Natural and anthropogenic pyrogenic carbon in Mediterranean ecosystems: the need for interdisciplinary learning and collaboration

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Charred vegetation residues derived from natural and prescribed burning play an important role in ecology and soil biochemistry and as an archaeological record. Indeed, vegetation fires shape our Earth and produce charcoal that has been accumulating in sediments and soils since geological times. Nevertheless, only since recently, pyrogenic organic matter (PyOM) has received more attention as an important constituent of the slow turnover pool of soil organic matter (SOM). Here, the term PyOM comprises the whole range of pyrogenic organic materials ranging from partially charred material to soot, which constitute the so-called black carbon (BC) *continuum*. Aside from increasing the overall stability of SOM, the input of ash and charcoal can positively affect nutrient availability and pH, but it can also alter the quality and quantity of SOM. The fertilizing effect of ash was a driving force for our Neolithic ancestors to develop fire-based agricultural practices. The soil conditioning properties of charred plant residues have been re-discovered only recently and investigated within the concept of biochar/biomass that has been pyrolyzed in a zero or low-oxygen environment in order to serve as soil amendment.

Although a strong political/policy and commercial demand to apply this concept exists, its novelty is responsible for the uncertainty regarding its ecological sustainability. Whereas some of the open questions may be answered by extrapolating existing knowledge in wildfire research, others may only be assessable from archaeology. Vice versa, wildfire science and archaeology can benefit from the strong efforts presently conducted in biochar investigation. Considering that possible synergies between those different research lines could overcome bottlenecks of each other, an exploratory workshop titled “Impact of natural and anthropogenic pyrogenic carbon in Mediterranean ecosystems”, financed by the European Science Foundation, was held in November 2013 in Seville, Spain. This meeting gathered selected investigators from all over Europe whose expertise covers a wide range of present PyOM research topics. The presented data were derived from investigations in Mediterranean ecosystems, as well as some from other ecosystems, which provided useful insights. Representatives from the COST Action TD1107 “Biochar as an option for sustainable resource management” also contributed to this knowledge. The main goal of this workshop was to further our understanding of the behaviour of different forms of PyOM in the environment, by integrating the latest advances of the chemical and physical nature of PyOM in the field of natural wildfires, biochar research and archaeology.

As an outcome of the workshop, this special issue brings together eight multidisciplinary works. They describe the application of contrasting techniques to characterize and quantify PyOM in sediments and soils located in the Mediterranean region as well as alpine and subtropical areas. The studies definitely contribute to a deeper knowledge and a wider perspective of the chemical composition, structure, functionality and abundance of the different forms of PyOM (including BC and biochar).

Studying the impact of vegetation fires on global C cycling, a pending question represents the persistence of PyOM to degradation, since its introduction into soil could contribute to the role of soil as a C sink. With respect to the use of biochar as a soil amendment, this question certainly has relevance as a suitable approach to reduce greenhouse gas emissions. However, on the other side of the coin, long-term survival of PyOM in soils implies that once biochar is added to the soil, both the desired but possibly also certain undesired, or potentially hazardous,

impacts on the environment may last for decades and longer. Unfortunately, due to the novelty of biochar research, long-term field experiments, which could predict the long-term behaviour of this soil amendment, are still missing. Thus, most of data available for the fate of biochars in soils are related to initial effects. However, many lasting impacts may be extrapolated from observations made during the investigation of ecosystems affected by natural fires and also by archaeology. One example represents the work by Sass and Kloss (2014). They sought to find out if and to which extent charcoal derived from former vegetation fires can survive and be stored on a long-term scale in Rendzic Leptosols in the Northern Limestone Alps of Austria. They observed that in areas of former forest fires, charcoal particles are frequently concentrated in a post-fire O horizon on top of the Ah horizon. Charcoal concentration and mean particle size were found to decrease due to erosion and translocation; however, when erosion was moderate, charcoal was conserved for centuries.

Focusing on the riverine transportation of charcoal from forest fires, the study of De la Rosa et al. (2015) focused on the distribution of pyrogenic carbon (PyC) in superficial sediments from the last 40 km of the Guadiana River (SW Iberian Peninsula). Determination of stable carbon isotope ratios together with chemo-thermal oxidation methods was employed to identify the possible origin of PyC, finding the highest concentration of PyC at sites located close to urbanized areas. Correspondingly, and confirmed by carbon isotopic ratio measurements, this material was derived mainly from fossil fuels but also had considerable contributions of charred biomass from C₃ plants. Most likely, the latter was derived from charred plant residues produced during vegetation fires of the mountainous area in the upstream parts of the river. The PyC to total organic carbon (TOC) ratio, and TOC contents, clearly indicated a selective preservation of PyC compared to sedimentary OM of the Guadiana estuary.

Mastrolonardo et al. (2014) characterized the chemical composition of organic matter in the top 10 cm of the mineral soil, and a covering charcoal layer, 2 months after an intense fire in a Mediterranean forest area. The intention of their work was to gain insight into PyOM formation in the Mediterranean environment and highlight the effects on charcoal structure and composition. Aside from confirming increasing aromaticity due to charcoal input, they found that charcoal was apparently quite sensitive to further combustion and oxidation by subsequent fires, even at moderate temperatures. This may affect OC stock estimations in environments where wildfires are frequent. Thermal laboratory treatments indicated further an increase of the N contents, which was explained by the formation of N heterocycles.

Many studies have demonstrated that an input of PyOM increases the aromaticity of SOM, but not all aromatic compounds in soils derive from charred material. In humic acids for example, aromaticity has often been considered as an independent index of biogeochemical maturity. Studying the structural characteristics of humic acids in soil with bi- and multivariate statistical exploratory analyses, Tinoco et al. (2014) sought relevant chemical descriptors that can be surrogated to aromaticity of humic acids. They found that the latter is responsive to the variability between environmental scenarios, in particular the effect of wildfires but also soil management (clearing and cultivation).

Transforming biowaste into biochar will not only allow the production of a value-added product but can also help to reduce waste disposal. However, in order to warrant an environmentally acceptable and sustainable application, a good understanding of the properties of such products is needed. With the intention to contribute to this knowledge, Pituello et al. (2014) investigated the properties of biochars obtained from different biowaste sources and at varying pyrolysis temperatures. They observed considerable chemical, structural and morphological differences between the artificial chars, depending strongly on the pyrolysis temperature and feedstock type. They concluded that it is not possible to identify a perfect biochar that can improve both soil nutrient content and soil structure. On the other hand, the fact that each biochar has specific features may allow creating products which are suitable for specific purposes.

An alternative source of charred soil amendments derived from waste may be charcoal fine residues. In Brazil, one of the largest charcoal producers, this by-product accumulates in large amounts and solutions for environmentally acceptable use are required. Leal et al. (2014) demonstrated the feasibility of applying this material as a soil fertilizer and as a stable C sink in subtropical Cambisols. They observed effects of charcoal input only in two soil layers, i.e. 0–5 cm and approximately 10–20 cm. However, no indication was found that charcoal residues leached below those first 20 cm of soil.

Applying the high-energy moisture characteristic (HEMC) technique and the powerful ¹H nuclear magnetic resonance (NMR) relaxometry to evaluate changes in aggregate stability and pore size distribution of biochar-

amended soils, Baiamonte et al. (2014) showed that aggregate stability improved as a biochar was progressively added to a sandy-clay soil. Since the recognition of the interaction mechanisms between water and biochar is of paramount importance to understand why biochar soil amendments improve soil fertility and crop production, a more detailed analysis of the ^1H NMR relaxation was performed. It was revealed that water dynamics were affected by the nature of biochar feedstock and that water undergoes an inner-sphere interaction mechanism with the biochar surface through formation of weak unconventional hydrogen bonds.

Most of the studies have been interested in the impact of biochar on the soils' concentrate on topsoils. In-depth analyses on alteration of C stability in subsoils are still scarce. Therefore, the study of Naisse et al. (2014), focusing on the effect of biochar addition on C mineralization and SOM priming in subsoils represents an important contribution towards a better understanding of the behaviour of anthropogenic chars in soil ecosystems. After applying ^{13}C -labelled biochar and plant material, Naisse et al. (2014) found only little biochar degradation and small priming effects in subsoils. They concluded that those processes are mainly affected by the composition of the added substrate and the soil parameters rather than by the microbial community characteristics.

During the workshop, considerable discussions evolved and led to a debate about the synergies and disparities between research on natural and anthropogenic PyOM forms. Although numerous studies on PyOM formed by natural fires have been carried out, the chemistry and properties of such materials are only scarcely understood. This is mostly because it is considered as a material that is too complex and heterogeneous to be well described. Here, the “natural PyOM” researchers could learn from the “biochar” scientists, which have recognized the essential need of a better knowledge of structural properties of the charred residues to be able to predict their behaviour in the environment. It became clear that considerably more effort is needed to understand the “inside” of natural and anthropogenic charcoal to advance from an observation point of view to a more mechanistic and chemical understanding of why and how the observed behaviour occurs. A more detailed functional understanding could also help to explain the observation that under some conditions, PyOM is relatively quickly degraded, whereas under other conditions, PyOM can survive for millennia and longer.

As a conclusion, one can state that the new field of biochar research can learn from the experience of post-wildfire research, about how low-temperature biochars may act on a long-term scale after their application to soils. However, one has to keep in mind that due to the special production conditions, high-temperature biochars have features that differ substantially from those of natural chars. Most likely, this affects their behaviour in soils and sediments and, as a consequence, still requires a major research effort to warrant its environmental sustainability. In contrast to the research field concerned with the impact of natural PyOM, recent progress in biochar research is furthering our understanding of the chemical and physical structure of different types of biochar according to their feedstock and production conditions. This helps to improve a classification allowing a better prediction of their behaviour in the environment and during ageing.

In summary, we hope that the papers collected in this special issue will initiate more fruitful collaborations between biochar and PyOM researchers, the latter includes both wildfire researchers and archaeologists, to boost our understanding and contribute to achieve safe biochar application to soil under different environmental conditions.

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