Global and Planetary Change 148 (2017) 72–78

Contents lists available at ScienceDirect

Global and Planetary Change

journal homepage: www.elsevier.com/locate/gloplacha

Invited research article

Changes in atmospheric CO_2 levels recorded by the isotopic signature of *n*-alkanes from plants

Karina Scurupa Machado [a,*], Sandro Froehner [b]

[a] Department of Hydraulics and Sanitation, Federal University of Parana, Curitiba, PR 81531-980, Brazil
[b] Department of Environmental Engineering, Federal University of Parana, Curitiba, PR 81531-980, Brazil

ARTICLE INFO

Article history:
Received 1 June 2016
Received in revised form 16 September 2016
Accepted 26 November 2016
Available online 03 December 2016

Keywords:
$\delta^{13}C$ signature
Little Ice Age
Atmospheric carbon dioxide
Volcanism

ABSTRACT

The isotopic signature of sedimentary organic matter acts as a tracer for past changes in the terrestrial and aquatic carbon cycles. The temporal variation in $\delta^{13}C$ values of *n*-alkanes from plants was assigned as resulting from changes in atmospheric composition in the study area, due to both global and local influences. Two rises in atmospheric CO_2 concentration were assigned from the variation in *n*-alkane $\delta^{13}C$ values for the periods between 1600 and 1880 and from 1930 to the present. In the first period, the sources of excess CO_2 were predominantly natural, mainly volcanism, while in the second period local anthropogenic emissions were the major reason.

1. Introduction

Knowledge about the evolution of atmospheric CO_2 concentration throughout the Earth's history, mainly within the last millennium, is important for a reconstruction of the links between climatic and anthropogenic changes (Etheridge et al., 1996). Although human activity has at present, increased the CO_2 concentration in the atmosphere, several factors may in the past, have contributed to the variation in atmospheric composition (Crowley, 2000). Such variation is directly reflected in the isotopic discrimination of CO_2 by plants (Wiesenberg et al., 2008b). An increase in atmospheric CO_2 concentration causes a decrease in $\delta^{13}C$ values of *n*-alkanes from terrestrial and aquatic plants. Here, we assessed the temporal trend in the isotopic signature of long chain and mid-chain *n*-alkanes from terrestrial and aquatic plants, respectively. Meaningful fluctuations were assigned to the variation in atmospheric CO_2 400 years ago during the cooling episode of the Little Ice Age (Mann, 2002). We also used more reliable palaeogeochemical proxies to assess the sources of the CO_2 potentially responsible for these fluctuations.

1.1. Biomarkers with palaeoenvironmental importance

The Earth has undergone significant changes in all environmental compartments during the last centuries. Due the spatial variability of the effects of this changes, it has been quantified at the continental scale. It is important to distinguish anthropogenic impact from the background range of natural variability, which needs to be considered to predict future scenarios. Understanding of natural events in the past may be obtained through geological archives containing sensitive indicators used to reconstruct past scenarios.

The natural variation in the ratio of carbon stable isotopes ($\delta^{13}C$ values) in different components of the environment (soil, air and water), acts as a tracer of physical, chemical and biological processes and determines the proportion of the lighter and heavier isotopes (Weisenberg et al., 2008a). Isotopic analysis of sediment can be associated with chronological data to obtain information about: changes in the vegetation composition, effects of the land management, changes in the atmospheric composition and also to quantify the rates and patterns of these changes in natural ecosystems (Tipple and Pagani, 2010). Biomarkers represent one way of investigating the isotopic fractionation between different environmental compartments of *n*-alkanes from terrestrial plants.

Atmospheric CO_2 plays an important and complex role in photosynthesis since several steps are involved in the pathway before the carbon is incorporated into plant tissue (Tipple and Pagani, 2010). $^{13}CO_2$ can be distinguished in all steps from the transfer of CO_2 from the atmosphere to the chloroplast and in the carboxylation reactions (Fung et al., 1997). Therefore, shifts in isotopic composition of atmospheric CO_2 strongly influence the isotopic discrimination by plants and are reflected in their $\delta^{13}C$ values.

Several studies report the influence of atmospheric CO_2 on the isotopic composition of plants (Berling and Woodward, 1995; Zhao et al., 2001; Tipple and Pagani, 2010). In fact, an increase in atmospheric CO_2 is considered to cause a decrease in $\delta^{13}C$ value in the *n*-alkanes from terrestrial and aquatic plants, making these values more negative

* Corresponding author.
E-mail address: ksmachado@hotmail.com (K.S. Machado).

http://dx.doi.org/10.1016/j.gloplacha.2016.11.015
0921-8181/

(Weisenberg et al., 2008a). Zhao et al. (2001) claim that the depletion of 2.5–2.8‰ in the $\delta^{13}C$ values in wheat after 153 yr is due the increase of atmospheric CO_2 in Rothamsted (England). Beerling and Woodward (1995) found a small decrease in $\delta^{13}C$ in C_3 plants exposed to an increase in CO_2 concentration in a growth chamber, while Weisenberg et al. (2008b) observed a depletion of 2–6‰ in the $\delta^{13}C$ values of *n*-alkanes from plant wax under ambient temperature with elevated CO_2 concentration.

Besides *n*-alkanes and their isotopic signature, another biomarker type with significant palaeoenvironmental importance is the glycerol dialkyl glycerol tetraethers (GDGTs), which are the polar part of basic constituents of the cell membrane of archaea (Blaga et al., 2010). These bacterially compounds are fluvially transported and often become part of the sediment. Their distribution in soils has been shown to relate to soils pH and annual mean air temperature (MAT) (Tierney et al., 2010). This property can be explored to provide paleothermometer information, expressed in the methylation index of branched tetraethers and cyclisation ratio of branched tetraethers (MBT-CBT), it has been used as a record of past soil pH and temperature change on land, both in geologically more recent times, including the last glacial – interglacial transition (Weijers et al., 2011).

2. Material and methods

2.1. Study area and sampling

Barigui watershed (25°13′24″ and 25°38′23″ S and 49°15′00″ and 49 22′29″ W) is one of most studied watersheds in the state of Parana (Froehner and Martins, 2008; Machado et al., 2014a,b). It corresponds to 35% of the total area of the municipality of Curitiba's watersheds and is a privileged area in terms of hydrometereological observations (Froehner and Martins, 2008). Barigui River is 67 km long, draining a watershed of 279 km^2, with 120 km^2 of drainage located in the municipality of Almirante Tamandare, 144 km^2 in the municipality of Curitiba and 15 km^2 in the municipality of Araucaria. It flows from north to south through the city of Curitiba and has been strongly influenced by urbanization throughout time, so has considerable potential to represent environmental shifts over time. The sampling station was located inside Tingui Park (Fig. 1) at a latitude of 25°23′55.81″ and a longitude of 37°35′33.84″. Monitoring studies have defined the area as reliable for sample collection and encompass the most significant data (Froehner and Martins, 2008).

Areas with dense terrestrial vegetation appear mainly to the north of the watershed, while aquatic macrophytes are present throughout the river. C_3 plants are predominant, basically trees and some species of scrubs, while C_4 plants play a minor role in the present vegetation and are summarized as being herbaceous, mainly from the pteridophyte group (Cerling et al., 1997)

The study area is located in the south Tropic of Capricorn and First Parana Plateau (900 m), where atmospheric intertropical and polar systems clash, resulting in a humid mesothermal climate (Silva and Guetter, 2003). Currently, four streams, controlling the climate in southern Brazil: Tropical Atlantic, Atlantic Polar, Tropical Continental and Equatorial Continental, which are formed in active centers such as: the Intertropical Convergence Zone (ITCZ) migration and Southern Oscillation (SO). These streams directly affect the temperature and moisture in the study area (Hendy et al., 2002).

In 2011, a sediment core (PT) 100 cm long was collected using a small gravity corer with a 6 cm diameter barrel. The core was extruded, sectioned at 2 cm intervals (resulting in 50 samples) and stored at 4 °C during transport to the laboratory, where the samples were frozen (−20 °C) and lyophilized prior to analysis.

2.2. Sedimentary environment of the study area

Sand (63–2000 μm) and silt (4–63 μm) size fraction predominate in most of the Barigui river basin, while clay (<4 μm) is found in minor proportion. The sedimentation rate on the basin is relatively constant, over time (0.44 $g\ cm^{-2} \cdot yr^{-1}$, ±0.09) and the drainage pattern is predominantly dendritic (Froehner and Martins, 2008; Machado et al., 2014a). The organic matter preserved in the fluvial sediment originates from aquatic and terrestrial sources in the basin. Due to several factors including the different types of land use in the basin, and absence of hydrologic seasonality, limnologic conditions significantly vary along the Barigui river's length (Machado and Froenher, 2016). Total organic carbon range at 428 $\mu mol \cdot g^{-1}$ to 2694 $\mu mol \cdot g^{-1}$ in the whole basin, while at Tingui Park, values around of 1138 $\mu mol \cdot g^{-1}$ (± 34) of total organic carbon may be found (Froehner and Martins, 2008). The Barigui river basin is a sub-basin of the Iguaçu River basin and the Barigui River is a right bank tributary of the Iguaçu River. There are no tributaries that contribute significantly to the Barigui River's inflow.

2.3. Chronology

The core was analyzed for ^{210}Pb by way of direct gamma assay using an EG&G ORTEC® model GMX25190P hyperpure Ge detector with mean resolution of 1.90 ke GMX25190P for the 1332.40 keV photopeak of ^{60}Co. ^{210}Pb activity was measured at 46.52 keV, according to the methodology and data acquisition described by Figueira et al. (2007). In this study, the sedimentation rate was calculated from the unsupported ^{210}Pb via CIC (constant initial concentration) model and CRS (constant rate of supply of unsupported ^{210}Pb). The chronological analysis is described in detail by Machado et al. (2014a,b).

2.4. Stable carbon isotopic analysis

Extraction and analysis of *n*-alkanes are described in detail by Machado and Froehner (2016). Briefly, each sample (5 g) was extracted using accelerated solvent extraction (ASE; Dionex) with a mixture of dichloromethane (DCM) and acetone (1:1 v/v). A silica column (1.5 g, 7 mm i.d.) and hexane as eluate (3 × 4 ml) were used to isolate the alkane fraction. The *n*-alkanes were separated from the branched and cyclic hydrocarbons, via urea adduction as follows, according the procedure proposed by Kristy et al. (2002) with minor modification. Urea was first cleaned with DCM for 24 h and then dissolved in MeOH until the solution was saturated. An aliquot (1 ml) of the methanolic solution was added to the aliphatic fraction, previously dissolved in 4 ml hexane: DCM (1:1), leading to the immediate formation of a white crystalline precipitate. The solution was centrifuged at 3000 rpm for 10 min and the solvent removed. Another aliquot (4 ml of hexane: DCM (1:1) solution was added. The adduct crystals were then dried under gentle N_2 flow. In order to remove the remaining contaminants, 4 ml hexane were added to the adduct crystals, and the mixture centrifuged and the solvent removed. This procedure was repeated. The non-adduct fraction was obtained by adding 5 ml of water (previously cleaned with DCM) to the crystals, breaking up the urea adduct crystals and releasing the *n*-alkanes. Liquid-liquid extraction was used to separate the *n*-alkanes from water by adding 4 ml of hexane (2×). Finally, in order to remove any remaining water, the organic fraction containing the *n*-alkanes was passed through a column of Na_2SO_4 and completely dried under N_2. The stable carbon isotopic composition of individual *n*-alkanes was determined at University of Liverpool (United Kingdom), using isotope ratio gas chromatography-mass spectrometry (IR-GCMS; Delta V Advantage (Thermo Fisher, Bremen) linked to a Trace Ultra GC instrument with a ConFlo IV interface. The sample in hexane/EtOAc was loaded onto a TriPlus auto sampler and 1 μl injected in splitless mode onto a DB5 fused silica column (30 m, 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific). The GC oven temperature was programmed from 45 °C (held 1 min) to 295 °C (held 15 min) at 6 °C/