Exploratory Workshop Scheme

Scientific Review Group for Life, Earth and Environmental Sciences

ESF Exploratory Workshop on

IMPACT OF NATURAL AND ANTHROPOGENIC PYROGENIC CARBON IN MEDITERRANEAN ECOSYSTEMS

Seville (Spain), 5-7 November 2013

Convened by:

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Consejo Superior de Investigaciones Científicas (CSIC)

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS)

SCIENTIFIC REPORT

The scientific workshop report of this ESF-exploratory workshop is divided in the following 6 sections:

1. Executive summary

Organisation details:

This exploratory workshop was held at the main meeting room of "Casa de la Ciencia", which belongs to the CSIC organisation in Seville. It started with a welcome dinner on the 5th of November and finished at 16h of the 7th of November. A total of 21 delegates representing 9 different European countries were present.

Accommodation of the delegates was carried out at Hotel "Alcázar", which was covered by the organization, as well as all the meals through the meeting:

-Dinner on the 5th of November was held at "Restaurante La Raza".

-Lunch on the 6th of November was held at the University of Seville ("*antigua fábrica de Tabaco*" building).

-Dinner on the 6th of November was held at "Restaurante Enrique Becerra".

-Lunch on the 7th of November was held at "Restaurante San Marco".

-Breakfasts were carried out at "Hotel Alcazar".

-Morning and afternoon coffee-breaks were provided at the conference venue (Casa de la Ciencia-CSIC).

Technical support (registration, checking of presentations, helping desk, technical support, etc) was carried out by 2 PhD students and 1 postdoc from IRNAS-CSIC.

The wokshop was divided into six sessions of oral presentations and one poster session. After each talk, questions and answers were carried out under a very active and dynamic way. The fact that every single talk had several questions carried out by the rest of delegates is a detail showing the interest of the talks and the active participation of the delegates during the entire workshop.

Session 1. Pyrogenic C: Distribution and stability (Chair: H. Knicker)

This session was composed by 6 oral presentations devoted to explain the distribution and fate of different forms of pyrogenic organic matter in the environment.

They comprised results from natural fire affected areas and incubation studies. On the other hand the stability in natural and antropogenic pyrogenic organic carbon samples of pyrogenic organic matter was assessed.

Session 2. Characterisation of pyrogenic C forms (Chair: P. Buurman)

In this session 3 oral presentations were shown. They presented novel technologies such as the TG-DSC, the Fast field cycling relaxometry NMR and the 15N soli state NMR spectroscopy. They demonstrated to be useful techiques for determining changes into the soil organic matter properties, measuring biochar surface properties and the induced changes into the soil organic quality due to the addition of pyrogenic organic matter respectively.

Session 3. Effects of pyrogenic C on soil organic matter (Chair: J.A. González Pérez)

Four oral presentations were given in this session. They covered wild-fire induced changes into the soil organic matter, the effects of fires in central Europe, the presence of Black Carbon and other forms or refractory organic matter derived from fires in Alpine regions and the effects of adding pyrogenic C on soils from southern Spain.

Session 4 was entitled: Charcoal in archaeology (Chair: C. Doukas). The title of the presentation was “Charcoal in archaeological research-why preservation matters" given by Eileen Eckmeier (Aachen University, Aachen Germany). This talk provided to the rest of the delegates an overview of the significance of those archeological sites. In addition, those charcoal samples could be used to predict the behaviour and recalcitrance of pyrogenic organic matter under certain deposition conditions

During the **poster session** each poster was presented during 3-5 minutes. After that, a short round of questions was carried out. This session also favoured a close interaction between the delegates.

At the end of the first day, during 2 hours the delegates asked numerous specific questions to the speakers during a satisfactory open session.

Session 5. Biochar: Production and characteristics. Risks and benefits of its application to soils (Co-chairs: B. Glaser and H-P. Schmidt).

This session was composed by 4 presentations. It was entirely devoted to the different aspects of biochar, including characterisation, production, pollutions risks, potential constraints for low availability water supply and their effects on the hidrology under Mediterranean conditions.

Session 6 and round table-discussion.

The first part (session 6) was entirely devoted to discuss the remaining questions derived from the biochar session. After that the convenors explained to the delegates the possibilities of future joint collaboration and publications. Specifically, the delegates working in the characterisation of pyrogenic organic matter from fire affected soils were invited to join an already existing working wroup within the Biochar COST action. On the other hand, all the delegates were invited to submit their scientific works to an special issue on the Journal of Soils and Sediments which will be created for the communication presented to this exploratory workshop.

The second part was devoted to expone the remaining questions as well as the similarities and particular differences between natural pyrogenic organic matter and biochars and to elucidate what those two disciplines can learn from each other. The delegates agreed to prepare a joint review manuscript covering those questions. The last 2 hours of the workshop were devoted to identify key questions which should be included within the joint manuscript. In addition, the delegates exponed their point of view to each of these questions during the subsequent helpful discussions. Finally, more than 30 questions were selected to be included in the joint manuscript. Among others this future manuscript will cover:

-Updating definitions (biochar; pyrogenic organic matter; anthropogenic Carbon).

-How can we determine the C stability and partitioning of Pyrogenic Organic Matter (PyOM) forms? (Chemical and biological recalcitrance of PyOM; Mechanisms of stability and functionality).

-What is the chemical composition and structure of the different forms of PyOM (including natural and anthropogenic forms and how defines the structure the function?.

-What are the similarities and particular differences between natural PyOM and biochars and to elucidate what those two disciplines can learn from each other?

-Opportunities and limitations for research synergies between the 2 fields. Besides technical issues and analytical methods

-Benefits, potential risks and environmental impact of PyOM/biochar in soils
-Which techniques and new technologies are available to address these questions?.
-What are key knowledge bottlenecks in our understanding of the C sequestration potential of pyrogenic C forms (specifically including biochar)?.

2. Scientific content of the event

This Exploratory Workshop funded by the European Science Foundation and organised by the "Geoecología, Biogeoquímica y Microbiología Ambiental" Department of the "Instituto de Recursos Naturales y Agrobiología de Sevilla" (IRNAS-CSIC) permited the initiation of close collaborations between leading researchers from different european institutions and also with the network eBRN (European Biochar Research Network) of the COST Action to form a multidisciplinary team.
The oral contributions and posters presented during the workshop addressed important key questions concerning natural pyrogenic organic matter (PyOM) and biochar.Specifically they included,
i) the chemical composition and structure of the different forms of PyOM (including BC and biochar); ii)-chemical and biological recalcitrance of PyOM together with mechanisms of stability and functionality as well as the carbon sequestration potential and iii) the impact of PyOM in different Mediterranean soils.
In the next lines, the summary of each contribution is presented:

SESSION 1
WHERE DOES ALL THE PYROGENIC CARBON GO? ITS REDISTRIBUTION IN THE ENVIRONMENT. Presented by Prof. Stefan DOERR
This contribution presented the significance of post-fire transport of PyC and its redistribution within terrestrial environments. Post-fire landscapes are very susceptible to erosion due to the loss of protective vegetation and litter cover and the commonly observed reduction in soil stability and infiltration capacity, which further enhances runoff and erosion during rainfall. The low density of PyC makes it highly susceptible to both wind and water erosion and its often hydrophobic nature is likely to facilitate floating during water erosion. In the Mediterranean and many regions elsewhere, areas with significant topography are often those under dense vegetation cover, and hence most susceptible to fire, to high PyC production, To date, PyC fluxes by post-wildfire erosion have been poorly quantified and empirical relations between soil erosion and PyC movement need yet to be established. Knowledge of its erodibility, transport behavior, fluxes and the nature of its deposition sites is essential in understanding the ultimate role of PyC as a long-term C sink.

DEGRADATION VERSUS STABILITY: UNDERSTANDING THE SOURCE, FATE AND AGE OF PYROGENIC CARBON IN THE ENVIRONMENT. Presented by Philippa ASCOUGH
Pyrogenic carbon is frequently described as one of the most recalcitrant forms of environmental carbon, with estimated soil residence times on the order of 103 years forming a significant global carbon sink. Yet PyC remains a very poorly understood and poorly quantified factor in global biogeochemical cycles; current stocks and fluxes of some PyC components have high associated uncertainties of over ± 50% on global

scales (e.g. Ramanathan and Carmichael, 2008), much of which can be attributed to measurement uncertainties.
This presentation shoeed key knowledge gaps surrounding the source, fate, and turnover time of PyC in the environment, and presented new results from studies aimed at addressing these gaps. As a new approach, the hydropyrolysis, a relatively new technique in PyC investigations, which separates highly recalcitrant 'Black Carbon' from more labile material in PyC samples was presented.

CHEMICAL, PHYSICAL AND BIOLOGICAL STABILITY OF PYROGENIC ORGANIC MATTER IN SOIL. Presented by Prof. Cornelia RUMPEL
Prof. Rumpel presented a combination of physical, chemical and biological methods to identify physical and chemical properties determining their survival potential and to address their stability at different time scales to evaluate the C sequestration potential of pyrogenic C in soil, Her results showed a strong relationship between elemental composition and resistance to chemical oxidation suggesting that chemical oxidation may be used to characterise the degree of condensation of aromatic C.

FATE OF BIOCHAR CARBON FROM CORN STOVER AFTER A 510 DAY-INCUBATION IN AN ANDISOL AND ALFISOL. Presented by Prof. Peter BUURMAN
Prof. Buurman presented results from an incubation experiment carried out during 510 days investigating the evolution of CO2 from soils amended with fresh corn stover or with biochar produced from corn stover at either 350 or 550 °C (CS-350 and CS-550). The main goals were to evaluate the priming effect of these biochars on native organic matter (NOM) decomposition, and to elucidate the fate of biochar in physically- and chemically-defined fractions of organic carbon (OC).
At the end of the incubation with uncharred corn stover, a net positive priming effect on decomposition (enhanced the rate of decomposition) of NOM was observed in the two soils. In the presence of biochar, a net negative priming effect on NOM decomposition was observed in the TK soil, but no clear net effect was detected in the EG soil. A C balance indicates that the C lost from both biochar production and decomposition "breaks even" with that lost from residue decomposition in less than 35 weeks

PYROGENIC C AS A SOURCE OF MOLECULAR PROXIES FOR SOIL C STABILIZATION MECHANISMS. Presented by Prof. Francisco J. GONZÁLEZ-VILA
Prof. Gonzalez Vila presented a review on the specific chemical characteristics of pyrogenic C, other than those found in biomacromolecules present in natural soil organic matter (SOM). Special emphasis was paid to the possible meaning of these characteristics in the performance of the biogeochemical processes involved in soil C sequestration. In addition, a series of fire-induced effects modifying the composition, structure and properties of SOM leading to accumulation of resilient C-forms in soil were discussed from the results of field and laboratory studies.

CHEMICAL COMPOSITION AND BIOLOGICAL STABILITY OF PYROGENIC C FROM A NATURAL FIRE. Presented by Marie ALEXIS
The work presented was a synthesis of an article series conducted on natural charcoal in the environment with the objective of characterize the alteration of OM resulting from

thermal alteration and to follow the fate of the produced pyrogenic C in soil. This work was led in the oak scrub, located on the Merritt Island Wildlife Refuge in Florida.

SESSION 2

WHAT IS THE DIFFERENCE BETWEEN PYROGENIC CARBON OF NATURAL AND ARTIFICIAL SOURCES? A CASE STUDY FROM A PINE FOREST FIRE. Presented by Cristina SANTIN

This presentation aboarded the environmental recalcitrance of Pyrogenic Carbon (PyC), both produced in vegetation fires (charcoal), and man-made (biochar). Sustainable production of biochar and its addition to soils is currently debated as one of the most viable global approaches for carbon sequestration and climate change mitigation. Also the role of its 'natural counterpart', i.e. wildfire charcoal, as a long-term carbon pool in soils is recognized within the PyC research community. This presentation compared characteristics of man-made biochar and wildfire charcoal generated from the same material under known production conditions: charcoal generated in the forest floor of a pine forest (Pinus banksiana) during an experimental wildfire with monitored burn temperature/duration vs. biochar produced from the same feedstock under three pyrolysis conditions [2h at 350, 500 and 650°C]. Preliminary results indicated a high variability among the different types of PyC characterised. The wildfire charcoal does not only differ to the man-made biochar, but also the biochar characteristics vary depending on the production temperature.

PYOM CHARACTERISATION IN FIRE-PRONE MEDITERRANEAN PINE FORESTS. Presented by Giovanni MASTROLONARDO

Mr. Mastrolonardo presented the significance of fire as a driving factor of ecosystems in the Mediterranean basin. This works dealed with some wildfires occurred in Mediterranean pine forests of Tuscany, central Italy, and it was aimed at disentangling the composition and structure of PyOM produced during wildfire. To overcome the complexity of the investigated matter, they used various techniques and fractionated charcoal according to particles size, starting from the assumption that those fractions have different composition and reactivity, which is plausible on the basis of previous studies.

By thermal (thermogravimetry, differential scanning calorimetry) and spectroscopic (FT-IR, Raman, NMR) techniques, they observed that fire caused an accumulation of recalcitrant and refractory compounds at the expense of the SOM fraction most labile to thermal degradation.

BIOCHAR SURFACE PROPERTIES THROUGH APPLICATION OF AN INNOVATIVE NMR TECHNIQUE: FAST FIELD CYCLING RELAXOMETRY. Presented by Prof. Pellegrino CONTE

Prof Conte presented the use of fast field cycling relaxometry to reveal changes into the biochar chemical physical properties. Dynamics of water at the liquid-solid interface of water saturated biochars is discussed. Results revealed that water dynamics is affected by the nature of biochar parent biomasses. It was understood that water undergoes to an inner-sphere interaction mechanism with biochar surface through formation of weak unconventional hydrogen bonds. Recognition of the interaction

mechanisms between water and biochar is of paramount importance in order to understand why biochar soil amendments improve soil fertility and crop production.

SESSION 3

CHARCOAL – A SOIL FORMING FACTOR IN FREQUENTLY BURNT SOILS?. Presented by prof. Heike KNICKER

Prof. Knicker dealed with the long-term impact of PyOM this material on SOM and on general soil properties. In order to fill this gap, she presented 3 case studies of soils with expected and known fire-history. They were characterized by solid-state nuclear magnetic resonance (NMR) spectroscopy. Their respective pyrogenic organic matter (PyOM) content was elucidated after their chemical oxidation with acid potassium dichromate and the quantification of chemical oxidation resistant aromatic carbon (CORECarom).The studied profiles indicated that charcoal input alters the chemical composition of SOM on a long-term scale. Whereas in the agriculturally used Vertisols with their low input of fresh litter, this is clearly expressed by a high aromaticity of the SOM of both sub and topsoil, in soils with frequent input of fresh litter the alteration of SOM composition is mainly manifested in the subsoils. With respect to modern agriculture, the possible transport and stabilization of PyOM residues has also to be considered if one intends to elucidate the sustainability of artificially produced biochars as possible soil amendments.

WILD-FIRE INDUCED CHANGES IN THE QUANTITY AND QUALITY OF ORGANIC MATTER ASSOCIATED TO THE MINERAL PHASE. Presented by María LÓPEZ-MARTÍN

This study combined routine and advanced solid-state 13C and 15N NMR spectroscopy with wet chemical analysis to characterize the organic N in the density and particle size fractions of fire-affected soils from the Sierra de Aznalcóllar, Southern Spain. First results confirmed that both, the quality and quantity of N are affected in all particle size fractions. Some studies revealed the formation of carboxylic groups during the microbial transformation of charcoal. Such groups can increase the solubility of charred residues in the soil solution but can also interact strongly with the mineral phase. On the other hand, respiration experiments indicated that those soils charcoal was biochemically less recalcitrant than commonly assumed. The mean residence times of the charcoal fraction in fire-affected soils were only slightly longer than those observed for fire unaffected organic material.

CAN N-RICH CHARCOAL BE USED AS AN EFFICIENT N FERTILIZER?. Presented by José M DE LA ROSA

Mr. De la Rosa presented an incubation study with N-enriched pyrogenic materials to assess their potential as slow release N fertilizers, which would be of significant interest in Mediterranean ecosystems due to the general poor content in organic matter and low nutrient bioavailability of those soils

Solid-state 15N NMR spectroscopy revealed that some of this N derived from the degradation of pyrrole-type structures was used for new plant material.

Results suggested that this material may not as recalcitrant during long-term humification as formerly thought, in fact, N-rich PyOM operated as an organic N-fertilizer.

OBSERVATIONS ON WILDFIRE BLACK CARBON IN SHALLOW SOILS OF THE NORTHERN ALPS. Presented by Prof. Oliver SASS

Prof. Saas exposed that in spite of the low frequency of fires the Northern Limestone Alps (Austria), they can trigger severe erosion and vegetation destruction with the possibility of secondary natural hazards like rockfall, debris flows and avalanches. The aim of this study was to find out if, where, and to which extent charcoal is stored in the Rendzic Leptosols of the affected slopes and if the charcoal can be used to reconstruct the location and the extent of earlier wildfires.

The results showed that significantly elevated BC concentrations can be found on known historical wildfire sites, even if there is a certain ubiquitous background concentration which is probably due to aeolian transport and to earlier fires. The position of BC fragments within the soil profiles is influenced by fire characteristics and by the intensity of erosion; with vegetation and soil recovery, zones of maximum charcoal accumulation shift further downwards in the soil profile. Charcoal concentration and mean BC particle size decrease with age due to erosion and translocation; however, if erosion is moderate, charcoal can be conserved for centuries. A conceptual model was developed which shows where BC can probably be found in the profile considering fire intensity, erosion and translocation.

SESSION 4

CHARCOAL IN ARCHAEOLOGICAL RESEARCH – WHY PRESERVATION MATTERS. Presented by Eileen ECKMEIER

Ms. Eckmeier presented the use of macroscopic charcoal to reconstruct past environmental conditions, the vegetation and fire history as well as for radiocarbon dating and building chronologies of past events. She also presented the problems related to the use of charcoal on those proxies. In terrestrial archives, several diagenetic processes affect charcoal preservation. If charcoal is missing in archaeological or environmental records, it should be investigated if the charcoal has always been absent, or if it was removed from the site by degradation or erosion. It was shown that older charcoal is prone to chemical decomposition (e.g. Cohen-Ofri et al., 2006, Braadbaart et al. 2009). Charcoal preservation in soils or sediments is therefore affected by a variety of natural, but also anthropogenic factors, which needs to be considered when reconstructing past fire events.

SESSION 5

INFLUENCING BIOCHAR CHARACTERISTICS THROUGH PYROLYSIS CONDITIONS, FEEDSTOCK BLENDING AND POST-PRODUCTION TREATMENT
Presented by Hans-Peter SCHMIDT

Mr. Schmidt presented the complexity and heterogeneity of biochar materials. Its chemical and physical properties vary enormously. Besides the biomass feedstock composition, the pyrolysis temperature curve, the residence time in the pyrolysis chamber, the pressure and gas flow in the chamber and particularly the cooling regime of the dissipated educts have a major influence on the properties of a biochar.

An extremely important and so far also often neglected non-aromatic constituent of biochar is its mineral matter. This can range from less than 5 wt.% in wood-derived

biochars to more than 10wt.% in biochars produced from crop residues and manure. The degree of mineral-carbon-complexes within the biochar can be adjusted by blending the biomass feedstock with clay minerals, as it happens naturally in a forest or steppe fire where organic matter smoulders without oxygen on top and within the first few centimetres of the soil.
Using modern pyrolysis techniques, biochar-mineral-complexes with varying VOC content can now be produced under highly controllable process parameters. Based on these new experimental possibilities, new models on how biochar-mineral-complexes were and are produced in natural forest and steppe fires and how to predict their behaviour in the natural environment might be created. Moreover, first trials with the addition of clay minerals to the biomass feedstock have resulted in biochar-complexes with high fertilizing potential. Diring the subsequent discussion, it was exponed that in order to enhance the agronomic effects of biochar several post production treatments might be considered: (1) adding nutrients, (2) inoculating it with beneficial microorganisms, (3) improving its surface reactivity and porous volume and thus its sorption dynamics through traditional activation techniques, and/or (4) accelerated biological aging through composting or fermentation. The different post-production techniques can be classified according to the resulting physical and chemical alteration of the biochar:

THE JANUS FACE OF PYROGENIC CARBON REGARDING THE DISTRIBUTION AND AVAILABILITY OF ORGANIC POLLUTANTS. Presented by Thomas BUCHELI.
This presentation exponed the ambivalent role of pyrogenic organic matter for the fate and behaviour of organic pollutants in the environment. On the one hand, it acts as a strong sorbent for many organic contaminants on the other hand, it may contain such pollutants itself. In any case, it greatly influences the distribution, bioavailability and bioaccessibility of these chemicals
Addition of pyrogenic carbon will pull them even more into soils and thereby reduce exposures. Pollutants co-produced with pyrogenic carbon, such as PAHs are expected to largely remain sorbed.
This contribution presented several examples of pyrogenic carbon used for remediation of polluted soils or sediments, and highlighted the potential and limitations of this approach

POTENTIAL AND CONSTRAINTS OF BIOCHAR FOR PLANT-AVAILABLE WATER SUPPLY. Presented by Prof. Bruno Glaser
This presentation highlighted the porous physical structure of biochar, which can absorb and retain water although its chemical structure is dominated by condensed aromatic moieties suggesting hydrophobicity. In addition, the pore size distribution of most biochars is dominated by pore diameters of < 0.2 µm bind water with high capillary forces so that this water must be considered inaccessible for plants. On the other hand, obtained results from real measurements strongly suggest positive effect of biochar for plant-available water supply.
He presented that biochar can indeed increase plant-available water supply. However, underlying mechanisms are not clear and theoretical contradictions need further attention.

POSTER SESSION

POSTER 1

THE EFFECT OF HEAT IN SOIL ORGANIC MATTER (SOM). EXPERIENCE FROM CONTROLLED BURNING EXPERIMENTS OF UNALTERED SOIL BLOCKS. Presented by José A. GONZÁLEZ-PÉREZ

This poster reflected the effect of fire to different soil properties and in particular to the quantitative and qualitative changes exerted to SOM in two different soil types; a gypseous soil (Hypergypsic Gypsisol) and a renzina (Rendzic Phaeozem). With respect to C quantity, in general in the burned blocks a decrease in soil organic carbon (CO) was observed in the O horizon and down till the 1st cm in the mineral Ah horizon where a maximum temperature was 250 °C. No appreciable quantitative differences were observed in the inorganic C content (CI) at any depth.

With respect to C quality, soil organic matter alteration caused by fire was studied at a molecular level using direct analytical pyrolysis (Py-GC/MS). The technique was useful in assessing fire severity in terms of soil organic matter molecular structural shifts. Among organic compounds, hydroaromatic structures (steroids) are found particularly resistant to heat, not only in the burned soils studied here, but also frequently observed by us to persists practically unaltered in other heavily charred matrices (biochars) obtained from a variety of substrates (LAR's, biomass, wood, etc.). The steroids are typical biomass markers with specific chemical structures informative of origin i.e. vegetation, animals including humans, mosses or fungi. Several steroids and related compounds are well known physiologically active substances that play different roles in eukaryotic organisms. In the future it may be prudent to consider the potential effects of such substances when present in biochars, particularly when the intended use implies the release of large quantities into nature i.e. as amendments in

POSTER 2

TOTAL ORGANIC CARBON, TOTAL NITROGEN AND CHEMICAL CHARACTERISTICS OF AN HAPLIC CAMBISOL AFTER BIOCHAR INCORPORATION. Presented by Heike KNICKER.

This poster presented the resuls of the use of different biochar as a soil conditioner to a subtropical Cambisol.

The main alterations in soil characteristics were observed in the superficial depth (0 - 5 cm) probably due to the permanence of the biochar fine particles at the soil surface. In addition, the contents of available P, exchangeable K and Ca where higher under treatment of 40 t ha^{-1} in comparison to treatment of 10 T ha^{-1}. In opposition, exchangeable Mg content, Al+H, V% and CEC were not altered by any treatment. After two years of biochar application an increase of soil organic carbon and a positive impact on the soil chemical characteristics at the soil surface were attained, but only with the highest tested dose (40 t ha-1).

POSTER 3

THE EFFECTS OF BIOCHAR AMENDMENT ON SOIL EROSION AND INFILTRATION. Presented by Frank VERHEIJEN

This poster presented the results of a pilot study that aims to identify if biochar mixed into soil affects the soil hydrology (infiltration and runoff), and if these effects correlate changes in soil structure. A 'perforated tray rotating disc type rainfall simulator' allows

for collecting both the run-off and the water percolated through the soil from a series of replicated rainfall simulation experiments (RSEs), under controlled conditions. Both types of water samples will be analysed for particle size (soil and biochar). The water samples were analysed for turbidity with a new plastic optical fibre-based sensor (Bilro et al. 2010), which was developed at the University of Aveiro. The results still need further analysis and the data process are still under development.

POSTER 4

ASSESSMENT OF EFFECTS IN THE GERMINATION AND AGRONOMIC PRODUCTION OF FOUR CONTRASTING BIOCHARS. AN INCUBATION STUDY. Presented by José M. DE LA ROSA.

This poster evalluated the effect of the application in a typical Mediterranean agricultural soil of four contrasting biochars produced from different feedstocks (a) wood biochar, b) paper-sludge-bran biochar, c) sewage-sludge biochar. In addition "Bodegas Torres Company, Spain" provided the sample d) of grapevine wood biochar). This experiment was carried out at 25 ºC for 79 days (14 h light day-1) and water supply equivalent to 800 mm yr-1 in quadruplicate with amounts equivalent to 10, 20 and 40 T Ha-1 ob biochar amendment. Control experiments (without biochar amendment) were also settled for comparison purposes. Results released from this experiment confirmed that beneficial effects of biochar in agriculture vary according to the kind of biochar used and its application rates. Germination and plant-survival increased significantly in the cases of wood biochar and sewage-sludge biochars (samples a and c respectively). However, grapevine wood biochar resulted in similar germination rates than un-amended pots. In addition, biomass production raised significantly in presence of all biochars.

POSTER 5

CHARCOAL INPUT INCREASES C SEQUESTRATION POTENTIAL OF SUBSOILS IN UMBRIC FERRALSOLS. Presented by Heike KNICKER.

This poster studied the effects fires and the subsequent input of charcoal on the SOM from profiles of Umbric Ferralsols from Atibaia, Campinas (São Paulo State) and Chapecó (Santa Catarina State). Soil OM was characterized by solid-state NMR spectroscopy. Their respective pyrogenic organic matter (PyOM) content was elucidated after their chemical oxidation with acid potassium dichromate and the quantification of chemical oxidation resistant aromatic carbon (CORECarom). In order to reveal possible interaction with the mineral phase, iron and aluminium oxides were extracted with different extracting solutions (sodium pyrophosphate, ammonium oxalate and dithionite-citrate-bicarbonate solution) and related to SOM quality and quantity.

As it is typical for such soil, SOM concentrations in the A horizons of the studied soils are about times higher than those of other Ferralsols. Pyrogenic organic matter (PyOM) was identified down to the 2 meters depth. Interestingly, PyOM contributions were less in the top soils than in the deeper horizons, most tentatively because of efficient charcoal oxidation at the surface and the subsequent removal of the degradation products by further mineralization or by transport to deeper soil regions. According to solid-state NMR spectroscopy, the SOM of several deeper horizons was almost exclusively composed of PyOM. This observation demonstrates its preferential

preservation in deep soils, possibly supported by its stabilization through the mineral phase.
Data clearly supported that frequent charcoal addition can have a long-term impact on both the quality and quantity of organic matter in particular of deeper soil horizons. Here the oxidized PyOM is selectively preserved and seems to play a key role for increasing the amount of sequestered C in fire affected soils.

POSTER 6
PRIMING EFFECT AFTER ADDITION OF PYROGENIC CARBON IN A SANDY SOIL MATRIX. Presented by Tatiana F. RITTL.
This study aimed to investigate the effect of biomass type on pyrogenic C and native SOM decomposition rate in a sandy soil by using elemental (CHN) and structural (13C nuclear magnetic resonance (NMR) spectroscopy) composition. On the other hand, the decomposition rate was measured by CO2 evolution and each source of CO2 released was distinguished by the CO2-13C signatures, because native SOM was dominated by the signature of C4-plants.
Results showed (i) differences in the C:N ratio and chemical groups of the three pyrogenic C; (ii) differences in CO2 evolution between treatments and control; (iii) preferential decomposition of compounds present in the pyrogenic C against the native SOM in soil and; (iv) samples richer in amorphous alkyl groups presented a higher decomposition rate of pyrogenic C than samples richer in aryl groups, indicating a preferential decomposition of these aliphatic compounds. As a main conclusion the application of pyrogenic C in this sandy soil resulted in an substantial early negative priming effect in the decomposition of native SOM.

SESSION 6 & IDENTIFICATION OF COMMON ISSUES, FORMULATION OF AGENDA FOR JOINT REVIEW MANUSCRIPT AND WOKSHOP REPORT.
During the first part of this session the discussion started with issues which arose during session 5 and led to a debate about the synergies and disparities between research on natural and anthropogenic pyrogenic organic carbon forms. It was stated that although numerous studies on pyrogenic organic carbon formed by natural fires have been carried out, the chemistry and properties of such materials are only scarcely understood, mostly because it is considered as a material which is to complex and heterogeneous to be well described. Here, the “natural-PyOM” researcher 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 was suggested to perform ring trail experiments to elucidate usable analytical techniques. It was further considered that the production and analysis of reference material with known feedstock and under different but controlled charring conditions could greatly improve the prediction of the fate of natural PyOM in different environments. It became clear that considerable 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 why and how the observed behaviour occurred. Those issues include i.e. the movement of nutrients and water in the pores and their interactions but also the biochemical accessibility of functional groups in the charcoals and the impact of the latter on charcoal stability. A more detailed functional understanding could help to

explain the observation that under some conditions pyrogenic organic matter is relatively quickly degraded, whereas different conditions can support its survival for millennia and longer. The delegates recognized that the latter is certainly also an important question in archaeology. It was also remarked that the presence and formation of dissolved and water extractable forms of pyrogenic organic matter needs more consideration since it seem to play an important role for soil forming processes in the subsoil of charcoal affected soils but also in the contamination of the aquifer and waters fed by water runoff after heavy rains. A further point of discussion was that the inherent variability of biochars due to different feedstock and production conditions coupled with different properties of different kinds of soils to which they are applied implies a high variability of the effect of those materials on soil properties and productivity. This strongly suggests that the production and use of biochars, as a carbon sequestration strategy and a soil amendment needs to be customized for each situation. However, up to now, the study of biochar effects is mostly limited to agricultural productivity and C-sequestration but is only poorly assessed with respect to impacts on different ecosystems or on the food chain, particularly under different climatic conditions, soil types and land management systems. A major problem of present biochar research is that available data are mostly related to initial biochar effects, since long-term experiments are not available, yet. However, many long-term impacts may be extrapolated from observations made during the investigation of ecosystems affected by natural fires and even by archaeology. On the other hand the strong efforts presently conducted to increase our knowledge about, the fate of biochar in soils can serve for scientists which are seeking a better understanding of the ecological impact of vegetation fires.

The second part of this session was dedicated to the development of an outline of a joint publication as a focus paper in an internationally well recognized research journal.

3. Assessment of the results, contribution to the future direction of the field, outcome

A major benefit of this workshop was the interaction of experts in the field of impact of natural fires on soils and ecosystems and in the field of biochars. This exchange of knowledge was complemented by researcher in the field of archaeology. It became clear that the new field of biochar research can learn from the experience after natural fire, how low temperature biochars may act on a long-term after their application to soils. However, due to the special production conditions, high temperature biochars has features which differ largely from those of natural chars, which may affect their behaviour in soils and still needs major research effort to warrant its environmental sustainability.

In contrast to the field of natural pyrogenic organic matter impact, recent progress in biochar research is going towards a better understanding of chemical and physical structure of the different types of biochar according to their feedstock and production conditions in order to improve a classification allowing a better prediction of their behaviour in the environment and during aging. Also, The role of the pore system for water and nutrient transport and as important interface for chemical, physical and biological processes was identified An improved understanding of the those aspects becomes of even higher importance if one turns to a development of functionalize

biochars where their properties are adapted to the needs of their users. Considering that such a knowledge could also facilitate the prediction of the impact of different fires on environmental aspects and the definition of groups within the BC continuum, it was agreed that this should be a focus of future charcoal research.

Dissolved or water extractable PyOM was recognized as a formerly neglected but nevertheless important fraction of charcoal both after natural and anthropogenic production. Its formation, behaviour and interactions in soil and the soil solution were defined as essential future research efforts.

Future actions:

In order to summarize and disseminate the research presented at the workshop a special issue in the Journal of Soild and Sediments will be prepared. However, since we agreed that our joint efforts allowed to extract sufficient evidence for the need of a better communication between the field of biochar, impact of vegetation fires and archaeology we agreed on preparing a focussed paper for a well recognized scientific journal highlighting the emerging science of the respective research fields and the synergies which are expected from if their interactions are improved. An outline of such a paper was achieved. After revision by the workshop conveners this draft will be send to the workshop participants which have to define their possible contributions according to their expertises. Subsequently, work groups will be assigned which are responsible for the preparation of specific paper section. The overall coordination will be handled by the workshop conveners.

In order to initiate future collaboration, it is intended to improve the integration of archaeology and wild fire research in the already existing ESF-COST action “European Biochar Research Network” (eBRN) by encouraging students and scientists to participate in the program for short term scientific visits and in the next Focus meeting of work group 1 of that COST action.

4. Final programme

WORKSHOP PROGRAMME

Tuesday, 5th November 2013

Afternoon	*Arrival, hotel registration and welcome (Hotel Alcázar)*
20.30	*Get-together. Dinner at Seville city center (Restaurante La Raza)*

Wednesday, 6th November 2013

8.30-8.50	***Registration at "Casa de la Ciencia-CSIC"***
8.50-9.00	***Opening by convenors***
	José M. De la Rosa & Heike Knicker (IRNAS-CSIC, Seville, Spain)
9.00-9.10	***Welcome by CSIC representative***
	Prof. Miguel A. Ferrer (CSIC- Institutional Coordinator, Andalucía, Spain)
9.10-9.20	***Welcome by IRNAS representative***
	Prof. José M. Pardo (IRNAS-CSIC Director)
9.20-9.40	***Presentation of the European Science Foundation (ESF)***
	Prof. Constantin Doukas (representative of ESF Science Review Group for Life, Earth and Environmental Sciences; University of Athens, Greece)
09.40-12.10	**Session 1. Pyrogenic C: Distribution and stability (Chair: H. Knicker)**
09.40-10.00	***Presentation 1 "Where does all the pyrogenic C go? Its redistribution in the environment"***
	Stefan Doerr (Swansea University, Swansea, UK)
10.00-10.20	***Presentation 2 "Degradation versus stability: Understanding the source, fate and age of pyrogenic carbon in the environment"***
	Philippa Ascough (University of Glasgow, East Kilbride, UK)
10.20-10.40	***Presentation 3 "Chemical, physical and biological stability of pyrogenic organic matter in soil"***
	Cornelia Rumpel (CNRS-BIOEMCO, Thiverval-Grignon, France)
10.40-11.00	***Presentation 4 "Fate of biochar carbon from corn stover after 510 day-incubation in an andisol and alfisol"***
	Peter Buurman (Wageningen University, Wageningen, The Netherlands)
11.00-11.20	***Coffee break***
11.20-11.40	***Presentation 5 "Pyrogenic C as a source of molecular proxies for soil C stabilization mechanisms"***
	F.J. González-Vila (IRNAS & representing CCMA, CSIC, Spain)
11.40-12.00	***Presentation 6 "Chemical composition and biological stability of pyrogenic C from a natural fire"***

	Marie Alexis (Biogéochimie et Ecologie des Milieux Continentaux, Paris, France)
12.00-13.00	**Session 2. Characterisation of pyrogenic C forms (Chair: P. Buurman)**
12.00-12.20	***Presentation 1"What is the differences between pyrogenic carbon of natural and artificial sources? A case study from a pine forests"***
	Cristina Santín (College of Science-Swansea University, Swansea, UK)
12.20-12.40	***Presentation 2"PyOM characterisation in fire-prone Mediterranean pine forests"***
	Giovanni Mastrolonardo (Università degli Studi di Firenze, Firenze, Italy)
12.40-13.00	***Presentation 3 "Biochar surface properties through application of an innovative NMR technique: Fast field cycling relaxometry"***
	Pellegrino Conte (Università degli Studi di Palermo, Palermo, Italy)
13.00-14.10	***Lunch (University of Seville, "Antigua Fábrica de Tabaco")***
14.10-14.20	*Group meeting photo*
14.20-15.40	**Session 3. Effects of pyrogenic C on soil organic matter (Chair: J.A. González Pérez)**
14.20-14.40	***Presentation 1 "Charcoal- a soil forming factor in frequently burnt soils"***
	Heike Knicker (IRNAS-CSIC, Seville, Spain)
14.40-15.00	***Presentation 2 "Wild-fire induced changes in the quantity and quality of organic matter associated to the mineral phase"***
	María López (Instituto de Recursos Naturales y Agrobiología, Seville, Spain)
15.00-15.20	***Presentation 3 "Can N-rich charcoal be used as an efficient N-fertilizer?"***
	José M De la Rosa (IRNAS-CSIC, Seville, Spain)
15.20-15.40	***Presentation 4 "Observations on wildfire black carbon in shallow soils of the northern Alps"***
	Oliver Sass (University of Graz, Graz, Austria)
15.40-16.00	**Session 4. Charcoal in archaeology (Chair: C. Doukas)**
15.40-16.00	***Presentation 1 "Charcoal in archaeological research-why preservation matters"***
	Eileen Eckmeier (Aachen University, Aachen Germany)
16:00-17:00	**Poster session & coffee break**
17:00-17:20	*Planetarium session (offered by Casa de la Ciencia-CSIC)*
17:20-19:00	***Discussion from sessions 1-4 (Co-chairs: S. Doerr & P. Conte)***
20.45	*Dinner at "Restaurante Enrique Becerra" (Gamazo Street; City center)*

Thursday, 7th November 2013

09.00-09.10	*Opening and announcements by convenors*
09.10-10.50	**Session 5. Biochar: Production and characteristics. Risks and benefits of its application to soils (Co-chairs: B. Glaser and H-P. Schmidt).**
09.10-09.30	**Presentation 1 "Infuencing biochar *characteristics through pyrolysis conditions, feedstock blending and post-production treatment"***
	Hans-Peter Schmidt (Delinat Institut, Arbaz, Switzerland)
09.30-09.50	**Presentation 2 "The janus face of pyrogenic carbon regarding the distribution and availability of organic pollutants"**
	Thomas Bucheli (Agroscope Reckenholz-Tänikon Res. Stat., Zürich Switzerland)
09.50-10.10	**Presentation 3 "Potential and constraints of biochar for plant-available water supply"**
	Bruno Glaser (MLU Halle-Wittenberg, Halle, Germany)
10.10-10.30	**Presentation 4 "Biochar and soil hydrology under mediterranean conditions"**
	Frank Verheijen (CESAM, University of Aveiro, Aveiro, Portugal)
10.30-11.00	*Coffee break*
11.00-14.00	**Session 6. Discussion, consolidation and recommendations (Co-chairs: H. Knicker, J.M de la Rosa and B. Glaser)**
11.00-12.00	**Discussion from session 5**
12.00-14.15	**Identification of common issues, formulation of agenda for joint review manuscript and wokshop report.**
	Networking and closing remarks.
14.30	*Lunch at San Marcos Restaurant*
16.00	*End of workshop and departure*

5. Final list of participants

List of Participants

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6. Statistical information on participants

Number of participants excluding the ESF representative: 20.
Age bracket: 26-67 years old (26-46 years old; 10 participants. 46-67 years old, 10 participants).
Countries of origin of the participants (9 different countries): Austria, France, Germany, Italy, Portugal, Spain, The Netherlands, United Kingdom and Switzerland.
(In addition the ESF representative was from Greece).
M/F repartition: 12 men and 8 women.