

RECONSTRUCTING YOUNGER DRYAS TEMPERATURE VARIABILTIY IN CENTRAL EUROPE BASED ON BRANCHED GLYCEROL DIALKYL GLYCEROL TETRAETHERS (BRGDGTS) IN LAKE TRZECHOWSKIE, POLAND



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# Inhoud

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## Abstract

The cause of the onset of the Younger Dryas is still a topic of discussion. High-resolution temperature reconstructions are necessary to examine this cold and dry phase of the last glacial period. These temperature records are scarce for the Younger Dryas, especially in Central Europe. Lake Trzechowskie, Central Poland, is an excellent location for high resolution climate studies, due to the accurate age model based on varve counting and tephrostratigraphy. This study is one of the first studies to apply the improved chromatography method that separates the 5- and 6-methyl isomer brGDGTs on a sediment core of a lake. The results show a gradual decrease in MAT of about 1.5 °C during the Younger Dryas. An increase in wind strength and an increase in aridity, based on n-alkane  $\delta D$  data of Collins et al. (unpublished), are recognized about 150 years after the onset of the temperature decline. The results support the theory that the temperature decline at the onset of the Younger Dryas is likely caused by a large influx of fresh water into the North Atlantic Ocean. This could have resulted in a decreased strength of the AMOC, an increase in sea ice in the North Atlantic Ocean and southward shift of the polar front. All these climatic changes have had a large impact on the European environments. A decreased impact of the westerlies on climate has been recognized on a west-east transect through Europe. The possibility of in situ production is an important drawback of the use of brGDGTs in lakes. This report also examines several approaches to verify the origin of brGDGTs in the lake and concludes that the results for the Trzechowskie Lake are valid.

# 1. Introduction

## 1.1 Younger Dryas

The Younger Dryas (YD) is the last cold period of the Weichselian glaciation, and occurred between 12,896  $\pm$  138 years BP and 11,703  $\pm$  99 years b2k based on Greenland ice core data (Fig. 1; Rasmussen et al., 2006). The extent of the event is not certain. Peteet (1995) states that the YD is mainly recognized in areas adjacent to the North-Atlantic Ocean. However, there is evidence of a cold period at the end of the last glacial in other areas on both the northern and southern hemisphere as well (Peteet, 1995; Andres et al., 2003; Shakun & Carlson, 2010). While it seems that the cold phase was widespread, Williams et al. (2005) suggested that the YD was not a global event, as climate reconstructions for New Zealand do not show a decrease in temperature around 12 kyr BP.

The abrupt cooling had an extensive impact on the climate and ecosystems around the North Atlantic. Pollen evidence in Europe shows a sudden southward shift in terrestrial plant communities at the onset of the YD (e.g. Brauer et al., 1999; Ammann et al., 2000; Slowinski et al., 2017). Similar evidence has been found on the North American continent (e.g. Shuman et al., 2002). Some taxa even migrated more than 300 km south within 100 years. The ecological changes were likely to be very rapid at the beginning and the end of the Younger Dryas, probably even within decades, due to the rapid rate of climate change (Brauer et al., 1999).

Only few temperature reconstructions exist for the Younger Dryas in Central Europe (e.g. Isarin & Bohncke, 1999; Dziedusynska et al., 2014). The existing temperature reconstructions for Poland during the YD are based on palynology and chironomid data. Isarin & Bohncke (1999) examined pollen data from northwestern and central Europe. They inferred that the mean July temperature in Poland should be around 13 °C for the Younger Dryas. Based on chironomids, the mean July temperature in Central Poland could have ranged between 14 and 15.8 °C (Dziedusynska et al., 2014). In winters, Younger Dryas temperatures could have dropped to below -20 °C (Isarin & Bohncke, 1999). This is likely to have caused discontinuous permafrost in the area (Renssen & Vandenberghe, 2003). The existing temperature reconstructions for Poland and Central Europe only represent summer or winter temperatures.

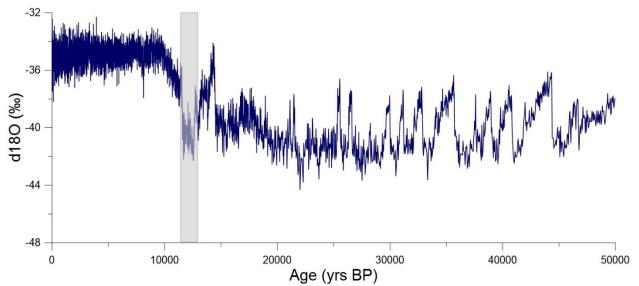


Fig. 1.  $\delta^{18}$ O record of the NGRIP ice core, Greenland, for the interval between 50,000 to 0 yrs before the year 2000. The grey rectangle indicates the Younger Dryas.

Furthermore, the cause for this cooling event is also much disputed. Broecker et al. (2010) suggests that the cooling during the Younger Dryas could be an integral part of the deglacial sequence of events. They state that a cold reversal equivalent to the YD occurred during the last four terminations. Therefore, the Younger Dryas may not have been an one-time event. The environmental changes during the onset of the YD occurred within a few years (Brauer et al., 2008), which makes this theory seem unlikely. The most widely accepted theory is that of an increase of glacial melting rates due to the increase in temperature, which caused a disturbance of the deep-ocean circulation (e.g. Fairbanks, 1989; Broecker et al., 1989). The origin of the fresh water is still unknown. Some studies suggest that a meltwater pulse from Lake Agassiz could have caused the increased amount of freshwater (e.g. Teller et al., 2002). Other studies suggest an increase in freshwater from glaciers and ice sheets on the northern hemisphere, as no morphological evidence has been found to support the hypothesis of a meltwater pulse at the start of the YD (e.g. Broecker, 2006). The increase of fresh water from melting glaciers and ice sheets on the northern hemisphere reduced the North Atlantic meridional overturning circulation (AMOC), and maybe even resulted in a complete shutdown (Broecker, 2003). The Gulf Stream transports heath from the lower latitudes towards Europe through the Atlantic Ocean. The water becomes heavy due to the cooling down of the water and increase in salinity due to formation of ice sheets in the northern part of the North Atlantic Ocean, and will sink to the bottom of the ocean. Increased freshwater results in less heavy water and a less strong overturning circulation. When the AMOC is weakened, as it might have happened during the YD, less heat could have been brought towards Europe (Broecker et al., 1990).

Not only temperature changed at the onset of the Younger Dryas, but wind strength and amount of precipitation are important environmental parameters which changed as well. It is thought that the wind strength increased abruptly around 12,679 yrs BP in Northwestern Europe (Brauer et al., 2008). The change in strength is attributed to a shift in the North Atlantic westerlies towards a stronger and more zonal jet (e.g. Isarin et al., 1997; Brauer et al., 2008; Lane et al., 2013). The influence of the westerlies decreases from western to eastern Europe. Hence, studying the evolution of temperature and precipitation along a W-E transect through time, and their relative phase relation at each site should provide new insights in the influence of disintegrating ice sheets and slow down of the AMOC on the remarkable cooling event during the YD. The amount of precipitation seem to decrease as well since the onset of the Younger Dryas in western Europe, based on hydrogen isotopes of plant waxes (Rach et al., 2014). Both the wind strength and change in aridity seem to be caused by an increase in sea ice in the North Atlantic Ocean. However, neither wind strength nor precipitation records are available for the Younger Dryas in Central Europe.

## 1.2 Lakes as sedimentary archives for past climate change

In order to create a dataset for temperature, precipitation and wind strength changes during the Younger Dryas, lake sediments are very useful. Lake records are excellent sedimentary archives that record past climatic changes, especially for the Late Quaternary. These sediments are relatively less affected by diagenetic process, and thus are more likely to still contain past climatic information. Lakes are very useful sedimentary records as they can be used as archive for many types of proxies, including palynological, organic, sedimentological, chemical and organic geochemical proxies. Extensive diagenetic losses of the organic matter, produced in or entering a lake, only takes place early after deposition (Meyers & Lallier-Vergès, 1999), but the majority of the material shows limited alteration after burial. Therefore, changes in the mineral, chemical and biological composition of the lacustrine sediments contain evidence of past environmental and climatic changes.

The use of varved lake sediments is in particular useful. Varves are annual sediment layers that are often deposited in deeper and oxygen depleted parts of lakes. The layers originate from seasonal alteration in which darker organic-rich layers alternate with light-hued mineral rich sediments (Ruddiman, 2001). Only few age constraints within the varved sediments are required to create an accurate age model for the lakes, as annual layers can be counted and the ages can be generated by AMS radiocarbon dating or Ar-Ar dating of volcanic ashes. Especially the last method is very useful for dating Younger Dryas-aged lakes in Europe. A large eruption of the Laacher See Volcano in Germany during late Allerød period was dated at 12,880 ± 40 varve yrs BP (Brauer et al., 1999). The dispersal of ash was widespread, as over a large part of northeast, south and southeast Europe a clear ash layer can be found back in the sedimentary record (Bogaard & Schmincke, 1985). This makes it possible to trace the volcanic ash layer in lakes across Europe and link the different lake records of the Younger Dryas.

## 1.3 Glycerol Dialkyl Glycerol Tetraeathers (GDGTs)-based proxies

Glycerol dialkyl glycerol tetraethers (GDGTs) based proxies can be used to create a record for temperature and wind strength changes. GDGTs are membrane lipids, and can be divided into two main groups: (1) isoprenoidal GDGTs (isoGDGTs), produced by archaea predominantly in the marine environment, and (2) branched GDGTs (brGDGTs), produced by bacteria primarily in peat bogs and soils (Sinninghe Damsté et al., 2000; Weijers et al., 2006). The TEX<sub>86</sub> index (TetraEther indeX of tetraethers consisting of 86 carbon atoms) was the first palaeothermometer that used membrane lipids of archaea to reconstruct past sea surface temperatures (Schouten et al., 2002). The index is based on the number of cyclopentane rings in the membrane lipids derived from marine Thaumarchaeota (isoGDGTs). These lipids are mainly produced in marine environments (Schouten et al., 2002), but are also found in soils (e.g. Weijers et al., 2006) and freshwater conditions (e.g. for lakes: Powers et al., 2004; Bechtel et al., 2010; Tierney et al., 2012, and for rivers: French et al., 2015). Branched GDGTs occur in various forms, with different amounts of methyl groups attached to the alkyl chains (4-6) and 0-2 cyclopentane moieties (Fig. 3). A survey of brGDGTs in globally distributed surface soils revealed that the amount of cyclopentane moieties (cyclisations) of the branched GDGTs, abbreviated as CBT, is primarily related to the pH of soils (Weijers et al., 2007). The relative amount of methyl branches (methylations) of the branched GDGTs, abbreviated as MBT, is correlated with annual mean air temperature (Weijers et al., 2007). Hence, analysing downcore changes in brGDGT distributions in a sedimentary archive can generate records of palaeoenvironmental and palaeoclimatic changes. However, the exact group of bacteria that produce these lipids is still unknown, so that cultivation experiments to validate the factors controlling brGDGT distributions is not (yet) possible.

A new type of branched GDGT was discovered, after the recent introduction of a new analytical method with improved chromatography, i.e. brGDGTs with a methyl branch on the 6-position rather than on the 5-position (De Jonge et al., 2013; Fig. 3). The discovery of these isomer aids in the accuracy of the brGDGT-based transfer function for palaeotemperature reconstruction (De Jonge et al., 2014a). Recent studies shows that brGDGTs in lakes do not only originate from catchment soils only, but are also produced in the lakes themselves (Tierney and Russel, 2009; Sinninghe Damste et al., 2009; Weber et al., 2015). The in situ contribution of lacustrine brGDGTs to the soil brGDGTs can complicate paleoclimate reconstruction, as lacustrine brGDGTs appear to have a different composition than the brGDGTs that originate from soils (e.g. Weber et al., 2015). It is likely that not all GDGTs that are produced in lakes are recognised, ss this is only a recent discovery. Nevertheless, caution needs to be taken with the use of the brGDGTs from lake

sediments, as it is still impossible to separate the possible lacustrine overprint from the soil brGDGT record.

The changes in GDGT distribution also record changes in the environment other than the temperature changes. Another important environmental indicator is the GDGT-0 over crenarchaeol (GDGT-0/cren) index (Sinninghe Damsté et al., 2009; Blaga et al., 2009) as the isoprenoid GDGT does not contain any cyclopentyl rings, is known to be predominantly produced by Euryarchaeota (Pancost et al., 2001) and Group I Thaumarchaeota (Sinninghe Damsté et al., 2002). These Euryarchaeota are known to be capable of performing anaerobic oxidation of methane (Pancost et al., 2001; Aloisi et al., 2002). Crenarchaeol is an unique GDGT as it contains a cyclohexane moiety, aside from four cyclopentane moieties (Sinninge Damsté et al., 2002). At the time of its identification, it was thought that crenarchaeol was specific for Group I Crenarchaeota. However, it is now thought to be specific for the phylum Thaumarchaeota (Schouten et al., 2013).

The rationale behind the GDGT-0/cren ratio is that both lipids can be derived from Group I Thaumarchaeota, whereas Euryarcheota synthesize GDGT-0, but no crenarchaeol. If the ratio is >2, anaerobic oxidation of methane likely takes place on substantial scale (Blaga et al., 2009; Sinninghe Damsté et al., 2009). Normally, the largest part of the methanogenesis takes place in the anaerobic lake sediments as mineralisation process. However, if a part of the water column is anoxic, the methanogenic activity could also occur there (Sinninghe Damsté et al., 2009). The cause for an anaerobic water column is often stratification. Through bad mixing of the water column, the deeper part will not be replenished with oxygen from the atmosphere. Due to oxidation of organic matter, the oxygen in the lower part of the water column will run down and will cause stratification of the water column. The degree of mixing of the water column is influenced by (1) wind strength, (2) temperature and (3) in salt water bodies, the influx of fresh water. Therefore, the GDGT-0/cren ratio could also be an indicator of wind strength and temperature in lakes.

## 1.4 Objectives and research questions

The main aim of this project is to generate a high resolution temperature record for the Younger Dryas in Central Europe using downcore brGDGT distributions in sediments from Palaeolake Trzechowskie in Central Poland to gain better knowledge on the processes that were driving and affecting the cooling during the YD. In order to do so, firstly the origin of the brGDGTs should be determined, as brGDGTs are mainly produced in soils, but are also synthesized in the water column and lacustrine sediments themselves (Tierney & Russell, 2009; Sinninghe Damsté et al., 2009). Therefore, this study aims to contribute to our understanding of the source of brGDGTs in lake sediments, as only few studies have used the method with improved chromatography on lake sediments. Changes in the occurrence of brGDGTs in the Trzechowskie Lake can aid in assessing the sources of brGDGTs, and help improving the accuracy of brGDGTs as a proxy for paleotemperature. The generated temperature record will subsequently be compared with an existing precipitation record based on the hydrogen isotopic composition of plant waxes (δD<sub>wax</sub>) obtained from the same sediment core (Collins et al., unpublished) to examine the relationship between variations in temperature and precipitation during the YD in Central Europe. The results of the GDGT analysis will also be compared to lithological changes and changes in pollen assemblage (Slowinski et al., 2017) at the onset of the Younger Dryas. Additionally, the temperature record will be compared to other temperature records across Europe to assess the influence of the Atlantic Ocean and the westerlies wind system along an east-west transect in Europe during the Younger Dryas.

# 2. Methods

## 2.1 Site description and sample collection

Recently, a varved sedimentary record from the Trzechowskie palaeolake (TRZ) has been recovered from the Tuchola Pinewoods in northern Poland (Wulf et al., 2013). The palaeolake Trzechowskie (53°52'22 N/18°14'58 E) is located about 60 km southwest of Gdańsk (Fig. 2). The present MAT in the Tunchola Pinewoods is approximately 7 °C (Kozlowska-Szczesna, 1993). The Trzechowskie palaeolake has been discovered close to the still existing Czechowskie Lake with which it formed a larger lake during the last glacial period. The palaeolake has recorded the Allerød-Younger Dryas boundary up to the Early Holocene. Wulf et al. (2013) has shown that the lake has annual layering in response to the seasonal temperature and precipitation changes. The presence of annual varves enables the generation of an age model with high accuracy. Hence, the lake sediments are likely to have an exceptional record of the sudden climatic changes that happened during the termination of the last glacial.

During the Weichselian period, the lake was formed in a subglacial channel (Ott et al., 2016; Slowinski et al., 2017). The size of the lake is 73 ha and it has a maximum water depth of 32 m. Due to this relatively small size, the lake predominantly records annual lamination, which are calcite varves. The age model for the core is based on a combination of varve counting, AMS <sup>14</sup>C dating of organic material,

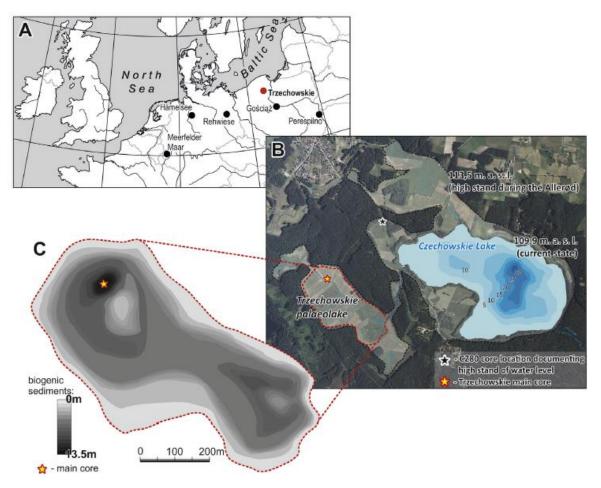


Fig. 2. Location of the Trzechowskie palaeolake, a) map of Europe with the location of the lake, b) air photo of study area and c) thickness of biogenic sediments, after Slowinski et al. (2017).

tephrostratigraphy and biostratigraphy (Slowinski et al., 2017). Varve counting has been performed for the laminated section of the core between 12.62 and 12.45 m depth. A total of 9 samples has been used for AMS <sup>14</sup>C dating and calibration with OxCal v4.2 software (Ramsey, 2001) with the IntCal13 dataset (Reimer et al., 2013). The Laacher See Tephra has been identified in the core at 12,880  $\pm$  40 varve yrs BP (Wulf et al., 2013). The boundary between the Younger Dryas and the Holocene is defined according to pollen data and synchronised with the Lake Gosciaz sediment record (Slowinski et al., 2017).

A total of 260 samples from the interval between 10.4-13.3 kyr BP, covering the entire Younger Dryas, was selected for biomarker analysis, resulting in an average resolution of 5-30 yrs. The samples have been collected by the team of Wulf et al. (2013), using a Livingstone type piston corer to core three parallel and continuous composite cores (TRZ-1a, TRZ-2a and TRZ-3a). A composite sedimentary profile was established and sampled for multi-proxy analyses. Details on the composite profile construction and the preparation of samples, other than for biomarker analysis, are described by Wulf et al. (2013) and Slowinski et al. (2017).

## 2.2 Sample preparation and GDGT analysis

Lipid biomarkers have been extracted from the lake sediments a mixture of dichloromethane (DCM) and methanol (9:1, v/v) at GFZ Potsdam. The obtained total lipid extract (TLE) was evaporated under near vacuum and separated in an apolar and a polar fraction over an activated  $Al_2O_3$  column by using hexane:DCM 9:1 and DCM/methanol 1:1, respectively.

The polar fractions were analysed for GDGTs during this project. First, an internal C<sub>46</sub>-GDGT standard (99 ng/vial) was added to the polar fraction for the quantification of the brGDGTs of the lake sediments. After drying under a continuous N<sub>2</sub> flow, the fractions were re-dissolved in a hexane/propanol (99:1) mixture, and filtered over a 0.45  $\mu$ m PTFE filter prior to analysis using high performance liquid chromatography mass spectrometer (HPLC-MS) at GML Utrecht. The HPLC-MS applies the latest method with improved chromatography by Hopmans et al. (2016), separating the 5- and 6-methyl brGDGTs. A few samples had particles in the solvent that were too large. Therefore, these samples were required to have an additional column filtration to remove these particles.

## 2.3 Proxy calculations

Multiple proxies are used to understand the distribution of the GDGTs through time. For the calculations of these proxies, the integrated areas of the GDGT peaks in the HPLC chromatograms were used. The Roman numerals and letters in the equations below indicate the type of GDGT, as shown in figure 3. A few of the equations are not yet calibrated to the newly used method to separate the 5-methylated and 6-methylated brGDGTs (De Jonge et al., 2013). Therefore, these equations should be applied with caution. The following equations were used to quantify the proxies:

$$MAT_{mr} = 7.17 + 17.1 (Ia) + 25.9(Ib) + 34.4(Ic) - 28.6(IIa)$$

 $R^2$  = 0.68, RMSE = 4.6 °C (De Jonge et al., 2014a), this equation uses the abundances of each brGDGT relative to the total amount of brGDGTs

$$MBT'_{5ME} = \frac{Ia + Ib + Ic}{(Ia + Ib + Ic) + (IIa + IIb + IIc) + IIIa}$$

De Jonge et al. (2014a)

$$CBT' = \log(\frac{Ic + IIa' + IIc' + IIIa' + IIIb' + IIIc'}{Ia + IIa + IIIa})$$
$$pH = 7.15 + 1.59 \cdot CBT'$$

R<sup>2</sup> = 0.85, RMSE = 0.52 units (De Jonge et al., 2014a)

$$BIT = \frac{Ia + IIa + IIa' + IIIa + IIIa'}{Crenarchaeol + Ia + IIa + IIa' + IIIa + IIIa'}$$

Modified after Hopmans et al. (2004)

$$Methanogenesis = \frac{GDGT - 0}{Crenarchaeol}$$

Blaga et al. (2009), Sinninghe Damsté et al. (2009)

$$\#rings_{tetra} = \frac{Ib + 2 \cdot Ic}{Ia + Ib + Ic}$$
$$\#rings_{penta 5me} = \frac{IIb + 2 \cdot IIc}{IIa + IIb + IIc}$$
$$\#rings_{penta 6me} = \frac{IIb' + 2 \cdot IIc'}{IIa' + IIb' + IIc'}$$

Sinninghe Damsté et al. (2016)

$$IR_{penta} = \frac{IIa' + IIb' + IIc'}{\sum pentamethylated brGDGTs}$$
$$IR_{hexa} = \frac{IIIa' + IIIb' + IIIc'}{\sum hexamethylated brGDGTs}$$

Sinninghe Damsté (2016), modified after De Jonge et al. (2014a)

$$sum_{tetra} = \frac{Ia + Ib + Ic}{\sum brGDGTs}$$

$$sum_{penta} = \frac{IIa + IIa' + IIb + IIb' + IIc + IIc'}{\sum brGDGTs}$$

$$sum_{tetra} = \frac{IIIa + IIIa' + IIIb + IIIb' + IIIc + IIIc'}{\sum brGDGTs}$$

Sinninghe Damsté (2016)

$$5 - me = \frac{IIa + IIb + IIc + IIIa + IIIb + IIIc}{\sum brGDGTs}$$
$$6 - me = \frac{IIa' + IIb' + IIc' + IIIa' + IIIb' + IIIc'}{\sum brGDGTs}$$

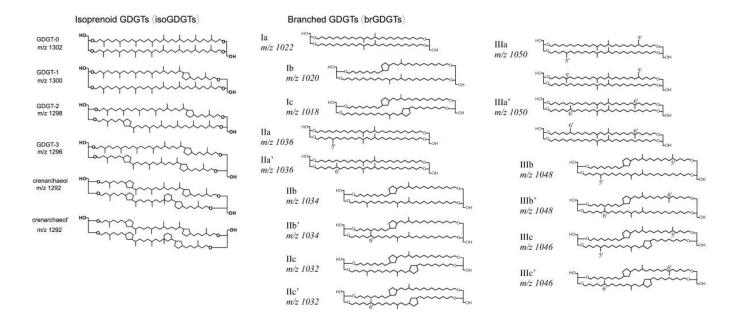


Fig. 3. Chemical structures of Glycerol Dialkyl Glycerol Tetraether (GDGT) membrane lipids, modified after Pearson et al. (2011) and De Jonge et al. (2014a).

## 3. Results

The following results have been produced with the improved chromatography method that separates the 5- and 6-methyl isomers of the brGDGTs, as described by De Jonge et al. (2013). The area under the chromatogram peaks have been integrated and used in the equations for the proxies. Some chromatograms showed a 'spike' around the peak of the 1050 GDGTs. The spike is recognized in chromatograms of 86 samples around the retention time of 25-27 min. The cause of the spike is unknown, but is likely to be sought in the performance of the HPLC-MS machine. The spike causes the peak of the 1050 GDGT to be distorted. This resulted in incorrect integrations of the peaks in the chromatogram. Therefore, these samples will not be used in the plots. The removal of these samples do not affect the resolution of the record too much, as still 141 samples can be used. The results of the calculations have been plotted in figure 4.

## 3.1 Presence and abundance of brGDGTs

BrGDGTs are present in the entire sedimentary column. The absolute amount of branched GDGTs in the samples varied significantly through time, between 13,500 and 49 ng brGDGTs per gram sediment (Fig. 4). The amount of branched GDGTs is low during the first part of the record. A rapid rise in the absolute amount is recognised around 11,523 yrs BP. The amount of brGDGTs during the Allerød period and the first 200 years of the Younger Dryas is slightly higher than during the other part of the Younger Dryas. Crenarchaeol is also present during the complete measured interval. However, some of the chromatograms had a peak of crenarchaeol that was too small to integrate. This is why these samples have been removed from the plot as they would bias the interpretation of the plots. The lowest amounts of crenarchaeol are found between 12,799 and 11,523 yrs BP. Both ends of the interval are marked by an abrupt drop or rise in value.

## 3.2 Distributions brGDGTs (BIT, GDGT-0/cren, IR, #rings)

The Branched and Isoprenoid Tetraether (BIT) index values are very high during the whole sampled time interval. The values range between 0.99 and 1.00 (Fig. 4). The samples with a BIT index value of 1.00 have a crenarchaeol concentration below the detection limit. Therefore, these samples have been removed from the plot. The lowest values of the index are recorded between 13,022 and 11,655 yrs BP, with a period of higher values between 12,779 and 12,595 yrs BP. Remarkable is the sudden rise of the BIT index at 11,655 yrs BP. The abundance of the GDGT-0 relative to crenarchaeol (GDGT-0/cren) varies widely, with values of 21 at 13,022 yrs BP to 905 at 11,486 yrs BP. This index shows higher values between 12,799 and 12,669 yrs BP. The values of the proxy are low during the Allerød and Younger Dryas periods, but rises abruptly at the start of the Holocene (at 11,645 yrs BP).

The Isomer Ratio (IR) is the fractional abundance of the penta- ( $IR_{penta}$ ) and hexamethylated ( $IR_{hexa}$ ) 6-Me brGDGTs divided by the total of penta- and hexamethylated brGDGTs (Sinninghe Damsté, 2016). Values for soils range between 0 to 1 for both, the  $IR_{penta}$  and the  $IR_{hexa}$ . For the Trzechowskie Lake, the values vary on average between 0.5 for the YD and 0.6 for the Allerød and Holocene. The  $IR_{penta}$  shows a clear drop in values from 12,669 to 11,655 yrs BP (Fig. 4). A decline for the  $IR_{hexa}$  starts around 12,843 yrs BP, but intensifies around 12,664 yrs BP. The termination of these low values is recognised around 11,645 yrs BP, practically the same age as for the  $IR_{penta}$ . The position of the methyl branch (5-me and 6-me) indicates the percentage of GDGTs that contain the 5-methyl and 6-methyl group, respectively, compared to the total amount of brGDGTs. That is why both indices show a simultaneous but inverse reaction to the

environmental changes during the late Pleistocene-early Holocene. The 5-me index is high between 12,669 and 11,655 years BP, while the 6-me is low during this interval.

The number of rings (#rings) in the tetramethylated brGDGTs is always lower than 0.3, and lower than 0.4 for the pentamethylated brGDGTs (Fig. 4). The highest values for these indices are recognized during the Younger Dryas, where the values are about 0.1 higher than during the Allerød and Holocene. The onset of the increase in values for both the tetra- and pentamethylated brGDGTs is around 12,642 yrs BP.

## 3.3 Temperature and pH

Reconstructed mean annual temperatures (MAT<sub>mr</sub>) in the period between 13,360 and 10,457 yrs BP range from 5.2 °C to 8.4 °C (Fig. 4). The lowest temperature of 5.2 °C has been recorded during the Younger Dryas at 12,153 yrs BP, while the highest temperatures of higher than 8 °C have all been recorded during the early Holocene. The average MAT<sub>mr</sub> for the reconstructed period is 6.6 °C. Another way to express temperature is with the Methylation of Branched Tetraether (MBT) index. A new MBT' ratio has been developed, based on the recognition of the 5-methyl and 6-methyl brGDGTs. The ratio that correlates the best with MAT is the MBT'<sub>SME</sub> (De Jonge et al., 2014a). This ratio excludes the 6-methyl brGDGTs. The MBT'<sub>SME</sub> ratio start to decline around 12,822 yrs BP and rises rapidly around 11,604 yrs BP in the Trzechowskie record. These ages are exactly the same as those for the MAT<sub>mr</sub>.

The degree of methyl branching is also affected by temperature (Weijers et al., 2007; Sinninghe Damsté, 2016) and therefore a useful proxy in the temperature reconstruction. The tetramethylated brGDGTs (Ia, Ib, Ic) are very abundant in tropical soils, relative to the total amount of brGDGTs. In contrast, the hexamethylated brGDGTs (IIIa, IIIa', IIIb, IIIb', IIIc, IIIc') have higher abundances in high-latitude soils (Weijers et al., 2007). Therefore, the degree of methyl branching does not indicate absolute temperature changes, but indicates warmer and colder periods. The most pronounced change is observed in the hexamethylated brGDGT (sum hexa) record. The percentage of these brGDGTs is averaged 40% during the Allerød and Younger Dryad periods (Fig. 4). No significant change is recorded at the boundary of these periods. However, around 11,604 yrs BP, this percentage changes. After 200 years, the percentage of hexamethylated brGDGTs is about 10% lower. This is a shift towards higher temperatures.

A new Cyclisation of Branched Tetraether (CBT') ratio was developed by De Jonge et al. (2014a), which includes the difference between the 5-methyl and 6-methyl brGDGTs. This ratio is used to calculate the pH of soils. The CBT'-based pH values of the samples are plotted in figure 3. The pH ranges from 6.8 to 7.3 during the time interval of the record. A sudden drop in pH is recognised around 12,669 yrs BP (Fig. 4). The values remain low until a slight rise around 11,655 yrs BP. The new MBT ratio, called MBT', as developed by Peterse et al. (2012), is not applied anymore to the improved chromatography method as an index for soil pH or MAT. De Jonge et al. (2014a) created a new method to calculate soil pH and MAT, as described above. Only the CBT' ratio is used for pH reconstructions.

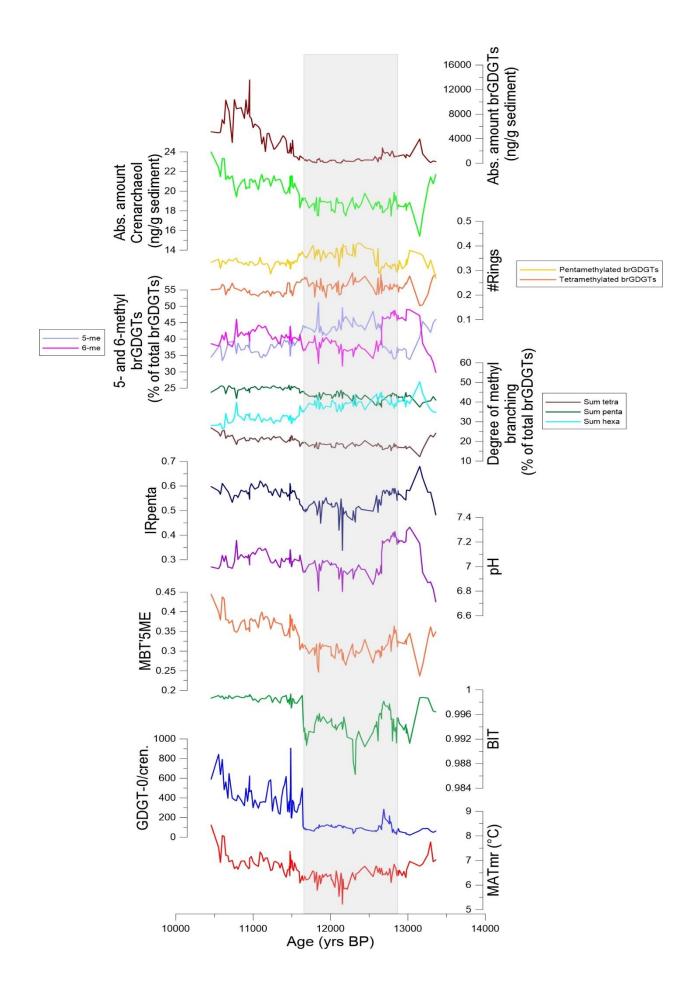
## 3.4 Timing of changes in indices

A change occurred in all indices during the interval of the sedimentary record. However, not all occur simultaneously with the starting and ending of the Younger Dryas, which have been defined by Rasmussen et al. (2006) at 12,896  $\pm$  138 and 11,703  $\pm$  99 yrs BP. The table below provides an overview of the changes in indices of the GDGTs. These indices are not all driven by the same processes and could therefore change at different ages. The timing of the onset of the temperature decline during the Younger Dryas was not only based on the MAT<sub>mr</sub>, but also on the MBT'<sub>SME</sub> index. The MBT'<sub>SME</sub> index correlates well with

temperature and therefore can be used as indicator for the timing of temperature change (De Jonge et al., 2014a). An important note is the fact that the GDGTs have different sources. Branched GDGTs are predominantly produced in soils and may therefore have a time lag to be introduced into the lake, while the archaeal GDGTs are synthesized within the lake.

	Start change (yrs BP)	Ending change (yrs BP)
MAT <sub>mr</sub>	12,822	11,604
GDGT-0/cren.	12,669	11,645
BIT	13,152 and 12,688	12,831 and 11,645
МВТ′5ме	12,822	11,604
рН	12,669	11,655
IRpenta	12,669	11,655
Sum hexamethylated brGDGTs	-	11,604
Position of methyl branch	12,669	11,655
#rings	12,642	11,645
Absolute amount of cren.	12,799	11,523
Absolute amount of brGDGTs	12,669	11,523

Fig. 4. On the next page. a) MAT<sub>mr</sub>, b) GDGT-0/cren, c) BIT, d) MBT'<sub>5ME</sub>, e) pH, f) IR<sub>penta</sub>, g) degree of methyl branching (as % of total brGDGTs), h) isomer location (as % of total brGDGTs), i) absolute amount of crenarchaeol, j) absolute amount of brGDGTs in Lake Trzechowskie.



#### 4. Discussion

#### 4.1 Source of the brGDGTs

It is essential to have knowledge about the source of the brGDGTs or the application of brGDGTs to a lacustrine environment. A recent discovery shows that we should take caution with applying brGDGT proxies, e.g. MAT<sub>mr</sub> and pH, for lake sediments. These proxies can only be applied when the brGDGTs are predominantly derived from soil erosion (Sinninghe Damsté, 2016). It was discovered that brGDGTs are not only produced in soils, as previously thought, but also in lake water and sediments (Tierney & Russell, 2009; Sinninghe Damsté et al., 2009; Tierney et al., 2010). Peterse et al. (2009) shows that the brGDGTs are also synthesized in marine sediments. The in situ produced brGDGTs could affect the distribution of the GDGTs in lakes and therefore the indices based on brGDGTs. It is important to validate that in situ production of brGDGTs does not affect the indices significantly as the biologic origin of the brGDGTs is still unknown (Weijers et al., 2006). Previously was thought that the BIT index could trace the input of terrestrial material to an aquatic basin (Hopmans et al., 2004). However, this index becomes less reliable due to the discovered in situ production. Therefore, multiple ways for the possible tracing of in situ production are proposed by Sinninge Damsté (2016). These approaches are based on coastal marine sediments and should therefore be applied with caution to lake sediments.

Sinninghe Damsté (2016) notes that calculated MAT, based on the De Jonge et al. (2014a) method, often underestimates the temperature. The underestimation could have been caused by a different response of the brGDGT-producing bacteria in aquatic environments to environmental parameters, e.g. temperature and pH, than soil bacteria. The mean annual temperature of the Trzechowskie Lake was at the coldest moment during the Younger Dryas 5.5 °C (Fig. 4). The recent MAT of Central Poland is about 7 °C (Kozlowska-Szczesna, 1993). Therefore, an under-estimation of the temperature seems unlikely as the temperature during the YD should be lower than the recent temperature. The consistent temperature is an argument for little to no in situ production of brGDGTs.

Another way to trace in situ production of brGDGTs, according

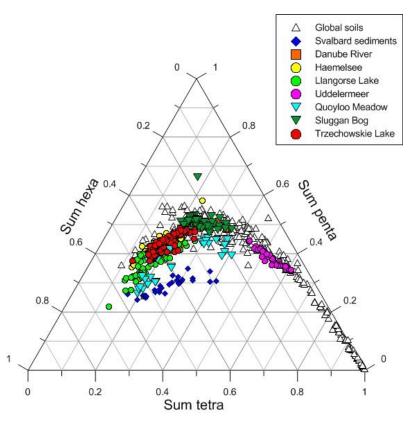


Fig. 5. Ternary diagram of the composition of brGDGTs showing fractional abundances of tetra-, penta- and hexamethylated brGDGTs of global soils (De Jonge et al., 2014a), Svalbard sediments (Peterse et al., 2009), Danube River (Freymond et al., 2017), Haemelsee (Bouwman, unpublished), Llangorse Lake (Maas, unpublished), Uddelermeer (Van den Bos, unpublished), Quoyloo Meadow and Sluggan Bog (Post, unpublished) and Trzechowskie Lake (this study).

to Sinninghe Damsté (2016), is to compare the values of the number of rings (#rings) of the tetramethylated and 5and 6-methyl pentamethylated brGDGTs of the Trzechowskie Lake to the global soil dataset. The values of the #rings do not exceed 0.4 for soils with a pH < 7, while the soils with a pH > 7 reach values up to 0.7 (De Jonge et al., 2014a). The pH values for the sediments in the Trzechowskie Lake are around the 7 and the #rings values rarely exceed the 0.4 (with exception of some values of the 5-methyl pentamethylated GDGTs) (Fig. 4). Therefore, it seems likely the #rings values also point to predominantly soil erosion as origin for the brGDGTs in the lake.

A third possible approach is to look at the degree of methyl branching of the brGDGTs (Sinninghe Damsté, 2016). The fractional abundances of the summed tetra-, penta- and hexamethylated brGDGTs of global soils (De Jonge et al., 2014a) show clearly defined boundaries, when plotted in a

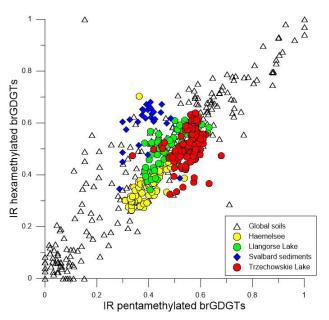


Fig. 6. Cross plots of the isomer ratio (IR) for penta- and hexamethylated brGDGTs. The datasets used are: global soils (De Jonge et al., 2014a), Haemelsee (Bouwman, unpublished), Llangorse Lake (Maas, unpublished), Svalbard sediments (Peterse et al., 2009), Trzechowskie Lake (this study).

ternary diagram (Fig. 5). As temperature is known to affect the degree of methyl branching, the tropical soils have higher abundances of tetramethylated brGDGTs (Weijers et al., 2007). In the temperate and cold soils, the penta- and hexamethylated brGDGTs become more important. It immediately becomes clear that the brGDGTs are produced in situ in the fjord sediments as they differ significantly with the brGDGT composition of the soils when the brGDGT composition of Svalbard fjord sediments (Peterse et al., 2009) is plotted. The data of other studies is also plotted on the ternary diagram, which confirms the presumption that the Llangorse Lake (Maas, unpublished) is influenced by in situ production and the Haemelsee (Bouwman, unpublished) is (almost) unaffected by in situ production of brGDGTs. It becomes clear that the data points of the Trzechowskie Lake fall within the boundaries of the global soil data set when plotting in the ternary diagram. These three approaches all indicate a terrestrial origin of the brGDGTs in the Trzechowskie Lake. Therefore, the results of the proxy analysis based on the brGDGTs are likely to be valid.

Sinninghe Damsté (2016) proposes a forth approach in order to trace the origin of the brGDGTs, namely to look at the Isomer Ratios (IRs). This approach was used by Bouwman (unpublished) to confirm the terrestrial origin. However, Sinninghe Damsté (2016) states that the IR is not helpful in identifying the source of brGDGTs in coastal sediments. Soils can cover the full range of IR values (0-1) for both the pentaand hexamethyladed brGDGTs (De Jonge et al., 2014a). Besides the degree of cyclisation of brGDGTs (Weijers et al., 2007), the dominance of 6-methyl brGDGTs is also thought to be an adaptation of brGDGTproducing bacteria to increasing pH (De Jonge et al., 2014a). When plotting the IR<sub>penta</sub> against IR<sub>hexa</sub> for the global soil data set (De Jonge et al., 2014a), the ratio is almost 1:1 (Fig. 6). The data of the Haemelsee (Bouwman, unpublished), Llangorse lake (Maas, unpublished), Svalbard sediments (Peterse et al., 2009) and Trzechowskie Lake (this study) are also plotted in the figure. It becomes evident from this plot that the Trzechowskie Lake, which is thought to have mainly terrestrial brGDGTs, plots closer to the Llangorse lake, which is thought to have in situ production of brGDGTs, than to the Haemelsee, which is also thought to have mainly terrestrial brGDGTs. Therefore, it seems likely to conclude that the IR is not helpful in determining the source of the brGDGTs in lakes.

## 4.2 Temperature record

## 4.2.1 MAT<sub>mr</sub> and MBT'<sub>5ME</sub>

The timing of the temperature decline precedes the change in lithology and change pollen assemblage of the sedimentary record with about 150 yrs (Fig. 7) (Slowinski et al., 2017). The lithology changes from laminated carbonate gyttja to weakly laminated carbonate gyttja and eventually to a carbonate gyttja without lamination. The difference in timing between the temperature decline and pollen change in Europe was also recognized at Lake Meerfelder Maar, Germany, by Rach et al. (2014). The abrupt cooling at the onset of the Younger Dryas in Greenland started at 12,846 yrs BP (Rasmussen et al., 2006). This falls well within the range of 40 yrs uncertainty for the age model of the Trzechowskie Lake. The simultaneous ages for the temperature drop during the onset of the YD of the Lake Meerfelder Maar (Rach et al., 2014), Greenland (Rasmussen et al., 2006) and the Trzechowskie Lake seem to confirm that the temperature decline in different areas in the northern hemisphere are likely to have the same origin.

The environment around the Trzechowskie Lake did not react to the temperature change immediately, as the sudden pollen change takes place approximately 150 yrs after the decline in temperature (Fig. 7). This could have been caused by the gradual cooling of Central Poland, as observed in the MAT<sub>mr</sub>. The delayed changes in pollen assemblage and lithology compared to MAT could also be caused by other factors, e.g. wind and precipitation (see sections 4.3 and 4.4). In other areas along the coast of the North Atlantic more rapid temperature changes have been recognized (e.g. Walker, 1995; Isarin & Bohncke, 1999; Blaga et al., 2013; Rach et al., 2014; Bouwman, unpublished). The gradual character of the temperature change in Poland could be attributed to the continental location of the lake.

The generated mean annual temperature record (MAT<sub>mr</sub>), based on the composition of the brGDGTs in the Trzechowskie Lake, shows a temperature decline of about 1 to 1.5 °C during the transition of the Allerød to the Younger Dryas. The most accepted hypothesis on the cause of the temperature drop isthat it is the result of large influxes of meltwater into the Atlantic Ocean (e.g. Fairbanks, 1989; Broecker et al., 1989). Little research has been done on the mean annual air temperature changes during the Younger Dryas in Central Europe. GDGT analysis, especially with the improved chromatography method as described by De Jonge et al. (2013), has only been performed on lakes a few times. Two datasets for the Holocene for the Uddelermeer, the Netherlands (Van den Bos, unpublished) and Llangorse Lake, Wales (Maas, unpublished) and one dataset for the Younger Dryas for the Haemelsee, Germany (Bouwman, unpublished) are available. Therefore, comparisons for the Younger Dryas in Central Europe have to be performed with other temperature proxies.

The data presented here shows a minimum mean annual temperature of 5.2 °C during the coldest phase of the Younger Dryas. This would mean that the seasonal temperatures fluctuated significantly, as summer temperatures were around 14 °C and winter temperatures up to -20 °C (Dziedusynska et al., 2014), whereas MAT changed only little over time. The increased seasonality during the Younger Dryas has been described by several authors. An amplitude increase of 10-20 °C during the YD is recognised on

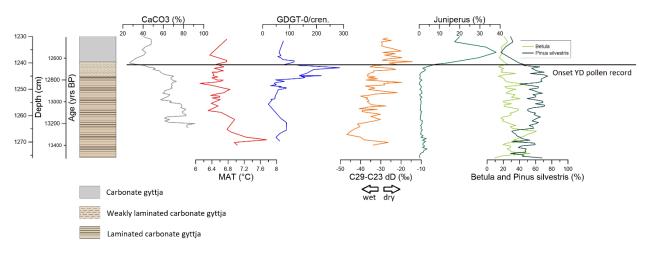


Fig. 7. Lithological section at the onset of the Younger Dryas, with a)  $CaCO_3$  (Slowinski et al., 2017), b) MAT<sub>mr</sub>, c) GDGT-0/cren, d)  $\varepsilon_{terr-aq}$  (Collins et al., unpublished), e) % Juniperus (Slowinski et al., 2017), f) % Betula and Pinus silvestris (Slowinski et al., 2017) for the Trzechowskie Lake.

the northern hemisphere (Denton et al., 2005; Lie & Paasche, 2006). The summers could be relatively mild and the winters could be cold, while the MAT only decreases little during the YD. The change in amplitude of seasonality supports the hypothesis of a fast-expanding ice cover as cause for the temperature change during Younger Dryas period (Lane et al., 2013).

The MAT has also been reconstructed in other parts of Europe. Blaga et al. (2013) concluded, based on a TEX<sub>86</sub> inferred temperature record of Lake Lucerne (Switzerland), that mean annual temperatures for Central Europe decreased with 2 °C at the onset of the Younger Dryas and a warming of 4 °C at the onset of the Holocene. Bouwman (unpublished) calculated the MAT<sub>mr</sub> for northwestern Germany based on brGDGTs in lakes. A decrease in temperature of about 3.5 °C was recorded during the Younger Dryas. Ideally, these results can be compared, while both methods to calculate temperature are different. These results might indicate an increasing MAT drop to the west on a west-east transect across Europe. The increased cooling to the west has also been described by other authors (e.g. Lowe et al., 1994; Coope et al., 1998; Van Asch et al., 2012). Van Asch et al. (2012) concluded, based on chironomid and pollen-based temperature reconstructions, that mean July temperatures decreased further west on a transect from Ireland to eastern Germany for the YD compared to the interstadial before the YD. The decreased temperature gradient can be explained by the decreasing influence of the westerlies in Poland due to continental location. The new evidence for the increased temperature gradient during the YD strengthens the theory that the influence of the Atlantic Ocean on climate and environments in Europe was more important during the Younger Dryas than during the previous interstadial.

There is no sign of a Mid-Younger Dryas Transition in the temperature record of the Trzechowskie Lake (Fig. 4.), which was recognized in the Haemelsee, Germany (Bouwman, unpublished). The transition is also not recognised in any of the other indices of the Trzechowskie Lake. The Mid-Younger Dryas transition is a sudden change in climate during the YD to a slightly warmer and drier climate (Isarin et al., 1998; Lane et al., 2013). The climatic changes halfway through the Younger Dryas could be caused by retreat of the Atlantic sea-ice margin during winter. This should have resulted in an increasing strength of the Atlantic Meridional Overturning Circulation and the retreat of the average polar front. The Mid-Younger Dryas Transition occurred at different times throughout a north-south transect of Europe. An offset of 120 yrs is found between Lake Maarfelder Maar in Germany and Lake Kråkenes in Norway, due to the gradual

retreat of the polar front (Fig. 9). The transition is dated at  $12,240 \pm 40$  varve yrs BP for the Lake Maarfelder Maar, precisely 100 yrs before the deposition of the Vedde Ash (Lane et al., 2013). The Trzechowskie Lake does not show this transition. The cause for this absence can again be sought in the continental location of the lake. The environment surrounding the lake could be affected less by the Atlantic westerlies and therefore shows less temperature fluctuations.

## 4.2.2 TEX<sub>86</sub> and other temperature indices in lakes

It has become possible to apply the TEX<sub>86</sub> index to lake sediments as recent studies show that crenarchaeol also is produced in freshwater environments (e.g. for lakes: Powers et al., 2004; Bechtel et al., 2010; Tierney et al., 2012, and for rivers: French et al., 2015). Multiple studies (e.g. Powers et al., 2004; 2010, Blaga et al., 2009; Pearson et al., 2011) have examined the applicability of the index for lake sediments. These studies agree that the index does generate reliable surface water temperatures for some lakes. However, the isoGDGTs were only detected in sediments from large lakes (>4,000 km<sup>2</sup>) (Powers et al., 2010). The influence of isoGDGTs from soil input is too large to calculate reliable water surface temperatures in smaller lakes.

The TEX<sub>86</sub> index should only be used in lakes with a sufficient production of GDGTs that are produced by Thaumarcheota relative to isoGDGTs from soil or aquatic sources (Blaga et al., 2009; Powers et al., 2010). The soil input affects the distribution of isoGDGTs and therefore a reliable TEX<sub>86</sub>. To examine the input of GDGTs from soils compared to the in situ production of GDGTs and therefore the applicability of the TEX<sub>86</sub> index in lakes, the BIT (Branched and Isoprenoid Tetraether) index can be used. The BIT index is used to determine the relative amount of fluvial input of terrestrial material in a sedimentary basin and is based on several brGDGTs and crenarchaeol (Hopmans et al., 2004). For oceanic basins, this BIT index is relatively straightforward as brGDGTs are mainly produced by bacteria in soils and therefore the index shows low values. The application of the BIT index in lakes becomes more difficult due to in situ production of brGDGTs (e.g. Bechtel et al., 2010; Tierney et al., 2012). A BIT index of <0.5 indicates a relatively low input of soil derived GDGTs and therefore a reliable TEX<sub>86</sub> for lakes(Powers et al., 2010). However, this statement comes with a note of caution that there is no substantial in situ production of GDGTs.

The Trzechowskie lake has a reconstructed surface area of approximately 19.7 km<sup>2</sup>. The surface area of the lake is many times smaller than the area of >4,000 km<sup>2</sup> which has been mentioned by Powers et al. (2010) as a minimum lake size for in situ production of isoGDGTs. It is also shown in the BIT index of the lake that there is little to no in situ production. The index reconstructed values between 0,986 and 1,00, indicating high runoff from the continent. Due to this high input of terrestrial material and the small surface area of the lake, it can be concluded that the TEX<sub>86</sub> cannot be applied reliably.

Other temperature calibrations for lake sediments have been introduced, for example by Powers et al. (2010), Tierney et al. (2010), Sun et al. (2011) and Pearson et al. (2011). These calibrations have been introduced, after Tierney & Russell (2009) and Sinninghe Damste et al. (2009) discovered that brGDGTs are also produced in the water column of lakes and/or lake sediments themselves (see section 4.5). The first calibration of the brGDGT-based MAT proxy of Weijers et al. (2007) is based on the assumption that brGDGTs are solely produced in soils, and not in lakes. The calibration for mean annual lake surface temperature (ALST), as created by Powers et al. (2010), is based on the TEX<sub>86</sub>. The calibration of Powers et al. (2010) cannot be used reliably for palaeotemperature reconstruction in the lake as the terrestrial input is too large for a reliable TEX<sub>86</sub> for Lake Trzechowskie. Subsequently Tierney et al. (2010), Sun et al. (2011) and Pearson et al. (2011) created new, lake-specific transfer functions to reconstruct mean annual

air temperatures (MAT) based on brGDGTs. Tierney et al. (2010) based their calibration on lake sediments from lakes in East Afrika and is therefore calibrated for (sub)tropical lakes. Sun et al. (2011) created a calibration for MAAT based on the MBT and CBT indices. The values range between 18 and 24 °C when this index is applied to the Trzechowskie Lake. This is almost three times as high than the reconstruction based on the method of De Jonge et al. (2014a). The overestimation is also recognized by Loomis et al. (2012). It is possible that the calibration of Sun et al. (2011) only applies for the old method, which does not separate the 5- and 6-methylated brGDGTs. The calibration will therefore not be used in this report.

The calibration created by Pearson et al. (2011) could be used for lakes worldwide, as a datasets from lake sediments on a transect from the Arctic to the Antarctic was used. The equation constructed by Pearson et al. (2011) is calibrated to summer air temperatures:

$$SAT = 20.9 + (98.1 * Ib) - (12.0 * IIa) - (20.5 * IIIa)$$
  
 $R^2 = 0.88, RMSE = 2.0 °C$ 

This transfer function is based on the classic chromatography method which does not separate the 5- and 6-methylated brGDGTs, but, as De Jonge et al. (2014b) states, the equation uses the 5methylated brGDGTs and not the 6-methylated brGDGTs. The results of this transfer function to the Trzechwoskie Lake (Fig. 8) show higher summer temperatures than reconstructions based chironomids have previously shown. on Temperatures range from 21.5 during the Holocene to 16.5 °C during the coldest phase of the Younger Dryas. Figure 8 shows that the summer temperature also declines between 12,822 and 11,604 yrs BP, which are the same ages as for which the decline in the  $MAT_{mr}$  were observed. Some studies recognize problems with the

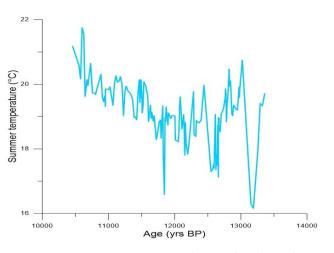


Fig. 8. Summer temperature at the Trzechowskie Lake, based on the temperature calibration of Pearson et al. (2011).

application of the calibration of Pearson et al. (2011) (e.g. Loomis et al., 2012; Sinninghe Damsté et al. 2012). Loomis et al. (2012) shows that the calibration generates temperatures that are too high, especially in cold lakes. The summer temperatures, based on the calibration of Pearson et al. (2011), of the Trzechowskie Lake come close to the summer temperatures reconstructed for Central Poland by Dziedusynska et al. (2014). The difference between the two temperature reconstructions could be caused the fact that the Trzechowskie Lake was a cold lake during the Younger Dryas. Therefore, the generated summer temperatures could be too high. Loomis et al. (2012) advise to use regional calibrations for palaeotemperature reconstruction, rather than global calibrations. Other causes for the difference can be sought in differences in proxy response to temperature

#### 4.3 Wind strength record

The GDGT-0/cren ratio is important in order to examine the wind strength during the Younger Dryas. The values of the GDGT-0/cren ratio are always above 2 during the whole interval in the Trzechowskie Lake (Fig. 4.), as the lowest value is 21 during the Allerød period. Therefore, the lake has likely been stratified for at least the entire Younger Dryas (Sinninghe Damsté et al., 2009). However, the degree of stratification

has varied significantly. The highest value for the ratio, during the early Holocene, is about 40 times higher than the lowest. The cause for the higher values of the ratio should be sought in either a temperature change or a change in wind strength. Based on the reconstructed MAT<sub>mr</sub>, the temperature has shifted a maximum of 1.5 °C over the whole period. This temperature change is relatively small in comparison to more westerly records (e.g. Haemelsee, Bouwman, unpublished), and it could therefore not explain the large changes in the GDGT-0/cren ratio. That is why the GDGT-0/cren ratio could mainly reflect wind strength for the Trzechowkie Lake or a combination of the two factors surpassing a certain threshold. The increase in wind activity has also been recognized in the Cladocera (water fleas) distribution in the lake, as species indicative of clear water conditions disappear (Slowinski et al., 2017). This strengthens the hypothesis that wind strength increased at the Allerød-YD boundary.

The onset of a potentially stronger wind system during the Younger Dryas in Central Poland is around 12,669 yrs BP, based on the GDGT-0/cren ratio of the Trzechowskie Lake. Geomorphological and sedimentological evidence confirms that Central Poland was affected by strong western and southwestern winds during the Younger Dryas, as wind dunes are aligned in this direction (Krajewski, 1977; Nowaczyk, 1986). The GDGT-0/cren ratio at the Haemelsee, Germany, also shows low values during the Younger Dryas (Bouwman, unpublished). The values are even lower than for the Trzechowskie Lake. This could be interpreted as stronger winds as it is closer to the Atlantic Ocean, or a larger temperature effect on the GDGT-0/cren ratio. The change in wind system has also been recognized in other parts of Europe (e.g. Isarin et al., 1998; Brauer et al., 2008; Lane et al., 2013; Rach et al., 2014). Brauer et al. (2008) reports an abrupt increase in storminess during the autumn to spring seasons, occurring from one year to the next in the Lake Maarfelder Maar, western Germany. The timing for this change is at 12,679 yrs BP, which falls within the uncertainty limit of 40 varve yrs for the Trzechowskie Lake. Therefore, multiple records on different proxies have recognized a large shift in climate at that time.

The cause for this abrupt climatic shift is still not completely known. The shift in wind strength could represent a change in the North Atlantic westerlies towards a stronger jet (Brauer et al., 2008). The increase change in the westerlies could be explained by changes in the North Atlantic Meridional Overturning Circulation (AMOC). The westerlies brings heath towards Europe, brought by prevailing southwesterly winds, in the modern wind-system (Thompson & Wallace, 2001). However, changes in the AMOC could have resulted into more zonal and less southerly winds (Fig. 9). This could have led to the cooling that is recognized in Europe. The changes in the AMOC could have been the result of a southward shift of sea ice (Kageyama et al., 1999). Brauer et al. (2008) states that an atmospheric trigger should not be ruled out even though the

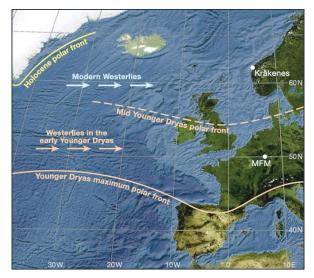


Fig. 9. Changes in AMOC leading to relocation of polar front and westerlies winds, after Lane et al. (2013).

oceanic trigger for the climate change is possible. The abruptness in the changes in wind strength observed at the Trzechowskie Lake suggest that sea ice played an important role, as sea ice is a rapid and

strong climate amplifier (Visbeck, 2002). The increase in sea ice seems to be the product of the cooling in Europe, based on the 150 years delay of the wind strength change compared to the temperature change.

The effect of the stronger winds could have an environmental effect on the region surrounding the Trzechowskie Lake. Slowinskie et al. (2017) examined the pollen assemblage around the lake. The main vegetation shift occurs when the percentage of Juniper (*Juniperus*) increases rapidly, while the percentage of Birch (*Betula*) and Scots pine (*Pinus silvestris*) decline. This occurred at 12,661 yrs BP, which is almost the exact time of the strengthening of the westerlies, based on the GDGT data. The timing of the onset of the pollen change is about 150 years after the decline of the MAT. Therefore, the change in wind system and possibly the amount of moisture which it brought, could have been the driving factor in changing the environment in Central Poland at the onset of the Younger Dryas.

The only aspect left unexplained is that during the Allerød period low values of the GDGT-0/cren ratio are found, while the sedimentary record was still varved in the Trzechowskie Lake. Therefore, the lake should have been stratified, while less methanogenisis had taken place. During this period the absolute values of GDGT-0 are as low as during the Younger Dryas, while the absolute amount of crenarchaeol during the Allerød is several times higher than during the YD. During the Allerød period, the brGDGT-based temperatures are higher and westerlies wind activity was likely to be less (e.g. Walker et al., 1994; Brauer et al., 2008). Therefore, it was expected that the lake was stratified, which did not occur. A possible explanation for the phenomenon is an increased easterlies in the summer (Ulden & van Oldenborgh, 2006) during the Allerød period. This could explain higher temperatures during the summer and lower values for the GDGT-0/cren ratio. However, the circulation of the water column would have been increased due to increased wind strength, which should have resulted in a sedimentary record without varves. Another explanation for the lack of methanogenic activity could be sought in the high amount of crenarchaeol during the Allerød period. This could indicate increased primary productivity and an increased oxygen concentration in the water column, resulting in less anaearobic oxydation of methane by Euryarcheota, and therefore lower a GDGT-0/cren.

## 4.4 Aridification record

## 4.4.1 $\delta D$ record of n-alkanes

Collins et al. (unpublished) created a hydrogen isotopic record ( $\delta$ D record) based on n-alkane lipids of plant waxes in addition to the GDGT record. n-Alkanes are a very useful proxy for climate reconstruction, because the compound is relatively easy to extract and are carbon-bound, which makes the hydrogen atoms non-exchangeable (Sachse et al., 2006). Also, the average chain length (ACL) of the plant waxes differs in different biological sources: (1) n-alkanes with 17 and 19 carbon atoms are derived from algae, (2) n-alkanes with 23 carbon atoms are produced by submerged aquatic plants (Ficken et al., 2000), (3) n-alkanes with 25-31 carbon atoms, but especially n-C<sub>27</sub> and n-C<sub>29</sub>, are synthesized by terrestrial higher plants (Eglinton & Hamilton, 1967) and (4) grasses produce especially n-alkanes with 31 carbon atoms (Maffei, 1996). For this report, I used the n-alkanes C<sub>23</sub> as indicator for aquatic plants and C<sub>29</sub> for terrestrial higher plants.

Ideally, the n-alkanes of plant waxes record the  $\delta D$  composition the of source water (Sessions et al., 1999). However, other factors, such as vegetation and relative humidity may also affect the  $\delta D$  values (Hou et al., 2008). n-Alkanes of mainly angiosperm leaves that are deposited in lakes are known to have recorded the meteoric water isotope composition (Sachse et al., 2004; Diefendorf et al., 2011), due to the fact that the fractionation between source water and n-alkanes is constant. The hydrogen source for submerged aquatic plants is lake water (Rach et al., 2014). n-Alkanes of terrestrial higher plants are enriched in deuterium  $(^{2}H)$  by between 10 to 60‰, compared to n-alkanes from aquatic plants. The isotopic difference does not originate from different biosynthetic pathways, but leaves from terrestrial higher plants are subjected to evapotranspiration (Leaney et al., 1985). Therefore, the difference between the  $\delta D$ values of terrestrial higher plants and aquatic plants ( $\epsilon_{terr-aq}$ ) could be a proxy for evapotranspiration. An important assumption that is made for the application of this proxy is that both plant types record  $\delta D$  values of the same source. This is very likely in a relatively small catchment area of meteoric water, e.g. for the Trzechowkie Lake. Seki et al. (2009) describes the difference between the n-alkane  $\delta D$  values of terrestrial and aquatic plants as an indicator of water level of the lake in which the aquatic plants live. Lower  $\delta D$  values should indicate wetter conditions. The  $\delta D$ 

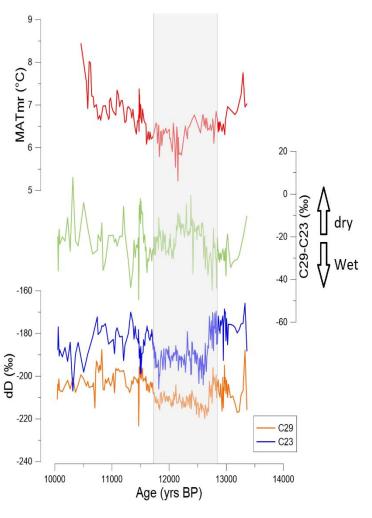


Fig. 10. a) changes in dD of aquatic plants ( $C_{23}$ ) and higher terrestrial plants (C29), b) changes in evapotranspiration based on  $\varepsilon_{terr-aq}$ , based on data from Collins et al. (unpublished).

values for both plant types and the relative difference between the terrestrial and aquatic plants ( $C_{29}$  minus  $C_{23}$  or  $\varepsilon_{terr-aq}$ ), indicating evapotranspiration, are plotted in figure 10.

The onset of the decline in absolute  $\delta D$  values for both the higher terrestrial and aquatic plants is at 12,704 yrs BP at the Trzechowskie Lake (Fig. 10). This would indicate that both plants types used had the same hydrogen source, namely meteoric water. Hence, the lake would have been fed mainly by precipitation and groundwater. The  $\delta D$  value of precipitation water is mainly controlled by condensation temperature, with lower values indicating lower temperatures (Dansgaard, 1964; Gat, 1996). An additional decrease in the  $\delta D$  values could be caused by meltwater release into the Atlantic Ocean (Lewis et al., 2010), which was likely to be the main source of precipitation for Central Poland based on the wind direction during the YD. This could also explain the apparent difference in timing of the temperature drop between the GDGT-based method and n-alkane-based method. The  $\delta D$  values of n-alkanes are mainly controlled by the water source and therefore the wind system. As the wind system, based on the GDGT-0/cren ratio, changed about 150 years after the initial temperature change around 12,822 yrs BP, the  $\delta D$  values of the n-alkanes, also changed 150 years later.

The onset of the increasing  $\varepsilon_{terr-aq}$  values is around 12,679 yrs BP, indicating the increasing evapotranspiration since that age. The timing corresponds almost perfectly with the shift in GDGT-0/cren index and therefore wind strength. The increasing evapotranspiration should have been primarily caused by aridity as temperature dropped during the YD. The aridity is likely to have been caused by the same mechanism as the change in wind strength, as the timing, about 150 yrs after the decline in temperature, is simultaneous with the expanding winter sea ice cover in the North Atlantic Ocean (Isarin et al., 1998) and subsequent southward migration of the westerly wind system (Lane et al., 2013). This could have led to a decreased uptake of moisture, as the wind passed over colder and potentially ice-covered water in the North Atlantic. Therefore, it could accumulate less latent heat and hold less water (Braconnot et al., 2007), which caused the dryer conditions at the European continent. The aridity did not seem to be severe during the Younger Dryas as the values of  $\varepsilon_{terr-aq}$  are not much higher than during the Allerød and Holocene periods. It is possible that the dryer conditions during the Younger Dryas, lake water evaporation has altered the isotopic composition of the lake water (Rach et al., 2014). This would have resulted in an underestimation of the depletion of  $\delta D$  values of the aquatic plant waxes and therefore less positive values of  $\varepsilon_{terr-aq}$ . The onset of the aridity and change in wind strength coincides with the onset of the pollen change and following the temperature decline (Fig. 7). This delayed hydrological response is also recognized on Greenland by Rach et al. (2014). All three changes are quite rapid, which would indicate that the environmental change is stronger influenced by the wind strength and amount of precipitation then by the temperature change.

## 4.4.2 BIT index

The BIT, PH and IR indices could possibly also be used as indicator for increased precipitation in the catchment area of a lake. The BIT index was originally developed for tracing soil organic matter in marine sediments (Hopmans et al., 2004). However, it is more frequently used in lacustrine environments as well. The BIT index can still be used to trace input of soil organic matter in lakes and therefore traces soil erosion and precipitation of the catchment area. There are two periods of decline recognized in the BIT index, one starts at 13,152 and the other at 12,688 yrs BP. The last age almost coincides with the age of the change in  $\varepsilon_{terr-aq}$ , which changes at 12,679 yrs BP. The 8-year difference could be caused by the time that was needed to transport the n-alkanes to the lake. A decline in BIT values could indicate decreased runoff from rivers entering the lake and therefore less input of brGDGTs into the lake. These results make it plausible that the BIT index could be used as a precipitation index. However, a drawback for the use of the BIT index as tracer for precipitation is the in situ production of brGDGTs, which could bias the index (see section 4.1). This could be an explanation for the first drop in BIT values at 13,152 yrs BP. Another cause for the decreased BIT index around that time could be the increase in absolute amount of crenarchaeol, while the amount of brGDGTs remains relatively constant (Fig. 4).

## 4.5 Implications on the termination of the Younger Dryas

The cold and arid climate lasted for about 1,000 to 1,200 yrs in Central Poland. Most GDGT indices in the Trzechowskie Lake show a termination of the Younger Dryas between 11,655 and 11,604 yrs BP. These changes in environmental parameters at the end of the YD at the lake Trzechowskie coincides almost perfectly with the increase in  $\delta^{18}$ O values of the Greenland ice core at 11,653 yrs BP (Rasmussen et al., 2006). The wind strength decreases abruptly within 20 yrs to a milder and less stormy regime at 11,645 yrs BP. The temperature increases with about 1 °C within 70 yrs. The n-alkane based evapotranspiration index increases rapidly around 11,614 yrs BP. This could be caused by a more arid climate, as for the onset

of the Younger Dryas. However, the increased evapotranspiration is more likely to be caused by the increased temperatures at the start of the Holocene.

Temperatures rose about 7 °C within 50 yrs in Greenland. The timing of the end of the Younger Dryas is thought to be synchronous over at least the Northern Hemisphere (e.g. Severinghaus et al., 1998). A possible explanation for the warming at the beginning of the Holocene is the rapid retreat of the sea ice margin, and thereby the polar front (Dansgaard et al., 1989). This also explains that the precipitation and wind strength changed approximately 40 yrs earlier than the temperature (Fig. 4 and 10), as precipitation and wind strength is directly affected by the amount of sea ice and polar front. The North Atlantic Meridional Overturning Circulation (AMOC) could have strengthened more gradual since the retreat of the sea ice and therefore could have increased the temperature more gradual.

# 5. Conclusion

The discovery of Tierney & Russell (2009) and Sinninghe Damsté et al. (2009) that brGDGTs are also produced in lakes themselves, instead of predominantly in soils, made an impact on the reliability of GDGT-based proxies. Sinninghe Damsté (2016) showed several approaches to determine whether significant brGDGT production in coastal marine sediments has taken place. It shows that the lake had little to no in situ production of brGDGTs when applying these approaches on the Trzechowskie Lake. The approach to use IR values to determine the origin of brGDGTs has been proven to be invalid for lakes. Therefore, the application of brGDGT-based proxies seem to be reliable to use with the improved chromatography method that separates the 5- and 6-methyl isomers of the brGDGTs. However, new calibration studies are still required to further investigate the changes in abundance of the 5- and 6-methyl brGDGT isomers with changing climate.

The analysis of the branched Glycerol Dialkyl Glycer Tetraether (brGDGT) composition of the Trzechowskie Lake shows a gradual temperature decline of about 1.5 °C during the Younger Dryas. The most accepted hypothesis on the cause for this temperature shift is sought in the influx of fresh water into the Atlantic Ocean, which decreased or stopped the North Atlantic Meridional Overturning Circulation (AMOC) (e.g. Lane et al., 2013). The change in amplitude of seasonality, based on my data, supports this hypothesis. The temperature decline in Central Europe is less strong than more westerly in Europe, suggesting that the influence of the Atlantic Ocean on climate during the Younger Dryas became less strong towards continental Europe. The gradual cooling of Central Poland did not have an immediate effect on the environment, as shown by the delayed changes in pollen assemblage and lithology of the lake (Slowinski et al., 2017). These changes are likely to be more influenced by the wind strength and amount of precipitation than by temperature. The decreasing temperature since 12,822 yrs BP precedes the changes in wind strength and aridity by about 150 yrs. This may indicate that the decreasing strength of the AMOC, due to increased fresh water input into the North Atlantic Ocean, resulted in an increase in sea ice, which affected the environment in Europe by inducing stronger winds and less precipitation.

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