NATURAL ORGANIC MATTER RESEARCH

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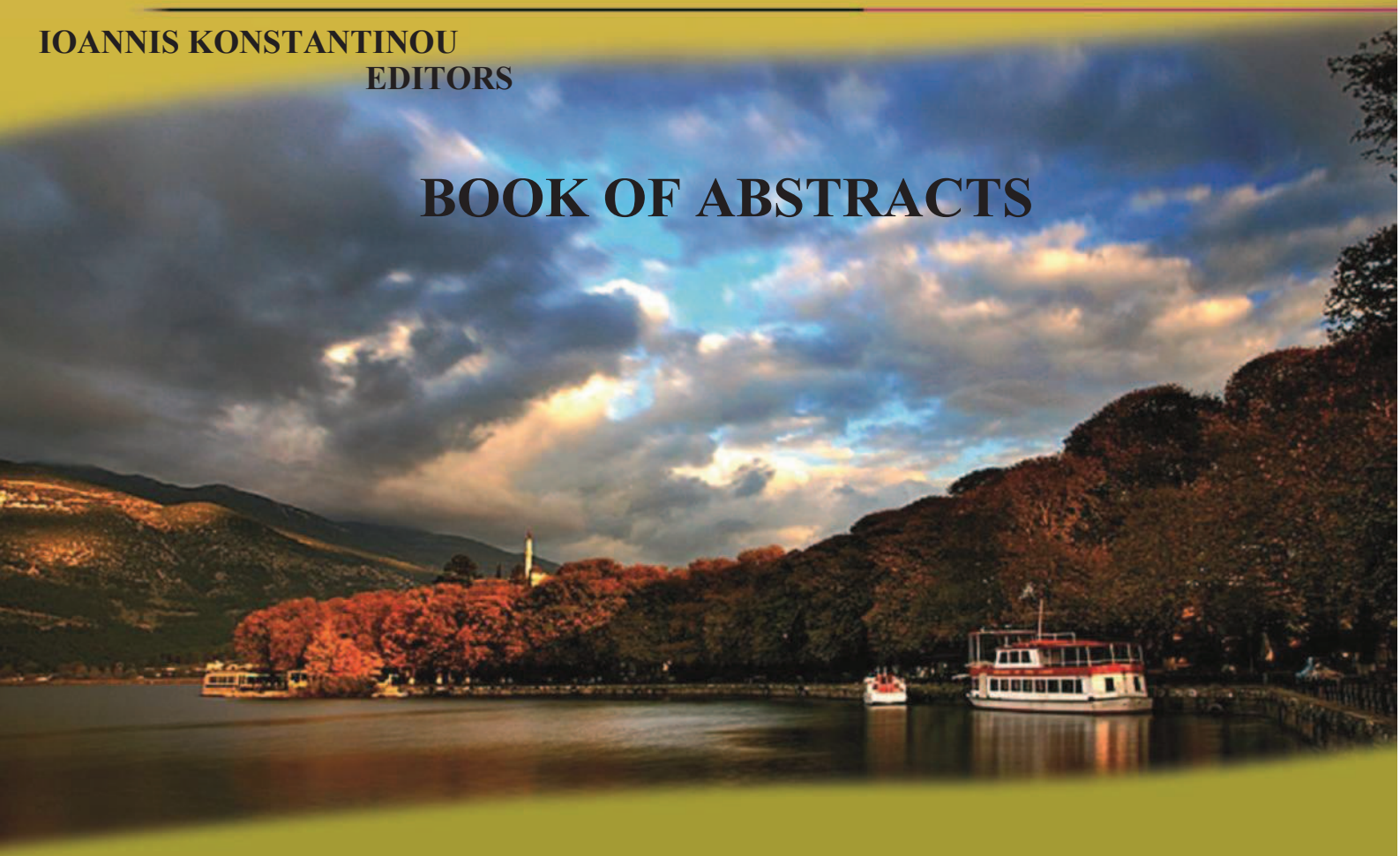

BOOK OF ABSTRACTS

NATURAL ORGANIC MATTER:

Structure-Dynamics

Innovative Applications

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Chemical composition of humic acids extracted from soils influenced by ancient charcoal production in Rio de Janeiro - Brazil

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Abstract During the late nineteenth century, some areas in Rio de Janeiro – Brazil – has undergone remarkable transformation of the forest arising from ancient charcoal activity carried out by ex-slaves. Nowadays, in the area of abandoned ancient kilns, it is possible identify charcoal in the soil. The charcoal weathering, in another anthropic soil, the Terra Preta de Índios (TPI), generated a peculiar soil organic matter, i.e very recalcitrant and with high cation exchange capacity (CEC), resulting in a resilient soil against degradation by intensive use. Thus, the structural comparison, by ^{13}C Nuclear Magnetic Resonance, of the humic acids (HA) from paleo-charcoal kiln and from TPI facilitate to confirm the hypothesis that the natural weathering of charcoal in the soil generate this peculiar organic matter. The result showed that the HA from paleo-charcoal kiln in Rio de Janeiro show similar features from TPI, i.e: policondensed aromatic rings heavily functionalised with carboxylic groups.

Introduction

From a historical perspective, the present environmental heritage is a product of past human populations' relationships with their environments (*1*). Our starting point in examining these interrelationships is the study of the paleo-territories of slaves, ex-slaves, and charcoal producers in the 19th and 20th centuries in Rio de Janeiro's mountain forests. Until the early 19th century, the mountains near the city, the Pedra Branca Massif, were largely used for sugarcane production and lumber and firewood extraction. In addition, our fieldwork indicated that the Pedra Branca Massif had been heavily populated from the 19th century until the beginning of the 20th century; our research located 157 abandoned ancient (paleo) charcoal kilns (*2*) and 61 home charcoal maker ruins among the forest slopes. Civil construction was one of the largest charcoal consumers at the turn of the 19th century (especially the stonemasons), and charcoal forges multiplied throughout the city with the exponential growth of industries and civil construction. The only traces that they left were vestiges in the landscape as the black soil in and around the paleo - charcoal kilns (*3*). So, the objective of this study was to investigate the consequences of the weathering of coal in the soil of the Pedra Branca Massif. Investigations on soils with charcoal presence have attracted the interest of scientist from different fields, such the literature has shown news perspectives of using this resource in improving soil quality and the potential to mitigate the anthropogenic green house effect, by the storage of the carbon in the soil (*4*). The Amazon TPI also are soils with charcoal residues, of anthropogenic origin from pre-Columbian period, which have higher fertility and resilience than the adjacent ordinary soils (*5*). These characteristics are provide by the peculiar organic matter of TPI, rich in pyrogenic C (*6*), important also for C sequestration. Therefore, we face the challenge of investigate humic acids from anthropic soils, as this influenced by ancient charcoal kiln, contemplated in the present work, drawing an analogy with TPI.

Experimental

It was selected a representative site from more than 157 charcoal kiln areas reported on the Pedra Branca Massif. However, update of this number indicates around 920 (data not published). It was sampled the center of the area under influence of the ancient charcoal kiln (center), and beyond two points: the dump (local deposition of charcoal residues not used for marketing); and surrounding soil, as control. In these points samples were collected at different depth: dump (0-10 cm, 10-20 cm and 40-60 cm), center of the paleokiln (0-10 cm, 10-20 cm and 20-40 cm); and control soil (0-10cm, 10-20 cm and 20-60 cm). The samples were dried and sieved (2 mm). After that, HA were extracted and purified by a selective extraction method (*6*). Briefly, an exhaustive extraction was done with NaOH solution adjusted at pH 7. HA samples were analysed by solid state ^{13}C Nuclear Magnetic Resonance (NMR) spectroscopy.

Results and Discussion

The ^{13}C NMR spectrum of HA extracted from control soil [Figure 1] is similar to the ones from ordinary HA from Tropical soils, exhibiting intense peaks from labile groups, such as: holocellulose (O and di-O- alkyl groups), probably partially oxidized to glucuronic acids (aliphatic carboxyl); lignin (aryl; O-aryl and methoxyl signals); and fatty acids (alkyl and aliphatic carboxyl). Already the HA samples rich in ancient charcoal, for example from dump site [Figure 1], display a significantly higher content of polycondensated aromatic structures than control samples, represented by the signal at 128 ppm, these structures give greater stability for the soil organic matter of these soils, and thus a greater potential for C

sequestration. Moreover, these samples exhibited carboxylic acids region (160-180 ppm) broader than control samples, due to an unresolved shoulder of upfield shifted carboxylic signal (around 165 ppm), this shoulder can be attributed to aromatic carboxylic acids. These structures guarantee a high fertility (high CEC) but in a recalcitrant form (aryl-carboxyl) resulting in a higher resilient soil, against cultivation, than the control one (*6*).

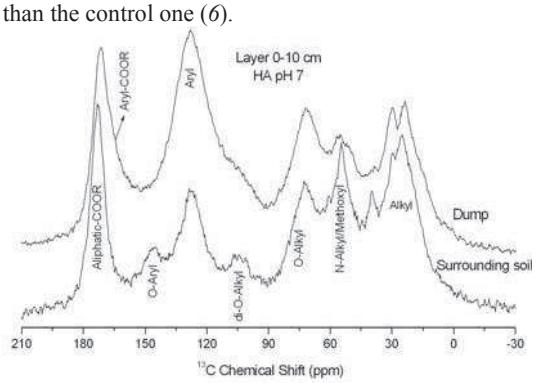

Figure 1. ^{13}C spectra of HA from ancient charcoal kiln and surrounding soil, in the 0-10 cm layer.

The spectra of the HA samples from the dump and center of ancient charcoal kiln (10-20 cm layer) [Figure 2] are similar, as both have carboxylic carbons from labile materials (aliphatic carboxyl – 172 ppm), as well as the typical aryl-carboxyl shoulder. In these samples the condensed aromatic structures are prevalent. However, these samples also shows peaks at 105 ppm (di-O-alkyl) and 72 ppm (O-alkyl), typical of carbohydrates (holocellulose), and the peak of the center of the kiln is narrower, indicating that the material is better preserved, while the broader peak of dump indicates that the material is more humified. This may be because the center is a flat area and thus a place of greater deposition of litter, less altered organic material.

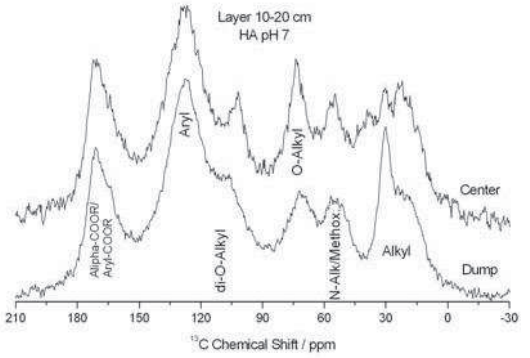

Figure 2. ^{13}C spectra of HA from ancient charcoal kiln and dump, from the 10-20 cm layer.

Comparing the ^{13}C spectra of the HA samples from the superficial layer of the area of dump with HA from TPI (*7*) [Figure 3], it is verified a high content of polycondensated aromatic structures (intense and broad band at 128 ppm) and carboxylic groups (band at 172 ppm) with typical broad and asymmetric signal of aromatic carboxyl in both samples.

However, the TPI HA does not have significant peaks of labile materials, seen in higher quantity in the dump, because this TPI is a cultivated area, with important lost of labile organic matter (*5*).

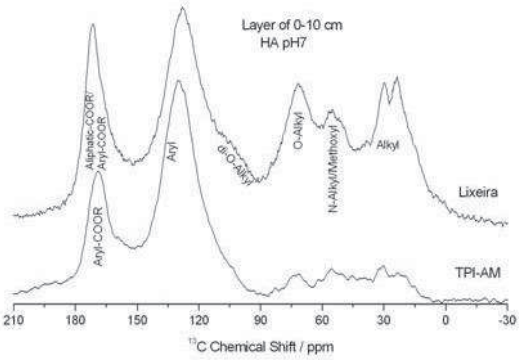

Figure 3. ^{13}C spectra of HA from dump and TPI, in the 0-10 cm layer.

The interaction human-nature not always is destructive (*Homo devastans*) and, in this studied case, produced HA structurally more recalcitrant (polycondensated aromatic structures) and with high capacity of adsorb nutrients cations (carboxylic groups), besides, this reactive groups probably are recalcitrant, since they are linked directly to the polycondensated aromatic structures, similar to HA found in TPI, another emblematic example of synergic interaction human-nature, since TPI are soils with higher: resilience; fertility and; sustainability than the adjacent control soils. It is important to highlight that besides the ex-slaves, have contributed to the construction of Brazil with its workforce, also left legacy (even if unintentional) soil with charcoal, which have peculiar characteristics and serve as model for thinking about more sustainable agricultural models, similar to the pre-Colombian Amazon indigenous people, and their TPI legacy.

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