NATURAL ORGANIC MATTER RESEARCH

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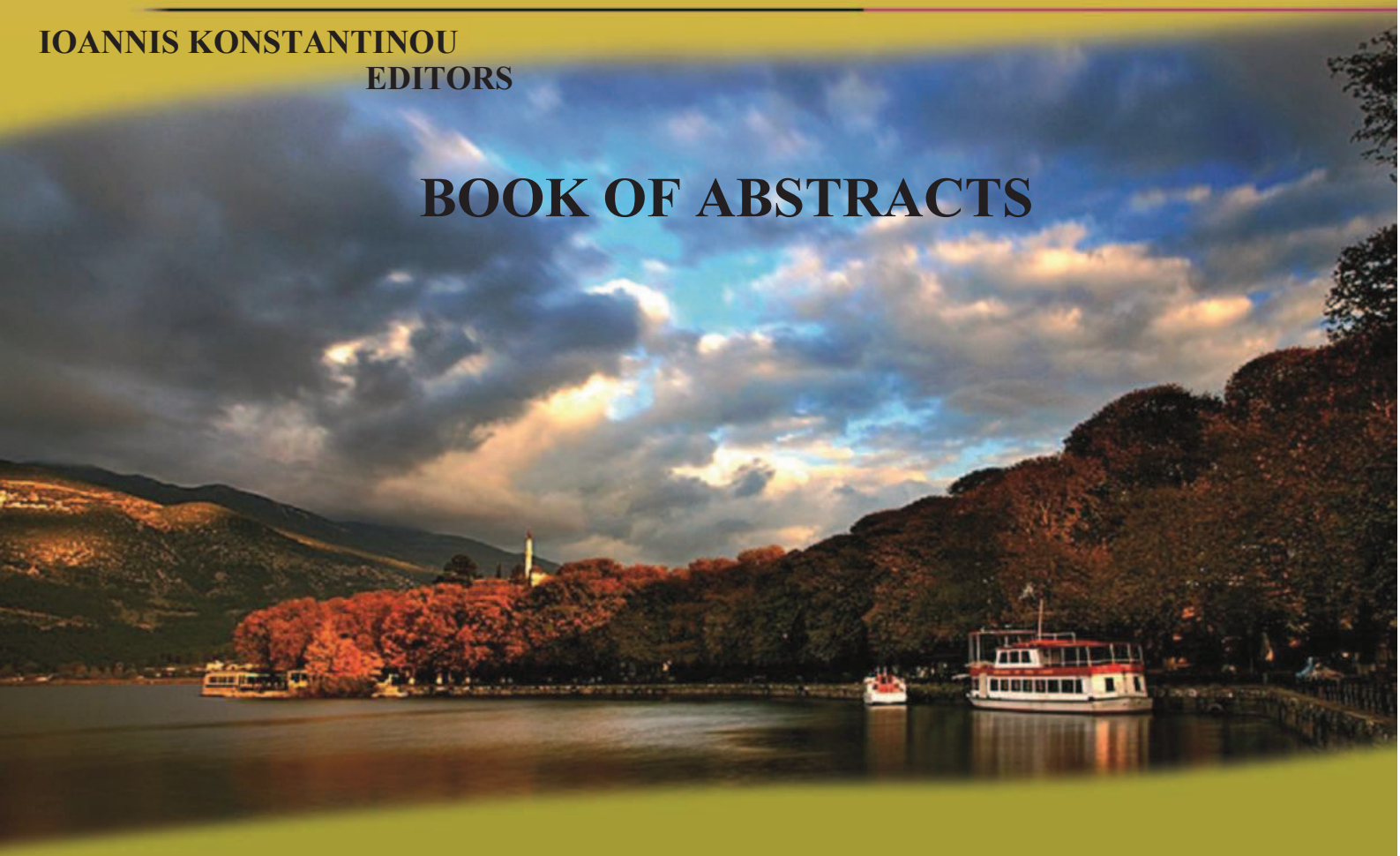

# BOOK OF ABSTRACTS

## NATURAL ORGANIC MATTER:

## *Structure-Dynamics*

## *Innovative Applications*

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# Effects of pyrogenic carbon feedstock and pyrolysis temperature on the oxidation kinetic and benzene polycarboxilic acids formation

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**Keywords:** oxidation kinetic; biochar; benzene polycarboxilic acids; pyrogenic carbon quantification

**Abstract** Pyrogenic carbon (PyC) has a high potential to soil carbon sequestration. Among the methods used to quantify PyC, the method of benzene polycarboxilic acids (BPCA) is well-established. The oxidation step of this method is essential for a reliable PyC quantification. Up to now there are no studies on the influence of feedstock and pyrolysis temperature in the oxidation kinetic of PyC and BPCA formation; and then these are the purposes of this study. For this, different PyC were oxidised at 170 ºC during different times. The data showed similar kinetic curves for all PyC, but different BPCA production depending upon feedstock and pyrolysis temperature. All PyC showed maximum production of BPCA at 6-8 h under nitric acid oxidation at 170 ºC. We concluded that 8 h of nitric acid oxidation at 170 ºC produces a reliable data to PyC quantification, thus representing a robust method.

## Introduction

Pyrogenic carbon (PyC), known as biochar, may play an important role in the global C cycle. When added to the soil, PyC is expected to contribute to the recalcitrant C pool and decelerate the soil organic carbon decomposition. Among the available methods of PyC quantification in soil, the BPCA method (*1,2*) is the most well-established. The BPCA first-step includes the oxidation of PyC by nitric acid at 170 ºC for 8 h. During this oxidation, the polycyclic or aromatic structures present in the PyC are converted to BPCA (Figure 1).

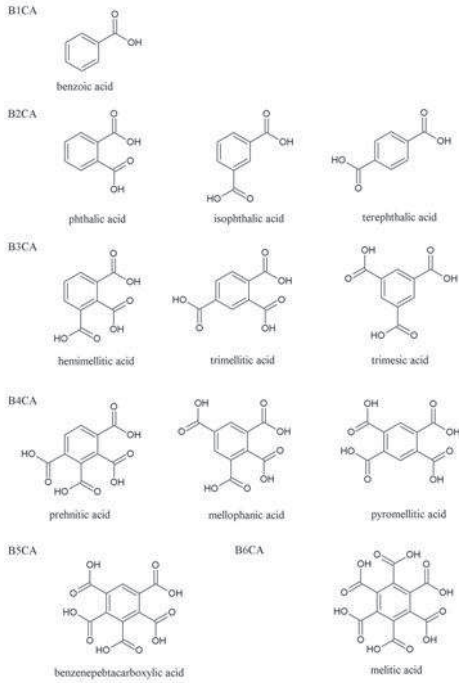


**Figure 1.** Chemical structures of BPCA (adapted from (*1*)).

The oxidation step is crucial for the BPCA method. The oxidation must assure that all aromatic structures will be converted to BPCA. Dittmar (*3*) observed a similar oxidation kinetic for three different samples (perylene, humic acid standard and marine dissolved organic matter) and a recovery of 92-100% for all samples after 9 h of oxidation. However, up to now there are no studies about how feedstock and the pyrolysis temperature affect oxidation kinetics and BPCA production. So, this study aimed to evaluate feedstock and pyrolysis temperature effects on the oxidation kinetic and BPCA production.

## Experimental

Biochar samples were obtained after 1 h pyrolysis of eucalyptus (*Eucalyptus dunnii)* wood and sugarcane (*Saccharum officinarum*) bagasse at 450 ºC; and from water hyacinth (*Eichhornia crassipes*); eucalyptus (*Eucalyptus dunnii)*; and pine (*Pinus taeda*) woods at 350 ºC.

Aliquots of 5 mg of PyC were weighed and filled into 5 mL glass ampoules, which were sealed after addition of 0.5 mL $HNO_3$ (65%). The ampoules were placed into microwave vessels and heated up to 170 ºC for 1; 2; 4; 6 and 8 hours using a laboratory oven. After oxidation, the ampoules were opened and the nitric acid evaporated under a gentle $N_2$ flux. The samples were diluted up to 1 mL in the mobile phase. The samples were analysed by the liquid chromatography with UV-DAD detection (RRLC-UV-DAD), using a Zorbax Eclipse C18 column

**Results and Discussion**

The yields of BPCA produced from eucalyptus and sugarcane bagasse increased with longer nitric oxidation times (Figure 2). After 8 hours, the production of BPCA for the two PyC reached the maximal.

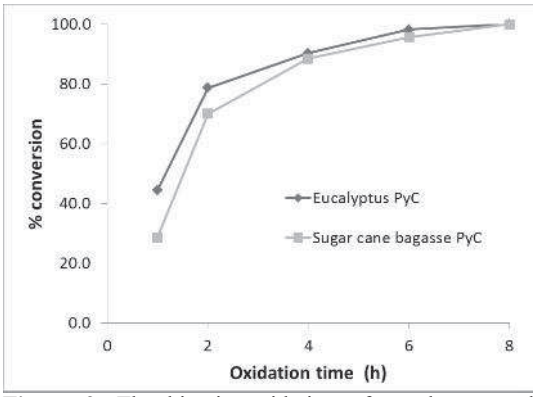


**Figure 2.** The kinetic oxidation of eucalyptus and sugarcane bagasse pyrogenic carbon (PyC) pyrolysed at 450 ºC. Both PyC had the maximum conversion of aromatic structures in benzene polycarboxilic acids (BPCA) at 8 h.

The oxidation kinetics was similar for the eucalyptus PyC pyrolysed at different temperatures (Figure 3). The temperature did not change the oxidation kinetic, however, as expected, eucalyptus PyC obtained at 450 ºC produced higher amount of BPCA than eucalyptus PyC pyrolysed at 350 ºC.

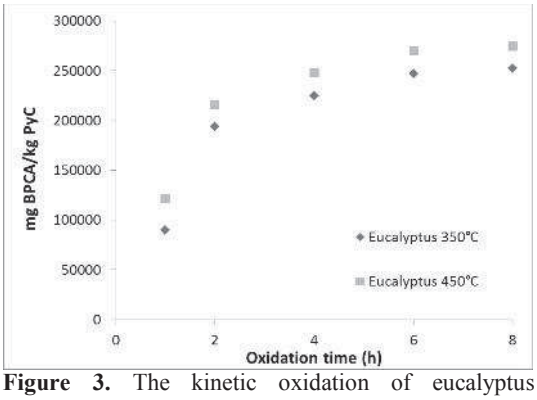


**Figure 3.** The kinetic oxidation of eucalyptus pyrogenic C (PyC) pyrolysed at 350 and 450 ºC. Both PyC had the maximum production of benzene polycarboxilic acids (BPCA) at 8 h.

The oxidation kinetics were similar for pine, eucalyptus and water hyacinth pyrolysed at 350 ºC, however they differed in the BPCA production. Eucalyptus produced the highest amount of BPCA, followed by pine and the water hyacinth (Figure 4).

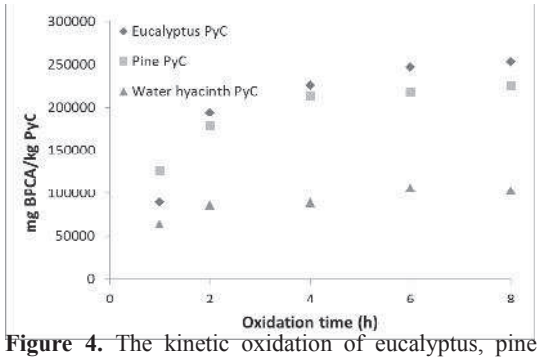


**Figure 4.** The kinetic oxidation of eucalyptus, pine and water hyacinth pyrogenic carbon (PyC) pyrolysed at 350 ºC. All PyC had the maximum production of benzene polycarboxilic acids (BPCA) at 8 h.

The water hyacinth produced a significant small concentration of BPCA, indicating that feedstock play an important role on BPCA formation.

Similar kinetics curve were found for most of the studied PyC, despite the feedstock and pyrolise temperature, indicating similar reaction mechanisms for these PyC. Although the pyrolys temperature and feedstock used influenced BPCA production, all PyCs had the maximum BPCA production after 6-8 h. These results are similar to those previously presented (3). Therefore, considering our results and the previous ones, we conclude that 8 h of nitric acid oxidation at 170 ºC is enough for maximal PyC conversion to BPCA and that these are robust oxidation parameters for the PyC quantification.

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