$ analyses of the DIC ($\delta^{13}C_{DIC}$) provide a powerful tool for tracing the lake carbon cycle and elucidating carbon fluxes (Quay et al., 1986; Herczeg, 1987; Stiller and Nissenbaum, 1999; Lei et al., 2012; Mu et al., 2016; Han et al., 2018; Shtangeeva et al., 2019). For instance, Striegl et al. (2001) compared the $\delta^{13}C_{DIC}$ values of 142 lakes during ice cover, suggesting that lakes with a higher CO_2(p CO_2) partial pressure had lower $\delta^{13}C_{DIC}$ values owing to the dominance of respiration of terrestrial organic material.

Lake ecosystems on the Qinghai-Tibetan Plateau are fragile and sensitive to changes in climate and environment (Fang et al., 2016). Lakes on the Qinghai-Tibetan Plateau account for approximately 50 % of the total lake area in China (Guan et al., 1984). Most studies on the $\delta^{13}C_{DIC}$ in lakes on the Tibetan Plateau have focused on the climatic and environmental implications of the carbon isotope compositions of lake sediments. Variations in the $\delta^{13}C_{DIC}$ of various lake types may have different responses to carbon cycle processes. For example, Lei et al. (2012) analyse the characteristics of the $\delta^{13}C_{DIC}$ of 24 lakes (mainly closed lakes) across the Qiangtang Plateau, finding that the high $\delta^{13}C_{DIC}$ values of closed lakes could be mainly attributed to significant catchment-scale contributions from carbonate weathering and the evasion of dissolved CO_2induced by enhanced lake water evaporation. Therefore, performing a more in-depth study on the changes in the $\delta^{13}C_{DIC}$ values of lakes on the Qinghai-Tibetan Plateau is necessary.

This study explored the relationships among the $\delta^{13}C_{DIC}$ values of the Genggahai Lake, the lake environment, and the watershed climate based on the observed water physicochemical parameters in areas with different types of submerged macrophyte communities, as well as the changes in the temperature and precipitation during the same period. Our objective was to provide a theoretical basis to elucidate the response mechanisms of $\delta^{13}C_{DIC}$ to the lake carbon cycle.

2. STUDY AREA

Gonghe Basin (35.45°–36.93° N, 98.77°–101.37° E) is located in the north-eastern Tibetan Plateau (Fig. 1a) at a mean elevation of approximately 3,000 m. This region is characterized by an alpine arid and semi-arid continental climate (Dong, Gao, & Jin, 1993). The basin has an elongated shape, which is surrounded by the Xiqing, Heka, Ela, Wahong, Waligong, and South Qinghai mountains (Fig. 1a) (Dong et al., 1993).

{Figure 1}

Genggahai Lake (36.18° N, 100.1° E) is located in the central part of the Gonghe Basin (Fig. 1a). The present-day area of the lake is approximately 2.0 km^2, with a surface elevation of 2,860 m, a maximum depth of 1.8 m, water salinity of 1 g L^{-1}, and a pH of 9.2 ± 0.5 (Qiang et al., 2013). The lithology of the Genggahai Basin is dominated by limestone, sandstone, marble, slate, and schist (Dong et al., 1993). Groundwater is the main water source in the Genggahai Lake (Qiang et al., 2013). Qiang et al. (2017) suggested that there is a close hydraulic link between the Shazhuyu River and Genggahai Lake. The lake is inhabited by a large number of submerged macrophytes, such as *Chara* spp.,*Myriophyllum spicatum L.* , and *Potamogeton pectinatus* L. (Fig. 1b), as well as gastropod molluscs (Qiang et al., 2013). The entire lake is surrounded by grassland, particularly the desert grassland ecosystem dominant in the Genggahai Basin. This region is characterized by strong wind-blown sand movement. Human activity in this region remains limited, with only a small number of Tibetan herdsmen, who graze their livestock on the grasslands surrounding the lake.

3. MATERIALS AND METHODS

Between 2012 and 2015, from May to September of each year, lake water samples were collected at a depth of 20 cm in three different areas characterised by *Chara* spp., *M. spicatum* , and *P. pectinatus* communities. At the same time, watershed groundwater samples and surface water samples from the Shazhuyu River were also collected. The collected samples were stored in 500 mL polyethylene plastic bottles; after adding 1 mL of $HgCl_2$ solution, each bottle was sealed with a sealing membrane. A total of 53 lake water samples, 19 groundwater samples, and 17 river water samples were collected. The physical and chemical parameters (i.e., the temperature, dissolved oxygen, and pH) were measured in situ using a portable water quality analyser (AquaRead-1000).

The plant samples, including *Chara* spp., M. *spicatum* , and P. *pectinatus* were sampled monthly adjacent to the lake water sampling point. Besides, *Gyraulus sibiricus* samples adhered to*Chara* spp. were collected. The fresh plant samples and shells were stored in polyethylene plastic bags and numbered. These samples were then transported to lab for further pre-treatment and analysis.

The water samples were subjected to the following laboratory pre-treatment procedure before DIC isotope determination. First, each sample was filtered through a 0.45-μm glass fibre filter and 4 mL of a saturated $BaCl_2$ solution was added to induce $BaCO_3$ precipitation (Wachniew & Różański, 1997). After the samples settled, the clear liquid was siphoned away; the remaining solids were placed in a drying oven to dry at a constant low temperature of 30 . Finally, the dried samples were ground to a uniform size and appropriate amounts were weighed for the DIC isotope determination. The prepared DIC samples were tested using a MAT-253 isotope ratio mass spectrometer (Thermo-Finnigan), together with a micro-carbonate sampling device (Kiel IV). Tests were performed at the Key Laboratory of Western China's Environmental Systems, MOE, Lanzhou University. Test results were reported relative to the PDB standard. Analytical precision values for $\delta^{13}C$ and $\delta^{18}O$ were ± 0.03 +- 0.05

To analyse the $\delta^{13}C$ of the plant bulk organic matter ($\delta^{13}C_{org}$), samples were pre-treated based on the methods reported in Song et al. (2012). The $\delta^{13}C_{org}$ was analysed using an on-line Conflo III-DeltaPlus isotope ratio mass spectrometry, combined with a Flash EA1112 elemental analyser at Lanzhou University. The results were reported in and wheat, whose standard deviations were 0.04, 0.07, and 0.05 respectively. All values are reported and discussed in the following section. Temperature data from the Gonghe Station were obtained from the China Meteorological Data Service Centre: 'Daily data from surface meteorological stations in China.'

4. RESULTS

4.1 Physical and chemical parameters of lake water

Together with the previously published physical and chemical parameters of water from the Genggahai Lake water from 2012 to 2013 (Jin et al., 2015), the overall trends for the temperature and pH of the lake water were relatively consistent in all three plant communities (Fig. 2a and 2b). More specifically, the overall temperature remained relatively constant throughout the entire monitoring period, but its annual fluctuations were more notable, with higher temperatures in June, July, and August, and relatively low temperatures in May and September (Fig. 2a). From 2012 to 2015, the lake water pH exhibited an overall gradually increasing trend from May to September, with only a few exceptions (e.g., June and July 2015; Fig. 2b). Beginning in May, both the number of aquatic plants and water temperature of the lake increased, which led to the increased consumption of CO_2 and HCO_3^- via plant photosynthesis. Moreover, the variation trend of dissolved oxygen (DO) was not notable, with all three plant communities showing inconsistencies, which may have been related to the high sensitivity of the DO to temperature changes (Fig. 2c).

{Figure 2}

A comparison of the three plant communities showed that, except for 2012, the lake water temperature and pH were slightly higher in the*Chara* spp. community than those in the *P. pectinatus* and*M. spicatum* communities throughout the testing period; however, these differences were not notable (Fig. 2a and b). In contrast, differences in the DO values of lake water in the three communities were more notable: the *Chara* spp. community had relatively higher DO values in June and July (Fig. 2c).

4.2 Spatial variations in DIC isotopic composition in the Genggahai Basin waterbodies

From 2012 to 2015, the $\delta^{13}C_{DIC}$ values of water from the Genggahai Lake ($\delta^{13}C_{DIC\text{-}L}$) ranged from –17.3 to 1.6 $\delta^{13}C_{DIC}$ of water from the Shazhuyu River ($\delta^{13}C_{DIC\text{-}R}$) ranged from –15.9 to –5.6 $\delta^{13}C_{DIC}$ for the groundwater spring, i.e., a lake water source, ranged from –17.3 to –1.1 value of –11.1 $\delta^{13}C_{DIC\text{-}L}$ values were the most positive, followed by the $\delta^{13}C_{DIC\text{-}R}$values, whereas the $\delta^{13}C_{DIC}$ values of the inflowing spring water ($\delta^{13}C_{DIC\text{-}I}$) were the most negative (Fig. 3). Jin et al. (2015) first reported the $\delta^{13}C_{DIC}$ values in the *Chara*spp. growth area and $\delta^{13}C_{DIC\text{-}R}$ values from 2012 to 2013.

{Figure 3}

The $\delta^{13}C_{DIC\text{-}L}$ values in the*Chara* spp. community were more positive than those in the*M. spicatum* and *P. pectinatus* communities. From 2012 to 2015, the $\delta^{13}C_{DIC\text{-}L}$ values in the*Chara* spp. community ranged from –9.9 to 1.6 value of –5.4 $\delta^{13}C_{DIC\text{-}L}$ values ranged from –15.2 to –3.9 spicatumcommunity, the $\delta^{13}C_{DIC\text{-}L}$ values ranged from –17.3 to –2.9 exception of one month (September 2012), the *P. pectinatus* and *M. spicatum* communities had similar $\delta^{13}C_{DIC\text{-}L}$ values: both communities had more negative values than the *Chara* spp. community (Fig. 3a).

4.3 Temporal variations in DIC isotopic compositions in the Genggahai Basin waterbodies

In the *Chara* spp. community, the $\delta^{13}C_{DIC\text{-}L}$ values were relatively positive in July from 2012 to 2014; in 2015, there was a gradual decrease in the $\delta^{13}C_{DIC\text{-}L}$ values. In contrast, the $\delta^{13}C_{DIC\text{-}L}$ values of the*P. pectinatus* and *M. spicatum* communities did not show a seasonal bias of more positive values (Fig. 3a). Figure 4a shows the interannual variations in the $\delta^{13}C_{DIC\text{-}L}$ values. From 2012 to 2015, the mean $\delta^{13}C_{DIC\text{-}L}$ values of the*Chara* spp. community were all more positive (–4.0 in 2013 and 2014, these values were more negative (–6.8 to 2015, the $\delta^{13}C_{DIC\text{-}L}$ values in the*P. pectinatus* and *M. spicatum* communities showed a gradual positive trend. In comparison, the $\delta^{13}C_{DIC\text{-}I}$ values from 2012 to 2015 showed an overall increase; however, in 2013 and 2014, these values became increasingly negative (Fig. 4b). During the same period, the $\delta^{13}C_{DIC\text{-}R}$ values showed a gradually increasing trend (Fig. 4b).

{Figure 4}

5. DISCUSSION

5.1 Φαςτορς αφφεςτινγ δ^{13}ΔΙ ιν τηε Γενγγαηαι Βασιν ωατερβοδιες

Several major processes affect the stable carbon isotope compositions of the lake water DIC, such as in-lake processes (including lake metabolism, organic matter decomposition, calcite precipitation, and exchange with atmospheric CO_2) and the climatic and geographical environment of the catchment (including carbonate rock weathering and dissolution and soil respiration) (Bade et al., 2004). The climatic and geographical environment in the catchment can alter the carbon isotope composition of the lake water DIC by influencing the aqueous CO_2 and alkalinity of inflowing water. Generally, the five following factors affect the isotope composition of the DIC.

1) Lake inflow carbon isotope composition. The isotopic composition of the lake inflow directly affects the isotopic composition of the lake. This is especially significant in exorheic lakes or lakes with a short water retention time. In the *Chara* spp. community, the $\delta^{13}C_{DIC\text{-}L}$ and $\delta^{13}C_{DIC\text{-}I}$ values were positively correlated ($r^{2} = 0.68$, $p < 0.01$), whereas in the *M. spicatum* community, these values were uncorrelated (Fig. 5). This is because the *M. spicatum* community was located far from the lake inflow in the south-eastern region, where exchange with spring water was weak (Fig. 1b). This reveals that the $\delta^{13}C_{DIC\text{-}I}$ values were key factors influencing the $\delta^{13}C_{DIC\text{-}L}$ values.

{Figure 5}

2) Exchange with atmospheric CO_2. The DIC pool in the lake tended to be in isotopic equilibrium with the atmosphere via CO_2 exchange. During the CO_2 exchange process, ^{12}C-rich CO_2 is preferentially released from the lake surface to the atmosphere, yielding a DIC pool enriched in ^{13}C. This exchange process is slow; therefore, its effect on the $\delta^{13}C_{DIC\text{-}L}$ values is more notable in endorheic lakes characterised by long retention time, whereas it is not as observable in lakes with short retention times or rapid circulation (Shen et al., 2010). When lake water to atmospheric CO_2exchange reaches an equilibrium, the $\delta^{13}C_{DIC\text{-}L}$ values range from 1–3 (Deuser and Degens, 1967; Leng & Marshall, 2004).

The exchange between the DIC of lake water and atmospheric CO_2 is continuous in exorheic lakes. At equilibrium, isotope fractionation occurs between atmospheric CO_2 and dissolved carbonate species, i.e., CO_2 (aq), HCO_3^-, and CO_3^{2-} (Zhang et al., 1995), as follows:

$\epsilon_{\text{aq-g}} = -(0.0049 \pm 0.003) \times T\ () - (1.31 +- 0.06)$, (1)

$\epsilon_{\text{HCO3-g}} = -(0.141 \pm 0.003) \times T\ () + (10.78 +- 0.05)$, and (2)

$\epsilon_{\text{CO3-g}} = -(0.052 \pm 0.03) \times T\ () + (7.22 +- 0.46)$ (3)

Temperatures recorded using a water level data logger showed that from May to September of 2013–2015, the mean water surface temperature of the Genggahai Lake was 17.0 . Based on Eqs. (1)–(3), the carbon isotope fractionation factors between H_2CO_3, HCO_3^-, and CO_3^{2-} and atmospheric CO_2 were –1.5, 8.38, and 5.89 isotopic composition of global atmospheric CO_2 is approximately –8.1 isotopic values of H_2CO_3, HCO_3^-, and CO_3^{2-} in lake water are –9.6, 0.28, and –2.21 $\delta^{13}C$ values at isotopic equilibrium; the magnitude of the $\delta^{13}C_{DIC}$ value depends on the proportions of the different DIC forms in lake water, which is related to its pH value (Stumm & Morgan, 1970). When the pH value was 5.5, 80 % of the DIC in a water body has an aqueous CO_2 form (aq). When the pH is 8.5, CO_2 (aq) accounts for < 1 % of the DIC, which predominantly takes HCO_3^- and CO_3^{2-} forms. When the pH reaches 10, HCO_3^- accounts for < 50 % of the DIC, whereas CO_3^{2-} dominates the DIC (Stumm & Morgan, 2012). The pH value of the Genggahai Lake varied from 8.1 to 10.6, which indicates that HCO_3^- and CO_3^{2-} were its dominant forms of DIC. Notably, the actual $\delta^{13}C_{DIC}$ values of the Genggahai Lake were generally more negative than the atmosphere-equilibrated $\delta^{13}C_{DIC}$.

3) Organic matter decomposition in lake sediments. Sedimentary organic matter in lakes includes native aquatic plants and terrestrial organic debris transported into the lake from the surrounding watershed. Once degraded, this organic matter increases the^{12}C-enriched DIC composition of lake water (Myrbo & Shapely, 2006). Organic matter decomposition in Qingmuke lake (i.e., a freshwater lake located on the Qiangtang Plateau) resulted in a DIC isotope value equal to or even lower than that of river water (Lei et al., 2012). In contrast, the isotopic composition of the DIC in the Genggahai Lake was significantly more positive than that of the Shazhuyu River, indicating that organic matter decomposition may have had a relatively small effect on the DIC composition of the lake. Additionally, methane produced by organic matter decomposition resulted in a more negative $\delta^{13}C_{DIC}$ value. Organic matter decomposition can cause a decrease in the $\delta^{13}C_{DIC}$ values to –50 2013). This value is significantly lower than the mean $\delta^{13}C_{DIC\text{-}L}$ value of the Genggahai Lake, which indicates that the CO_2 or methane produced via decomposition did not have a significant effect on seasonal or interannual changes in the $\delta^{13}C_{DIC\text{-}L}$values.

During the observation period, the mean carbon isotopic composition of organic matter ($\delta^{13}C_{org}$) in the*Chara* spp. community was –16.0 $\delta^{13}C_{org}$ in the *P. pectinatus*and *M. spicatum* communities were –12.7 and –11.4 If we neglect the effect of carbon isotope fractionation owing to organic matter decomposition, the $\delta^{13}C$ of the CO_2 released via organic matter decomposition is then equal to $\delta^{13}C_{org}$. According to Eq. (2), if HCO_3^- is the dominant form of DIC in the lake, then the equilibrium isotopic value of HCO3- in the lake water is 0.28 mean $\delta^{13}C_{DIC\text{-}L}$ value of the*Chara* spp., *P. pectinatus* , and *M. spicatum*communities would be –15.72, –12.42, and –11.12 respectively. However, the observed mean $\delta^{13}C_{DIC\text{-}L}$values for these three communities were –5.4, –7.4, and –7.9 matter decomposition has a limited effect on the $\delta^{13}C_{DIC\text{-}L}$ of the Genggahai Lake.

4) Lake photosynthetic activity. In highly productive lakes, photosynthesis is a key factor that affects the $\delta^{13}C_{DIC}$ values of the lake water (McKenzie, 1982, 1985). During photosynthesis, plants preferentially up-

take ^{12}C, which yields more negative $\delta^{13}C$ values for plants and the $\delta^{13}C_{DIC}$ of the water body becomes more positive (Andrews et al., 2004). Charaphytes are an important submerged aquatic macrophyte. Compared with vascular plants, charaphytes have a higher photosynthetic rate and lower respiration rate. The preferential uptake of $^{12}CO_2$ for photosynthetic purposes could have led to the ^{13}C-enrichment of the DIC in the lake water (Pełechaty et al., 2010). During intense photosynthesis, dissolved CO_2 in lake water is limited (Herczeg & Fairbanks 1987). When this occurs, charaphytes use HCO_3 for photosynthetic activity. Compared with vascular plants, charaphytes can use HCO_3^- for photosynthetic activity more effectively (van den Berg et al., 1999). According to Eqs. (1)–(3), the $\delta^{13}C$ values of HCO_3^- were more positive than those of H_2CO_3 and CO_3^{2-} in the lake water. In contrast, the photosynthetic activity of charaphytes results in carbonate precipitation in the surrounding waters, forming thick $CaCO_3$ encrustations (Pełechaty et al., 2010). This also led to ^{13}C-enriched water in the charaphyte growth area.

We found that the seasonal bias in the $\delta^{13}C_{DIC\text{-}L}$ values of the *Chara*spp. community were more positive in July (2012–2014) (Fig. 4a). Additionally, at the beginning of *Chara* spp. growth (in May), the $\delta^{13}C_{DIC\text{-}L}$ value of the *Chara*spp. community was equal to the value at the end of *Chara* spp. growth (in September), especially in 2012. In contrast, the $\delta^{13}C_{DIC\text{-}L}$ values in the *P. pectinatus* and *M. spicatum* communities showed no seasonality (Fig. 4a). This phenomenon may have occurred because *Chara* spp. has a higher photosynthetic rate and a lower respiration rate than that of the other communities (Van den Berg et al., 2002). Pentecost et al. (2006) also observed seasonal variations in the $\delta^{13}C_{DIC\text{-}L}$ values of the *Chara*spp. community in the UK. Pełechaty et al. (2010) suggested that an increase in $\delta^{13}C_{DIC}$ results from the intense photosynthetic activity of *Chara rudis* during the early summer. Moreover, we found that the differences in the $\delta^{13}C_{DIC\text{-}L}$ values between *Chara*spp. and vascular plants were smaller at the beginning and end of the growing season in the Genggahai Lake, but larger during the mid-growth season (July) (Fig. 4a). There may have been a limited impact from photosynthesis on the $\delta^{13}C_{DIC\text{-}L}$ values in areas with submerged vascular plants. This trend was not evident during certain months, e.g., in July 2015. Due to data limitations, we cannot provide an explanation for this phenomenon. Nevertheless, we can reasonably conclude that the variations in the $\delta^{13}C_{DIC\text{-}L}$ values of the lake water were related to the intensity of photosynthetic activity in different aquatic plants.

5) Water retention time. In arid regions, with extended lake water residence times, strong evaporation leads to the preferential loss of the lighter $^{12}CO_2$ and$^{16}O_2$ isotopes, yielding more positive $\delta^{13}C_{DIC\text{-}L}$ and oxygen ($\delta^{18}O$) isotopic lake water compositions; furthermore, there was a significant positive correlation between $\delta^{13}C_{DIC\text{-}L}$ and $\delta^{18}O_L$ (Li & Ku, 1997). Monitoring results revealed that the $\delta^{18}O_L$ values of the Genggahai Lake deviated significantly from the global meteoric water line, but were consistent with the local evaporation line (LEL), indicating that evaporation affected the $\delta^{18}O_L$ composition of the lake water (Jin et al., 2015; Qiang et al., 2016). However, this study found that the $\delta^{13}C_{DIC\text{-}L}$ and $\delta^{18}O_L$ values of the Genggahai Lake were not correlated (Fig. 6), which indicates that evaporation may have had only a minimal effect on the $\delta^{13}C_{DIC\text{-}L}$ value of the lake.

{Figure 6}

The preceding analysis demonstrated that the lake surface to atmospheric exchange of CO_2 and evaporation had a relatively minimal effect on $\delta^{13}C_{DIC\text{-}L}$; $\delta^{13}C_{DIC\text{-}I}$ primarily influenced the changes in $\delta^{13}C_{DIC\text{-}L}$. The high photosynthetic efficiency of *Chara* spp. indicates that the its corresponding $\delta^{13}C_{DIC\text{-}L}$ values showed a seasonal trend of more positive values, which were more positive than the $\delta^{13}C_{DIC\text{-}L}$ values of areas with vascular plants. This shows that the photosynthetic activity of vascular plants has a negligible effect on the $\delta^{13}C_{DIC\text{-}L}$ of lake water.

5.2 Isotopic composition of DIC in the Genggahai Basin groundwater and Shazhuyu River

The $\delta^{13}C_{DIC\text{-}I}$ and $\delta^{13}C_{DIC\text{-}R}$ values were significantly more negative than $\delta^{13}C_{DIC\text{-}L}$ during the same period, which suggests that isotopic fractionation owing to atmospheric exchange or the photosynthesis of aquatic plants occurred after groundwater inflow into the lake (Leng & Marshall, 2004). Compared with the $\delta^{13}C_{DIC\text{-}I}$ value, $\delta^{13}C_{DIC\text{-}R}$ was significantly more positive, possibly because the Shazhuyu River essentially forms via surface runoff, as well as the more frequent exchange of atmospheric CO_2 with surface water than groundwater.

We found a significant correlation between $\delta^{13}C_{DIC-I}$ and $\delta^{13}C_{DIC-R}$ ($n = 17, r^2 = 0.46$, and $p < 0.01$). Additionally, given that groundwater is the main water source of the Genggahai Lake, $\delta^{13}C_{DIC-I}$ was the main factor affecting the $\delta^{13}C_{DIC-L}$ values of the lake water (see section 5.1). Therefore, we further analysed the influencing factors of $\delta^{13}C_{DIC-I}$.

Three main species compose the DIC in water bodies: CO_2, CO_3^{2-}, and HCO_3^-. In this study, the titration method was used to determine the DIC composition of groundwater in the Genggahai Basin. We found that $HCO_3^-$was the dominant form of DIC. Additional research has shown that the primary source of HCO_3^- in the groundwater of the Genggahai Basin and the Shazhuyu River is the chemical weathering of rocks, especially carbonate rocks (Jin et al., 2019). Based on the reaction equation for chemical weathering, CO_2 is an essential component of this process. Dissolved CO_2 in groundwater originates from the atmospheric flux, watershed soil respiration, and organic matter decomposition (Gu, 2011). Atmospheric CO_2 normally has $\delta^{13}C$ values of approximately –8 stable. The $\delta^{13}C$ values of soil CO_2 from areas with C_3 and C_4 plants range from –32 to –20 respectively. The $\delta^{13}C$ value of HCO_3^- from carbonate dissolution during subsurface weathering is approximately 0 2016). The isotopic equilibrium between CO_2 and HCO_3^- from different sources can be attained through the following exchange reaction:

$^{13}CO_2(g) + H_2{}^{12}CO_3(aq) = {}^{12}CO_2(g) + H_2{}^{13}CO_3(aq)$. (4)

The fractionation factor of CO_2 and HCO_3^- in the CO_2–HCO_3^- system in soil is approximately 10 CO_2 is dissolved in water, its $\delta^{13}C$ value becomes more negative than that of HCO_3^-. However, carbonate rock dissolution increases the $\delta^{13}C$ value of HCO_3^-. Evidently, the carbon source that affects the isotopic composition of DIC in groundwater, $\delta^{13}C_{DIC-I}$, consists of two components: (1) ^{13}C from the weathering and dissolution of carbonate rocks, which possesses a more positive isotope ratio and (2) ^{12}C from CO_2 generated through soil respiration, which has a more negative isotope ratio. Therefore, the relative contribution of these two carbon sources to the groundwater DIC determines the composition of $\delta^{13}C_{DIC-I}$ in the Genggahai Basin.

6. IMPLICATIONS OF LAKE WATER DIC ISOTOPIC COMPOSITION ON CARBON CYCLE

Lake ecosystems are active components of the global carbon cycle as they continually fix and release carbon through various biological processes, including photosynthesis, food web activity, and bacterial degradation (Tranvik et al., 2009; Holgerson & Raymond, 2016). The lake carbon cycle is mainly composed of carbon input via runoff and atmospheric CO_2 diffusion, different forms of carbon transformation in the lake (including organic matter decomposition, photosynthesis/respiration of aquatic plants, and carbonate precipitation), and carbon output via runoff and gaseous CO_2 emissions through the water surface (Hu et al., 2014).

The DIC and its isotopes are an important tool to elucidate the carbon cycle of lake ecosystems (McKenzie, 1985; Quay et al., 1986; Herczeg & Fairbanks, 1987; Wachniew & Różański, 1997; Herczeg et al., 2003; Lei et al., 2012; Mu et al., 2016). Striegl et al. (2001) found that during the ice melting period, the average $\delta^{13}C_{DIC-L}$ value in 132 freshwater lakes in temperate and cold regions was –14 (2004) reported that the average $\delta^{13}C_{DIC-L}$ value in 108 freshwater lakes in different regions was –15 photosynthesis of aquatic plants and organic matter decomposition in sediments are active components of the carbon cycle (Lei et al., 2012). In freshwater lakes on the Qiangtang Plateau, variations in $\delta^{13}C_{DIC-L}$ also showed that organic matter decomposition significantly contributed to the carbon cycle of the lake ecosystems (Lei et al., 2012). However, Lei et al. (2012) found that the $\delta^{13}C_{DIC-L}$ values of endorheic lakes on the Qiangtang Plateau were relatively high, approaching the $\delta^{13}C_{DIC-L}$ values of equilibrated CO_2 in water to atmospheric exchange. Therefore, water surface to atmospheric CO_2 exchange drives the carbon cycle in endorheic lakes on the Qiangtang Plateau (Lei et al., 2012).

The $\delta^{13}C_{DIC-L}$ values of the Genggahai Lake significantly exceeded the $\delta^{13}C_{DIC}$ values of freshwater lakes

(> 8 Qiangtang Plateau (> –5.71 indicates that the carbon cycle of the Genggahai Lake significantly differs from those of freshwater lakes and lakes on the Qiangtang Plateau. Variations in the $\delta^{13}C_{DIC-L}$values of the Genggahai Lake indicate that organic matter decomposition and water to atmospheric CO_2 exchange are not likely the main components of its carbon cycle (section 5.1). Carbon input from inflowing groundwater and the photosynthesis of aquatic plants may be the main components of its carbon cycle.

Recent vegetation surveys have shown that the main terrestrial plants in the watershed of the Genggahai Lake are *Artemisia desertorum* ,*Oxytropis aciphylla* , *Achnatherum splendens* , *Orinus kokonorica* , and *Agropyron cristatum* . This is identical to that in the Qinghai Lake watershed (Duan & Xu, 2012; Liu et al., 2013). The $\delta^{13}C_{org}$ values of ^3C plants in the Qinghai Lake watershed varied from –27.7 to –24.5 of soil in the Qinghai Lake watershed varied from –26.9 to –24.8 (Liu et al., 2013). When the DIC in groundwater only originates from soil respiration and organic matter decomposition, if we neglect the effect of carbon isotope fractionation due to organic matter decomposition, the $\delta^{13}C_{DIC}$ of groundwater ranges from –27.7 to –24.5 fractionation between CO_2 (aq) and HCO_3^-(approximately –10 al., 1995), the $\delta^{13}C_{DIC}$ of groundwater ranges from –17.7 to –14.5 $\delta^{13}C_{DIC}$ values of groundwater in the Genggahai Lake watershed were more positive than –14.5 indicates that soil respiration and organic matter decomposition may not be the only carbon source for the groundwater DIC in the Genggahai watershed.

Significantly higher $\delta^{13}C_{DIC}$(approximately –3 to +3 values in groundwater can occur in karstic regions where a proportion of the carbon atoms derive from the dissolution of catchment limestones (Andrews et al., 1997). For example, the $\delta^{13}C_{DIC}$ of groundwater from the Donggi Cona catchment on the north-eastern Qinghai-Tibetan Plateau varies from 0.9 to 2.0 the early and middle Pleistocene are widely distributed throughout the Gonghe Basin (Dong, 1993). Here, HCO_3^- originates from the weathering of paleolake sediments and subsequent mineral dissolution, which is enriched in ^{13}C. Water and groundwater flows transport the HCO_3^-, thus yielding more positive $\delta^{13}C_{DIC}$ values. We suggest that HCO_3^- originates from paleolake sediment weathering, which affects the groundwater DIC pool in the Genggahai watershed and yields relatively positive groundwater $\delta^{13}C_{DIC}$ values. Thus, variations in the $\delta^{13}C_{DIC}$ values of groundwater may reflect the relative contributions of two carbon sources to the groundwater DIC pool. One carbon source is CO_2 that derives from soil respiration and organic matter decomposition while the other is HCO_3^- from paleolake carbonate sediments. Besides, we elucidated that carbonate weathering and soil respiration related to vegetation succession control the variations in $\delta^{13}C_{DIC-I}$. Therefore, variations in the $\delta^{13}C_{DIC-L}$ values of the Genggahai Lake may reflect the lake productivity and carbon cycle of the watershed. Clearly, more data are required to constrain the environmental significance of the $\delta^{13}C_{DIC-L}$ values of the Genggahai Lake.

7. CONCLUSIONS

1) For the overall DIC isotopic composition in the Genggahai Basin, we found that $\delta^{13}C_{DIC-I}$ was the most negative, with an average value of –11.1 $\delta^{13}C_{DIC-R}$, with an average value of –10.8 positive, with an average value of –6.91 fractionation resulting from the photosynthesis of aquatic plants after spring water inflow into the lake.

2) Owing to variations in the photosynthetic activity intensity of different aquatic plants, there were also significant variations in the $\delta^{13}C_{DIC-L}$ values in areas with different aquatic plants. We found that areas with *M. spicatum*and *P. pectinatus* communities had similar $\delta^{13}C_{DIC-L}$ values, with an average of –6.8 of the *Chara* spp. community was more positive, at –4.0 likely occurred because *Chara* spp. plants have a higher photosynthetic rate and are more capable of using $CO_2$for photosynthetic activity, converting them into plant organism.

3) Based on hydrochemical observations, we found that the $\delta^{13}C_{DIC}$ of the lake water was primarily affected by the $\delta^{13}C_{DIC-I}$and aquatic plant photosynthesis. The change in $\delta^{13}C_{DIC-I}$ to a more positive value resulted from carbon isotope equilibration between ^{13}C from carbonate weathering in the watershed and$^{12}CO_2$ from soil respiration.

4) The changes in the $\delta^{13}C_{DIC-L}$composition of the Genggahai Lake indicated that the DIC from lake inflow and the photosynthesis of aquatic plants were the key components in the carbon cycle of the lake.

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DATA AVAILABILITY

All data reported in this manuscript are available in Figure 2, 3, 5, 6, from which data on Figures 4 can be derived. For the data policy, all of the data above for this paper are available in Figshare (https://doi.org/10.6084/m9.figshare.11492313.v1).

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Figure Legends

Fig. 1. Setting and location. (a) Location of the Gonghe Basin (Google Earth^{TM}). The red rectangle and red circle indicate the study site. Circulation systems influencing the study area are also shown. Dashed and solid lines indicate the modern extent of the East Asian summer monsoon (EASM) and Indian Ocean summer monsoon (ISM), respectively (Winkler & Wang, 1993). (b) Genggahai Lake, its surrounding physical environments, and the spatial distribution of modern aquatic vegetation (Qiang et al., 2013).

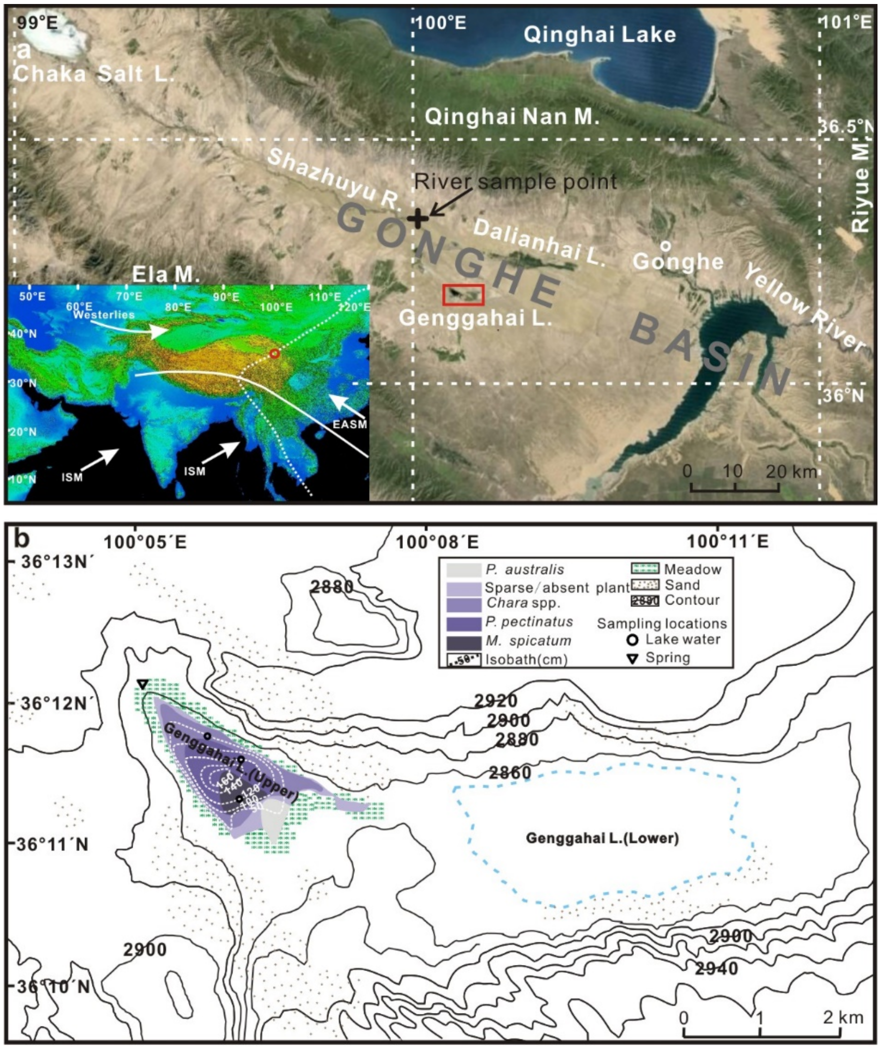
Fig. 2. Seasonal variations in the physical and chemical parameters of the lake water in different plant growth areas of Genggahai Lake from May to September (2012–2015). (a) Water temperature; (b) pH value; and (c) dissolved oxygen concentrations.

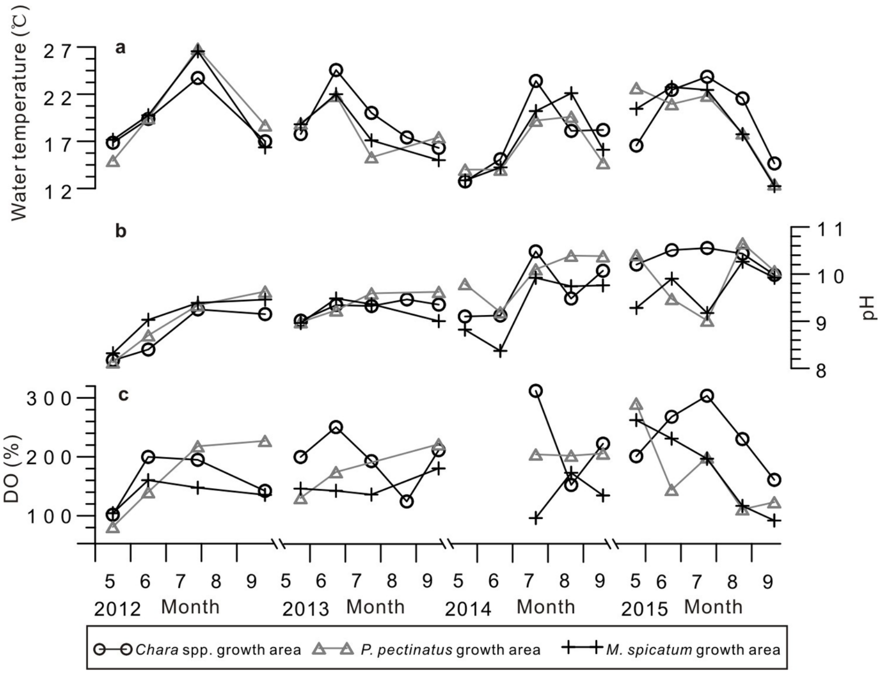
Fig. 3. Variations in the carbon isotopes of DIC precipitated from the (a)surface water in Genggahai Lake and (b) waterbodies within its catchment from May to September (2012–2015).

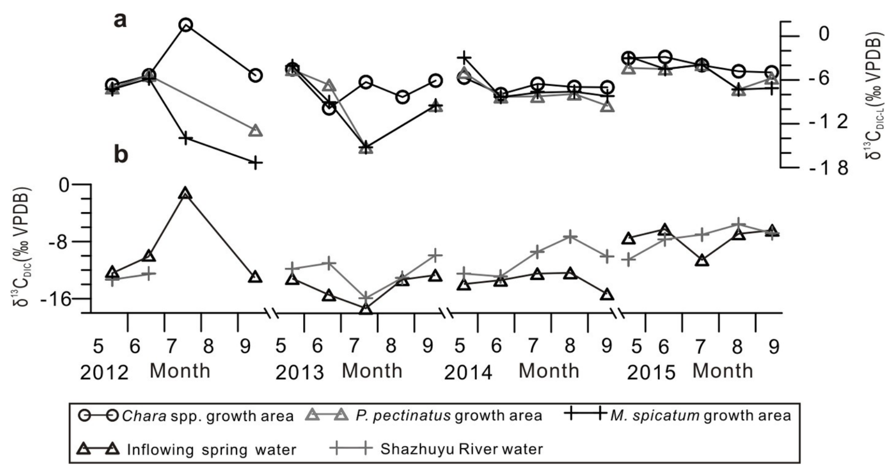
Fig. 4. Annual variations in the carbon isotopes of DIC precipitated from the surface water in Genggahai Lake and waterbodies within its catchment from 2012 to 2015.

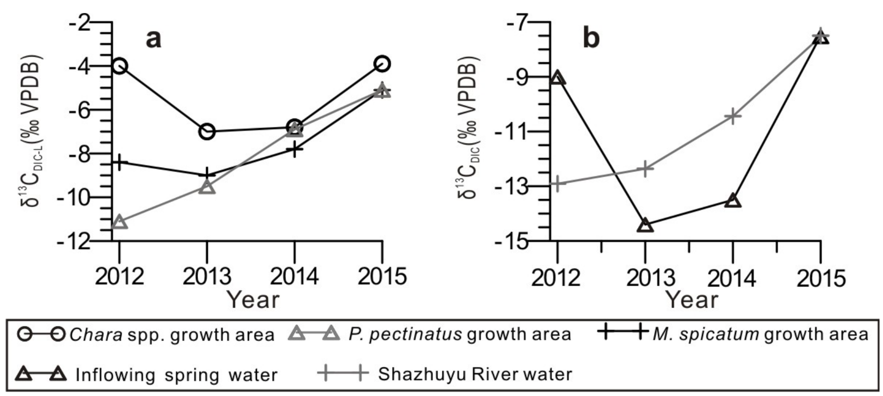
Fig. 5. Correlation between the carbon isotopes of inflowing water DIC and lake water DIC in (a) *Chara* spp., (b) *Potamogeton pectinatus* , and (c)*Myriophyllum spicatum* growth areas.

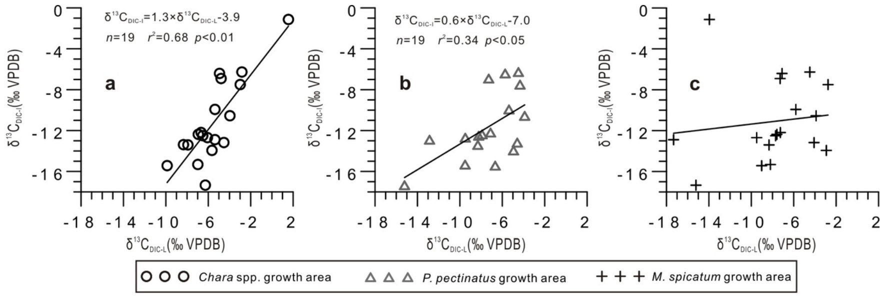
Fig. 6. Correlation between the carbon isotopes of the lake water DIC and oxygen isotopes of the lake water in the (a) *Chara*spp., (b) *Potamogeton pectinatus* , (c) *Myriophyllum spicatum* growth areas.

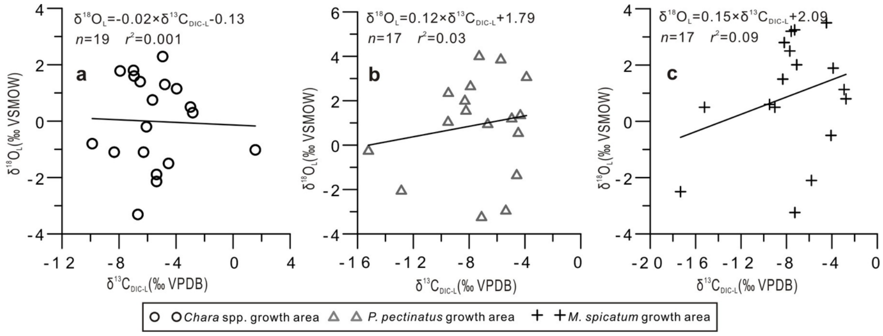

a
99°E
100°E
101°E
Qinghai Lake
Chaka Salt L.
Qinghai Nan M.
36.5°N
Riyue M.
Shazhuyu R.
River sample point
GONGHE BASIN
Dalianhai L.
Gonghe
Yellow River
Ela M.
Genggahai L.
36°N
0 10 20 km
50°E
60°E
70°E
80°E
90°E
100°E
110°E
120°E
Westerlies
40°N
30°N
20°N
10°N
EASM
ISM
ISM
b
100°05´E
100°08´E
100°11´E
36°13N´
36°12N´
36°11´N
36°10´N
P. australis
Sparse/absent plant
Chara spp.
P. pectinatus
M. spicatum
Isobath(cm)
Meadow
Sand
Contour
Sampling locations
Lake water
Spring
2880
2920
2900
2860
2900
2940
Genggahai L.(Upper)
Genggahai L.(Lower)
0 1 2 km


a
b
c
Water temperature (℃)
pH
DO (%)
Month
2012
2013
2014
2015
Chara spp. growth area
P. pectinatus growth area
M. spicatum growth area


a
b
δ13CDIC-L(‰ VPDB)
δ13CDIC(‰ VPDB)
Month
2012
2013
2014
2015
Chara spp. growth area
P. pectinatus growth area
M. spicatum growth area
Inflowing spring water
Shazhuyu River water


a
b
δ13CDIC-L(‰ VPDB)
δ13CDIC(‰ VPDB)
Year
Chara spp. growth area
P. pectinatus growth area
M. spicatum growth area
Inflowing spring water
Shazhuyu River water


δ13CDIC-I=1.3×δ13CDIC-L-3.9
n=19 r2=0.68 p<0.01
a
δ13CDIC-I=0.6×δ13CDIC-L-7.0
n=19 r2=0.34 p<0.05
b
c
δ13CDIC-I(‰ VPDB)
δ13CDIC-L(‰ VPDB)
Chara spp. growth area
P. pectinatus growth area
M. spicatum growth area


δ18OL=-0.02×δ13CDIC-L-0.13
n=19 r2=0.001
a
δ18OL=0.12×δ13CDIC-L+1.79
n=17 r2=0.03
b
δ18OL=0.15×δ13CDIC-L+2.09
n=17 r2=0.09
c
δ18OL(‰ VSMOW)
δ13CDIC-L(‰ VPDB)
Chara spp. growth area
P. pectinatus growth area
M. spicatum growth area