CLIMATE CHANGE INFERENCES FROM STABLE ISOTOPES COMPOSITION OF TREE RINGS IN THE MEDITERRANEAN AREA

A DATABASE FOR PORTUGAL

Purpose of the visit

Tree rings can be used as high resolution proxies to reconstruct past temperature and precipitation conditions. Their use has been considered very useful in decreasing the uncertainty of climatic reconstruction analysis (Luterbacher et al. 2005).

The determination of stable isotope patterns in wood can greatly increase precision and confidence on climatic reconstruction by tree rings. Moreover as stable isotopes composition of wood in trees depend on the physiological response of trees to climate in the past they can also increase our knowledge on the feed back response of trees to climate in the future.

The purpose of this visit was to learn and practice laboratory techniques necessaries for mass spectrometry measurements of carbon and oxygen isotopes including the method of cellulose extraction from wood, which is fundamental for obtaining reliable results, especially for δ^{18} O measurements. During the stage that was realized at the Paul Scherrer Institute under the supervision of Dr. Rolf Siegwolf and Dr. Matthias Saurer, I also had the opportunity to improve my skills in dendrochronology.

Description of the work carried out during the visit

The tree species selected for this study were *Pinus pinaster* (Ait.) and *Pinus pinea* (L.) for showing easily identifiable tree rings and for being largely represented in Portugal.

Two sites were selected for showing similar temperature but different water availability. Site one was considered no-water limited for proximity to a water stream, whereas site 2 was considered severely water limited.

The objective of this study was to compare the relationship of $\delta^{13}C$ with climate on an annual

basis in two considered species and under conditions of different soil water availability.

Tree rings were first cross dated after discarding juvenile years and separated by the help of a magnifying glass to delimitate years. Material from each ring was then milled individually (ZM1000 (Retsch, Germany). Samples from the same site and corresponding to the same year were polled together. Pooling allows eliminate variability induced by genetic influences among trees while keeping differences related with environmental conditions which trees were subjected (Borella et al, 1998). For a greater homogeneity and a site representative sampling, we averaged the material from different radii and at least four trees of the same year. However, to be aware of the variability within each site 5 years were chosen for individual measurements in selected years.

The method used for cellulose extraction was the so-called ISONET (Waterhouse, 2004). This method is able to give α -cellulose with δ^{13} C values within 0.1‰, and was also selected for requiring only 20 mg of milled wood.

The cellulose extraction process began with washing samples with 0,8vol% NaClO₂ (10g/1000ml) and 4 ml of acetic acid per litre solution (the pH of the solution must be 4). This procedure eliminates the lignin and should be repeated 5 times at 70°C, until the samples fairly light in colour, and then the samples had to be washed with deionised water. Next step was to prepare the 17% NaOH solution. This chemical preparation needs to cold down for 3 hours and then samples should be washed for 45 minutes at 25°C, to removed fats, resins, oils, tannins and hemicelluloses. Rinse samples with 1% HCl solution and with deionised water later, was essential to neutralized NaOH from previous step. To finishing the process samples was to dry at 50°C in oven overnight. Obtained cellulose was then analysed by a mass spectrometer (delta-S, Thermo-Finnigan, Germany,) to achieve δ^{13} C and δ^{18} O.

Patterns of variation in the isotopic signal were compared with annual and seasonal climate records and annual growth after its correction for changes of atmospheric CO₂ and precipitation.

Description of the main results obtained

Portuguese climate is classified as Atlantic-Mediterranean, a maritime climate, strongly influenced by the Atlantic Ocean, cool and rainy in north, hot and dry in south (site average precipitation: 588mm; site average temperature 16.3°C) (Fig. 1) In these climatic conditions the main constrain to trees growth is water deficit together with high temperature and high vapor pressure deficit during the summer.



Figure 1: Total annual precipitation and average annual temperature recorded in Portugal in the last 40 years

In Figure 2 is visible the effect of water deficit on tree rings width. Trees from the site with higher water availability (site 1) showed much larger growth than trees water limited (site 2).



Figure 2: Average rings width of *Pinus Pinaster* (Ait.) and *Pinus Pinea* (L.) in a water limited (site 1) and non-water limited site (site 2).

Only preliminary data from mass spectrometry can be shown as, due to the large number of samples, analyses are still running.

One of the firsts conclusions of this work is that individual trees has the same pattern of pooling samples, suggesting that the polling process gives us the same information that individual measurements, and hence can be applied in climatic reconstruction, with the advantage to save time and eliminate genetic or site-specific influences (Figure 3).



Figure 3: Individual measurements of trees comparing with the polling values.

The correlation between carbon isotope composition measured (δ^{13} C) and climate data is shown in figures below (figures 4-7). This correlation was not very reliable when every year was considered (figures 4 and 6), probably partly because factors like resin extraction or cuts, affected trees physiological performance. In figure 5 and 7, is possible to see that the correlation coefficient increase when only years with extreme climatic conditions, extremely dry or wet were considered. This also suggest that possibly the climatic index applied is not the best representative of climatic changes. We propose to apply and compare results from different climatic indexes.



Figure 4 - 5 : Correlation between $\overline{\delta}^{13}$ C values and climate data, considering all years (left panel) and considering only years selected for being extremely dry or wet (right panel).



Figure 6-7: Correlation between δ^{13} C values and climate data, considering all years (left panel) and considering only years selected for being extremely dry or wet (right panel).

In addition, it is possible to appreciate that the two considered species showed similar pattern in relation to the climatic index selected, suggesting a similar response to climatic conditions.

Acknowledgments

Thanks are due to Dr. Rolf Siegwolf and Dr. Matthias Saurer for receiving me in Paul Scherrer Institute and for their technical help, to Anne Kress and Lucas for the careful in isotopic measurements and to Dr^a. Sofia Cerasoli for advice on a previous draft of this report. This work was financially supported by the European Science Foundation within the framework of the activity entitled "Mediterranean Climate Variability and Predictability".

References:

- 1. Luterbacher et al. (2005). J Geophysical Research 32: L15713.
- 2. Borella et al. (1998). J Geophysical Research 103: 19,519-19,526.
- 3. Waterhouse et al. (2004). Analytical Chemistry.

<u>Note</u>: Remaining samples are still being analyzed including ¹⁸O analysis.

Projected publications/articles resulting or to result from your grant

Results from the experience will be published in an international journal with reference and presented in an international meeting.