Sources of organic matter in the surface sediments from Lake Sihailongwan Maar and Lake Zhanjiang Maar (Lake Huguangyan Maar) in China

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ABSTRACT

Maar lakes are closed lakes that have a well-documented history of changes in organic matter (OM) production. The surface sediments from 2 typical maar lakes in China were analyzed for total organic carbon (TOC), total nitrogen (TN), $\delta^{13}C_{org}$, $\delta^{15}N_{total}$, aliphatic hydrocarbons (AHs), fatty acids (FAs) and alkanols. The FAs and alkanols were fractionated into two sub-fractions (free and bound) to investigate their sources. A higher TOC content was observed in the surface sediment from Lake Sihailongwan Maar than that from Lake Zhanjiang Maar. The molecular compositions of the *n*-alkanes, *n*-alkanols and FAs extracted from the surface sediments reveal different responses to environmental changes. The fatty acid distributions are dominated by short-chain components from algal and bacterial origins. However, the *n*-alkane and free *n*-alkanol distributions in the surface sediment from Lake Sihailongwan Maar are dominated by long-chain terrestrial source inputs, indicating that the secondary components of the post-depositional microbial activity are important for the FAs in the sediment from Lake Sihailongwan Maar. The aquatic FAs derived from algae and anaerobic bacteria are major components of sedimentary OM in all of the studied samples.

1. Introduction

The OM in maar lake sediment includes the original, biologically synthesized lipid materials that originate from the organisms within the lake and the secondary lipid compounds derived from the microbial activity in the water and sediment (Lu and Meyers, 2009). Maar lakes are mostly closed lakes, so there is little terrestrial OM input from the surrounding watershed that is introduced via stream/river inflows. Maar lakes are especially sensitive to environmental change because they have a small catchment area and limited inflow/outflow (Wang et al., 2012). Moreover, they often provide high-resolution records due to limnological processes favorable to the development and preservation of seasonally laminated sediments (Rasser et al., 2013).

Lipid biomarkers have been widely used to reconstruct the past changes in lacustrine ecosystems because these biomarkers contain abundant information about the original sedimentary source material and about the changes in the biogeochemical processes related to aquatic productivity, anthropogenic effects, climatic changes and postburial diagenesis (Lu and Meyers, 2009). The distribution and sources of lipids in the maar lake sediments might be influenced by

many factors, including the mean annual precipitation (MAP), mean annual surface water temperatures (MAWT), light intensity, nutrient salt level, pH, total dissolved solids (TDS), etc. The light intensity, day length, and nutrient salt level are important factors regulating the growth of phytoplankton. A longer day length and higher light intensities resulted in greater biomass production and a complete utilization of nitrate and phosphate in less time compared with shorter days and lower light intensities (e.g. Meseck et al., 2005).

Maar lakes are considered extreme environments. They are usually small ecosystems, with deep water. Most maar lakes are not exposed to direct anthropogenic impact, therefore, maar lakes can be used as indicators of environmental changes. This project conducted a comprehensive study of the composition, preservation and origin of the bulk OM and lipids in the surface sediments from 2 typical maar lakes in China. The lakes include Lake Sihailongwan Maar and Lake Zhanjiang Maar (Lake Huguangyan Maar), spanning 21°9′ (N) to 42°17′ (N). The factors that might influence the composition of the sedimentary OM, such as the light intensity, MAWT, MAP, pH and TDS, are apparently different between the two investigated lakes. In the present study, we report the concentrations of the TOC and TN, $\delta^{13}C_{org}$ and $\delta^{15}N_{total}$

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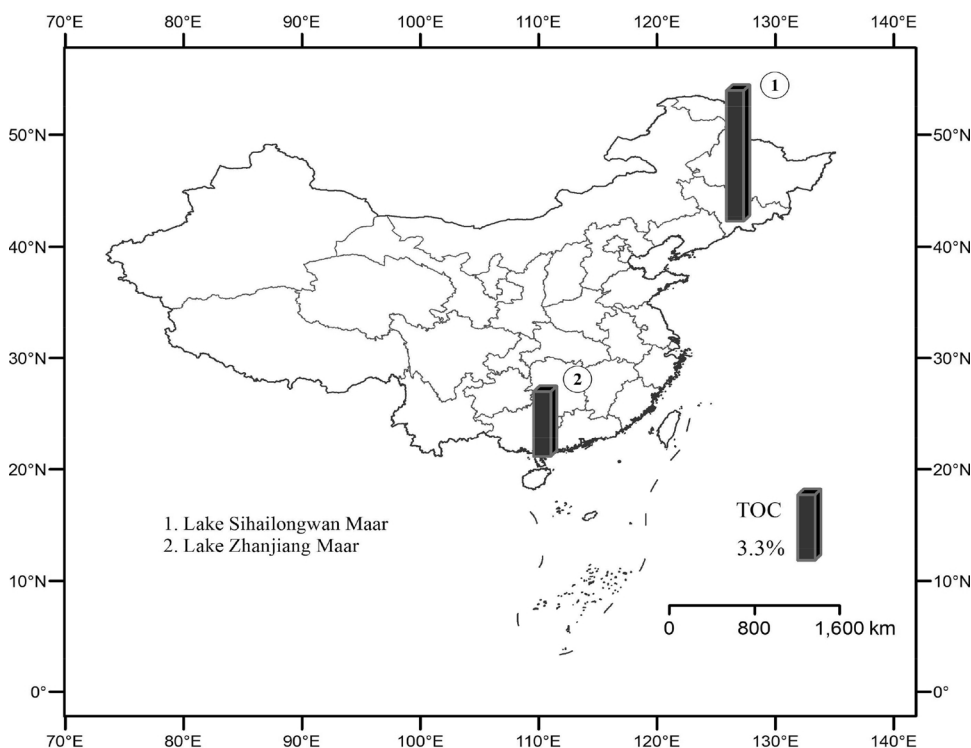 *E-mail address:* wufengchang@163.com (F. Wu).

Fig. 1. Sketch map of PR China, showing the locations and TOC distributions in the surface sediments from Lake Sihailongwan and Lake Zhanjiang Maar, China.

values and the composition of biomarkers (AHs, *n*-alkanols and FAs) in the surface sediments. The aim of this study was to search for the source changes of sedimentary OM with the changes of the influencing factors between two different maar lake areas.

2. Study site

The nearly circular Lake Sihailongwan Maar (42°17′ N, 126°36′ E, altitude: 791 m asl) is located in the Longgang Volcanic Field, northeastern China (Jilin province) (Fig. 1). The catchment area is 0.7 km², while the lake has a surface area of ~0.39 km² and a maximum depth of ~50 m (Parplies et al., 2008). The catchment is well covered with typical broadleaf–conifer mixed forest. Brown chernozem has developed in the catchment, with a thickness of 10–40 cm. A tephra layer (10–20 cm) is widely distributed below the brown chernozem in the catchment area (Zhu et al., 2013).

The Lake Zhanjiang Maar (Lake Huguangyan Maar) (21°9′N, 110°17′E), a typical volcanic maar lake located in Guangdong Province, is located at the central part of the Leizhou Peninsula, southeastern China (Fig. 1). The lake is surrounded by a high tephra wall (relative elevation of 10–20 m), which includes pyroclastic rocks, breccias, conglomerates, and tuffs. The present lake has a surface area of ~2.3 km², with a diameter of ~1.7 km and a maximum depth of ~20 m (Duan et al., 2014). Situated in a subtropical climate zone, Lake Zhanjiang Maar is surrounded covered by tropical semi-evergreen seasonal rain forest and soils from weathered volcanic rocks.

3. Material and methods

3.1. Lake selection and sediment collection

The lakes (Lake Zhanjiang Maar, Lake Sihailongwan Maar) were selected from southeastern and northeastern plains, as typical maar lakes, China, and represent a contrast of light intensities, MAWT, MAP, pH and TDS (Table 1). Four sediment cores were collected from the center of each lake in 2014 using a piston-percussion corer fitted with 58 mm i.d. Perspex tubes. The cores were sectioned into 1 cm intervals

and freeze-dried immediately after collection. In order to make the samples more representative, the surface sections (0–1 cm) of all four sediment cores from each lake were combined for analysis.

3.2. Elemental and stable isotope analyses

Sub-samples for elemental (TOC and TN) and bulk stable isotope composition analyses were acidified with 1 M HCl before analysis to remove carbonates. Concentrations of TOC and TN, as well as the C_{org}/N_{total} (atomic) ratios were determined using a CHNS Vario E1 III elemental analyzer. Carbon and nitrogen isotope analyses were conducted on a Thermo Finnigan Delta Plus XL mass spectrometer connected to a Flash EA 1112 elemental analyzer via a Finnigan MAT ConFlo III interface. $\delta^{13}C_{org}$ and $\delta^{15}N_{total}$ were reported relative to VPDB and air, respectively. The instrument analytical precision for $\delta^{13}C_{org}$ and $\delta^{15}N_{total}$ was 0.1‰ and 0.2‰, respectively.

3.3. Extraction and fractionation of free and bound lipids

Samples were Soxhlet extracted for 72 h with CH_2Cl_2/MeOH (9:1 v/v). Sulfur was removed by addition of activated Cu. The free lipids were fractionated using silica gel–alumina column chromatography (50 mm × 5 mm i.d.). The saturated hydrocarbons were eluted with 20 ml hexane, followed by free alkanols and free FA (FFA) fractions, which were successively eluted using 20 ml of 20% EtOAc in hexane and 20 ml MeOH, respectively. The extracted samples were saponified with 0.5 M KOH in MeOH under reflux for 2 h to release bound lipids. The mixtures were centrifuged and the supernatant decanted. The bound alkanols were extracted with *n*-hexane/Et_2O (9:1 v/v). After acidification to pH 1 by addition of HCl, bound FAs (BFAs) were extracted with CH_2Cl_2. All fractions were analyzed using gas chromatography (GC) and GC-mass spectrometry (GC–MS). Prior to GC and GC–MS, the free and bound alkanol fractions were derivatized with acetic anhydride/pyridine (1:1 v/v). The FFA and BFA fractions were methylated with saturated HCl-MeOH (100 °C, 1 h), to form the FA methyl esters (FAMEs).