Reconstructing the climatic history of an ancient monastic site in Bangladesh using lipid biomarkers

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Abstract

Long geological epochs can be preserved by lipids in sediments. Lipid biomarkers are important tools in the analysis of environmental and biotic change throughout Earth history, and they can provide insights into the co-evolution of life and environments both in deep time and on the modern Earth. The proposed method is applied to analyse Lipids on soils sampled and collected at different interval of time. Prior to ^{14}C analysis, charcoal samples were taken from soil samples and treated using the traditional acid-alkaline-acid method. Finally, the samples were subjected gas chromatography and gas chromatography/mass spectrometer for extraction. The results show that the treated soils experienced a range of cooler to warmer climate conditions throughout the Pala Dynasty (730-1080 AD). In this article, we examine how lipid biomarker data can be used to reconstruct the palaeoenvironmental conditions in archaeological soils. This study represents a major prerequisite for the future application of lipid biomarkers on sediments.

Keywords: *Palaeoenvironment, Lipid biomarkers, Sediments, archaeological soils.*

1. Introduction

Due to a dearth of researchers situated in the region, our current understanding of Bangladesh's Holocene climate history is restricted. In addition to providing valuable information for paleoenvironmental reconstruction, lipid biomarkers in soils and sediments can be a highly diagnostic tool for addressing particular queries about minor differences in organic matter brought on by anthropogenic activity and various overlying vegetation changes (van Bergen et al., 1997). Geological components known as lipid biomarkers can reveal an endless supply of information about biotic origins and environmental conditions. They include both functionalized biolipids and their hydrocarbon derivatives. Lipid biomarkers have been detected in rocks up to 1.6 billion years old and frequently maintain the hydrocarbon structure of their biotic counterparts despite diagenetic and catagenetic modification. These qualities have participated in the widespread adoption of lipid biomarkers across several fields.

At archaeological sites, lipid biomarkers are substances whose carbon skeletons imply a connection to natural products linked to previous human activity. Antiquity's lipid biomarkers are substances whose carbon skeletons point to a connection with naturally occurring products linked to past human activities. Similarmy, lipids are great candidates for use as biomarkers in paleoenvironmental and archaeological investigations due to their resistance to degradation and likelihood of survival at the original site of deposition due to their intrinsic hydrophobicity.

The use of biomarkers in late Quaternary paleoclimatology was innovative by Brassell et al. (1986). Since then, lipid biomarkers have been widely employed by researchers as environmental and paleoclimatic indicators in oceanic (Brassell et al. 1986; Volkman et al. 1995; Müller et al. 1998; Gong and Hollander 1999), lake sediments (Cranwell 1973, 1974, 1984; Meyers and Ishiwatari 1993; Street-Perrott et al. 1997; Meyers and Lallièr-Verges 1999; Huang et al. 1999; Ficken et al. 2000; Meyers and Teranes 2002; Schwark et al. 2002; Meyers 2003; Gayantha, 2020), peat deposits (Quirk et al. 1984; del Rio et al. 1992; Karunen et al. 1983; Dehmer 1993; Farrimond and Flanagan 1995; Avsejs et al. 1998; Lehtonen and Ketola 1990, 1993; Duan and Ma 2001; Xie et al. 2000, 2003a; Zhou et al. 2005) and loess–paleosol successions (Lin et al. 1991; Wang et al. 1997; Wang and Follmer 1998; Hatté et al. 1998, 2001; Liu et al. 2002; Xie et al. 2003b, 2003c; Zhang et al. 2003, 2006).

Additionally, lipid compounds frequently retain the original source's functional group features and fundamental skeleton structure (Venkatesan 1988). As a result, studying the lipid compositions in different recent depositional settings can reveal a lot about the origin and diagnostic processes of organic matter. Additionally, this data can be used to recreate the deposition conditions from the palaeoenvironment (Venkatesan 1988; Rieley et al. 1991; Logan and Eglinton 1994).

This paper presents the method of lipid biomarkers recovered from the late Holocene-aged archaeological soils of the Somapura Mahavihara archaeological monastery site, northwestern Bangladesh. The step-by-step procedure to collect soil samples, soil dating and analytical methods as well are discussed in the later sections of this article.

2. Study site location

Paharpur is one of the most important archaeological sites in Bangladesh where the remains of the most important and the largest known Buddhist monastery south of the Himalayas have been excavated. The great architectural attraction during the Pala period was the Somapura Mahavihara (Mahavihara meaning 'large monastery') is located in the northwestern Bangladesh. This site was occupied from prehistoric times until the early/middle of the 8th century.

The Somapura Mahavihara site is situated in the village of Paharpur, Badalgacchi Upazila of Naogaon District, between latitudes 25°1.79'–25°1.95'N and longitudes 88°58.50'–88°58.70'E (Figure 1). The site is 5 km west of Jamalganj railway station in Joypurhat District, 14 km west of Joypurhat and 28 km north of Naogaon District headquarters and it is connected with these places by railroad.

The location of the Somapura Mahavihara is approximately half way down an old road between Pundranagar (present Mahasthan), the ancient capital of Pundravardhana, and the secondary capital at Kolivarsa (modern Bangarh) a position which must have been strategically ideal to the founder of the monastery.

The Paharpur region is well-drained by numerous small, entrenched meandering streams and rivers. The Old Jamuna River flows from north to south and maintaining a meandering course, forming many Oxbow Lakes. The traces of relict watercourses are detectable from the air and mostly run in a north-south direction, although an east-west arm appears to have extended laterally just south of the monastery. At their lowest points, these water courses remains as 'bils' or catchment's ponds which flood to lakes, over many acres, during the monsoon period but cam dry up altogether in the winter. A small bil exists northeast of the monument and a much larger one to the southwest, but both are being reduced in size, each year, by silt and cultivation (Chowdhury 2003).

Figure 1. Location map. (A) General map of Bangladesh (after Khan, 1991); (B) More detailed view of the Paharpur study area showing the location of Trench 1 from which soil samples were collected (based on an ASTER FCC image)

3. Geology

The site sits on the Pleistocene-Holocene aged Barind Clay Residuum, which is the largest Quaternary physiographic unit of the Bengal Basin and comprises slightly elevated landform terraces within the alluvium. The underlying sediments - known as the Pleistocene-Holocene Madhupur Clay/Barind Clay - are considered to be marine-estuarine deposits (Brammer 1996). The Barind Clay Residuum is a strongly iron-stained, clay-rich unit of weathered alluvial sediment that is compact and resistant to erosion. In the study area it consists of two zones: an upper zone comprising a grey to yellowish brown mottled clayey silt/silty clay, with a lower zone of red and brownish-yellow mottled clayey silt; the amount of sand increases gradually with depth. Both zones feature abundant pottery fragments, brick chips and plant roots, and are described as archaeological soils belonging to the Holocene epoch (Figure 2).
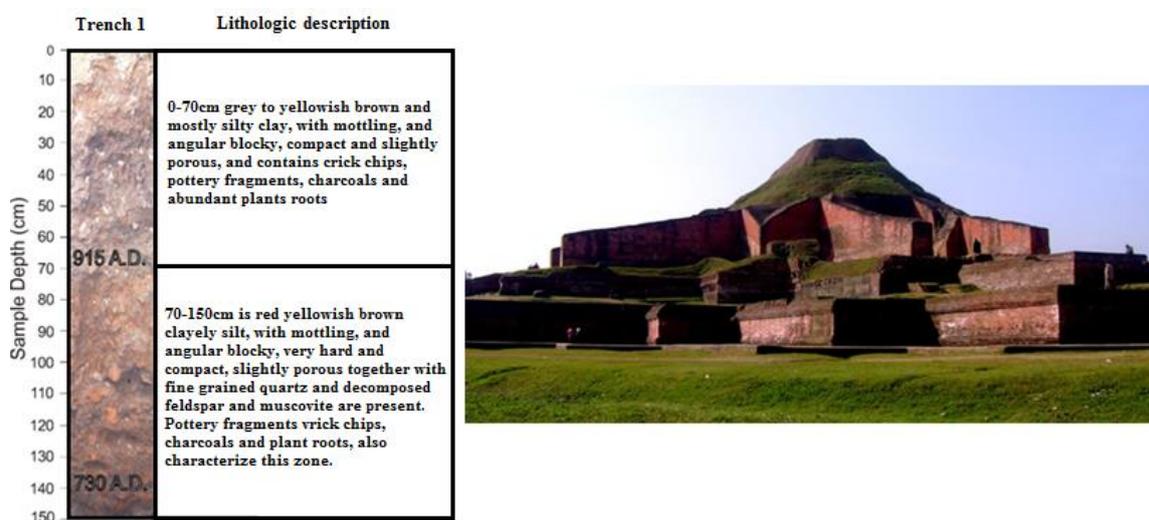
Figure 2. Photograph showing the archaeological ruins of the Somapura Buddhist monastery, Paharpur, Naogaon District, Bangladesh (right) and lithological description of Trench 1 section (left).

4. Materials and methods

4.1. Soil sampling

The archaeological soils of Somapura were sampled in May 2020 and later in August of the same year. For the collection of samples one trench (labeled Trench 1), was excavated from the surface to the first occupation level of the monastery. Trench 1 is located in the vicinity of the northern outer wall of the monastery (near the main entrance of the monastery), has a maximum depth of 1.50 m below surface, and the lower and upper zone of the Barind Clay Residuum is clearly present. Samples for lipid analyses were mostly collected at regular intervals of 5 cm (Figure 2).

4.2. Radiocarbon Dating

Charcoal samples were collected from soil samples and were subjected to the conventional acid–alkaline–acid treatment prior to 14C analyses. The sample was first gently crushed /dispersed in deionized water. It was then given hot HCI acid washes to eliminate carbonates and alkali washes (NaOH) to remove secondary organic acids. The alkali washes were followed by a final acid rinse to neutralize the solution prior to drying. Then the solution containing the alkali soluble fraction is isolated/filtered and combined with acid. The soluble fraction which precipitates is rinsed and dried prior to combustion.

4.3. Extraction and separation

Lipids can be extracted from soil by a variety of different methods including supercritical CO2 (Schulten and Schnitzer 1991), ethanol (Grimalt and Saiz-Jeminez 1989), toluene-methanol (3:1) (Simoneit and Didyk 1978), a benzene-methanol azeotrope (3:1 v:v benzene:methanol) (Rice and MacCarthy 1989), solvent extraction (Dinel et al. 1990) as well as sequential extractions such as n-hexane, chloroform and supercritical n-pentane (Schulten and Schnitzer 1990). Moreover, the complete extraction and separation procedure for soil lipids was previously described in detail (Wiesenberg et al. 2004). In this study, the extraction and separation of soil lipids were performed as described by Xie et al. (2003b, 2004b).

For lipid extraction and separation, initially 15 samples of Trench 1 were air dried at room temperature. All the air-dried soil samples were crushed with a pestle and mortar and subsequently sieved to a 100 mesh (0.154 mm) to remove root fragments and provide homogeneous samples. 80 gms of each crushed sample were then extracted using a Soxhlet apparatus with chloroform for 72 h and native copper also added to remove sulfur. The extract was then concentrated on a rotatory evaporator under reduced pressure and transferred to a small vial. Following evaporation of the remaining solvent, the total extractable lipid was weighed. The total lipid extracts were fractioned by flash column chromatography (filled with silica gel 60) into saturated hydrocarbons, aromatics, and non-hydrocarbons by successively eluting with n-hexane, benzene, and methanol. The saturated hydrocarbons were then directly analyzed by gas chromatography–mass spectrometry (GC/MS) while the non-hydrocarbons containing acids, alcohols and ketons were derivatized with N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) before GC/MS analysis.

4.4. Analytical methods

Gas chromatography (GC) has a role to play in the analysis of all the major classes of lipids that exist in biological materials (Figure 3). The development of modern capillary columns has greatly extended the scope of GC, offering the necessary resolving power to separate the individual compounds present in the complex mixtures of lipids that are often recovered from soil.

While, used in combination with mass spectrometry, termed GC/MS, the facility is provided for both separation and the on-line recording of mass spectra that are required to make the structure assignments necessary for the study of biomarkers. In this study, gas chromatography and gas chromatography/mass spectrometer were used for lipid biomarker analysis of soil.

A Hewlett-Packard 5973 mass spectrometer, interfaced directly with an HP6890 plus gas chromatograph equipped with an HP-5MS fused silica capillary column (30 m x 0.25 mm inner diameter, 0.25 mm film thickness), was used for saturated hydrocarbon and non-hydrocarbon fractions. The operating conditions were as follows: temperature ramped from 70º to 280º C at 3 C/min, held at 280º C for 20 min, with He as carrier gas; the ionization energy of the mass spectrometer was set at 70 eV, with a scanning range from 50 to 550 amu. The compounds were identified by comparison of their retention times and mass spectra with those of reference compounds.

Because of low contents of organic compounds in soil, necessary preventative measures were taken to minimize laboratory contamination. All glassware was sequentially washed with detergent/water, chromic acid and double-distilled water, and then annealed in an oven at 450ºC for 24 h. Organic solvents were double distilled. Silica gel, cellulose extraction thimbles and filter papers were Soxhlet-extracted with dichloromethane (DCM) prior to use. The mill disk for pulverization was washed with water and ethanol. In addition, blanks were simultaneously processed under the same conditions as the archaeological soil samples to evaluate possible laboratory contamination. The total ion current traces of the blank samples analyzed by GC/MS were used to confirm that target compounds were below detection levels in the blanks.
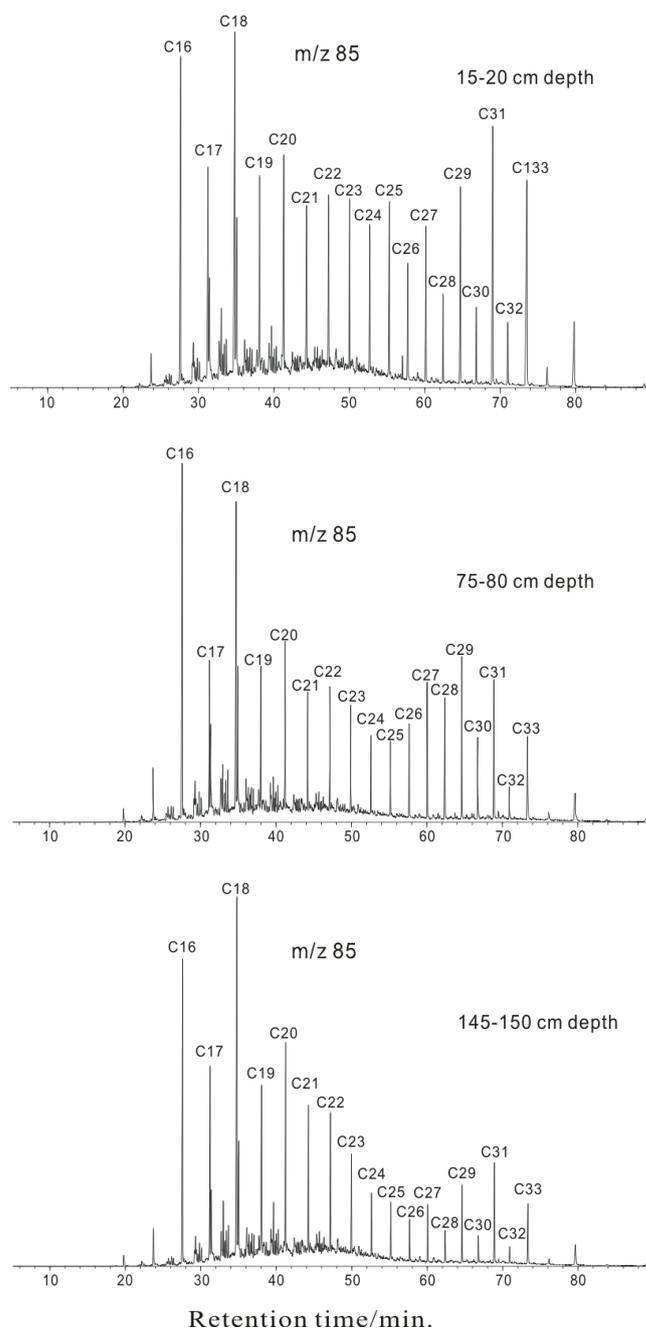
Figure 3. GC–MS mass chromatograms (m/z 85) showing n-alkane distributions of selected soil samples

5. Results

5.1. Dating

Two charcoal samples were analyzed for ^{14}C in the Quaternary age dating Lab. of Peking University, Beijing. The ^{14}C age of each charcoal sample was converted into a calibrated calendar age by OxCal software version 3.10 (Bronk-Ramsey 2005) using IntCal04 calibration curve (Reimer et al. 2004). The results of the OxCal calibration of the measured ^{14}C age are summarized in Table 1.

The radiocarbon dates thus obtained fit well with the known occupation history of the site based on written records, with archaeological sediment accumulation appearing to commence during the middle of the 8th century AD coincident with the first construction of the site.

Table 1. Radiocarbon dates from Trench 1, Paharpur archaeological site, Bangladesh

Lab. No.	Trench	Depth below surface (cm)	Material dated	Radiocarbon age (^{14}C yr B.P.)	Calibrated age (cal yr AD) (95.4% probability, 2 sigma)
BA 06800	1	67	Charcoal	1105±45	**915 AD** (810-1020)
BA 06801	**1**	**138**	**Charcoal**	**1295±40**	**730 AD** (650-810)

5.2. Climate reconstruction

All CPI values are greater than unity (≥2) suggesting a generally cooler climate throughout the time period, except for 77 cm depth where the CPI value was close to unity (1.8) suggesting accelerated microbial degradation and diagenesis of organic matter, implying a relatively warmer climate. The Pr/n-C_{17} and Ph/n-C_{18} ratios at the same depth where Pr/n-C_{17} and Ph/n-C_{18} ratios were high and varied from 6.2 to 8.6, suggesting a stronger microbial activity implied that a cooler to warmer conditions persisted around Paharpur and the surrounding region throughout the Pala Dynasty from 730 to 1080 AD (Figure 4). In this contribution, we present a climate conditions dominance from lipid biomarkers analysis. The technique of lipid biomarkers presented in this study represents a major prerequisite and useful for the future application of lipid biomarkers on a variety of sediments. Anyone correctly following this method article should be able to replicate the results obtained in this study.
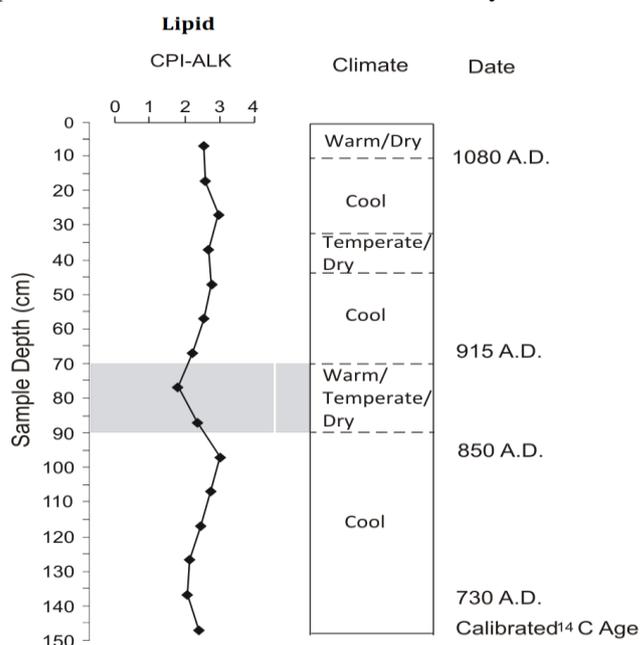
Figure 4. Composite graph of lipid analysis presenting the climate variability.

6. Conclusion

In this study, we present a climate conditions dominance from lipid biomarkers analysis in the city of Paharpur. From the results obtained, it is shown that the hydrocarbon fractions show a dominance of n-alkanes range from n-C_{16} to n-C_{33} with C_{max} at n-C_{18} and n-C_{31} or n-C_{33} in a bimodal distribution with distinct odd-over-even carbon predominance observed above n-C_{22} throughout the profile. All CPI values are greater than unity (≥ 2) suggesting a generally cooler climate throughout the time period, except for 77 cm depth where the CPI value was close to unity (1.8) suggesting accelerated microbial degradation and diagenesis of organic matter, implying a relatively warmer climate. The Pr/n-C_{17} and Ph/n-C_{18} ratios at the same depth where Pr/n-C_{17} and Ph/n-C_{18} ratios were high and varied from 6.2 to 8.6, suggesting a stronger microbial activity implied that a cooler to warmer conditions persisted around Paharpur and the surrounding region throughout the Pala Dynasty from 730 to 1080 AD. The technique of lipid biomarkers presented in this study represents a major prerequisite and useful for the future application of lipid biomarkers on a variety of sediments.

Acknowledgments

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