2nd Mediterranean Biochar Symposium
Environmental impact of biochar and its role in green remediation

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Università degli Studi di Palermo

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THE SYMPOSIUM

Biochar is a carbonaceous material obtained by pyrolysis of biomass feedstocks. It is applied to soils in order to improve fertility and mitigate greenhouse-gases emissions. In fact, on one hand, biochar changes physical-chemical soil properties, thereby affecting soil fertility. On the other hand, biochar is resistant to chemical and biochemical degradation. Therefore, its use allows carbon sequestration in soils and consequent reduction of carbon dioxide to the atmosphere. Moreover, biochar is a porous material showing good sorption properties for inorganic and organic pollutants. Because of this, biochar can be applied for environmental remediation.

Notwithstanding the positive effects in environmental applications, many studies report also about adverse issues deriving from biochar uses. In fact, literature is plenty of controversial results concerning use of biochar as amending material. Due to the direct relationship between structural/molecular characteristics and chemical/biochemical properties, it must be pointed out that a deep characterization either by innovative physical-chemical techniques or by traditional chemical investigations is of paramount importance in order to reveal biochar role in environmental compartments, to address its agronomical and environmental uses and to allow meaningful pre-application quality assessments.

The 2nd Mediterranean Biochar Symposium will be focused on the chemistry and biochemistry of biochar products retrieved by biomass feedstocks. Particular attention will be devoted to the environmental impact of biochar and to its use as a "green" amending material for environmental remediation, especially in the Mediterranean Region.

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Program

16/01/2014

8.00-10.00	Registration + welcome breakfast	
10.00-10.30	**Symposium opening**	
Session 1. Worldwide Biochar Assessment		
Chair	**Dr. Hans-Peter Schmidt** (Ithaka Institute, Switzerland)	
10.30-11.00	L. Genesio	2007-2013: 7 YEARS OF BIOCHAR RESEARCH IN ITALY
11.00-11.20	M. Iwaya	UTILIZATION OF CHARCOAL IN JAPAN
11.20-11.40	I. Teichmann	AN ECONOMIC ASSESSMENT OF BIOCHAR IN GERMANY
11.40-12.00	A. Wrobel-Tobiszewska	ECONOMIC PERSPECTIVE OF BIOCHAR APPLICATION TO FORESTRY PLANTATIONS
12.00-14.00	**Lunch + Poster session**	
Session 2. Biochar Characterization		
Chair	**Dr. Francesco Primo Vaccari** (National Research Council, Italy)	
14.00-14.30	H.-P. Schmidt	ANALYTICAL STANDARDS FOR BIOCHAR CHARACTERIZATION AND CERTIFICATION – LESSONS FROM THE COST BIOCHAR RING TRIAL
14.30-14.50	D. Fabbri	MOLECULAR CHARACTERIZATION OF BIOCHAR BY ANALYTICAL PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY
14.50-15.10	A. Dieguez-Alonso	POROSITY CHARACTERIZATION OF BIOCHAR SAMPLES WITHIN THE FRAMEWORK OF THE BIOCHAR COST ACTION TD1107

15.10-15.30	P. Conte	WATER DYNAMICS AT THE SOLID-LIQUID INTERFACE OF PYROGENIC CARBON MATERIALS
15.30-16.00	**Coffee Break + Poster Session**	
Session 3. Biochar Effect on Living Systems		
Chair	**Prof. Luigi Badalucco** (Università di Palermo, Italy)	
16.00-16.30	D.P. Rasse	MINERALIZATION KINETICS OF BIOCHAR SERIES AND ASSOCIATED CHANGES IN SOIL MICROBIAL COMMUNITIES
16.30-16.50	A. Maienza	ANTS AND BIOCHAR: A FIELD EXPERIMENT STUDY
16.50-17.10	S. Baronti	BIOCHAR APPLICATION AFFECTS PLANT-WATER RELATIONS IN Vitis vinifera (L)
17.10-17.30	S.S Akhtar	BIOCHAR IMPROVES PHYSIOLOGY AND BIOCHEMISTRY OF POTATO IN RESPONSE TO SALINITY STRESS
17.30-19.00	**Poster session**	

17/01/2014		
9.00-10.00	**Poster Session**	
Session 4. Agro-Environmental Effect of Biochar		
Chair	**Dr. Alessandro Pozzi** (ELY/AGT, Italy)	
10.00-10.30	El-Araby	BIOCHAR FOR DESERT RECLAMATION AND CARBON DIOXIDE SEQUESTRATION
10.30-10.50	M. Valagussa	BIOCHAR IN GREEN ROOFS
10.50-11.10	E. Pusceddu	CHANGES IN MORPHOLOGICAL AND PHYSICAL CHARACTERISTICS OF BIOCHAR AFTER LONG-AGING IN SOIL
11.10-11.40	**Coffee Break**	
11.40-12.00	M. Paneque Carmona	AGRONOMIC EFFECTS OF THE ADDITION OF BIOCHAR FROM DIFFERENT FEEDSTOCKS TO A TYPICAL MEDITERRANEAN AGRICULTURAL SOIL IN RELATION TO THE APPLICATION RATE
12.00-12.20	J.M. De La Rosa	ANALYTICAL CHARACTERISATION AND PAH ASESSMENT OF FOUR BIOCHARS AND A BIOCHAR AMENDED CAMBISOL FROM SOUTHERN SPAIN
12.20-13.00	**Symposium Closing and Remarks**	

POSTER SESSION

Biochar Characterization

PS.2.1 **Marsala et al.** CHARACTERIZATION OF A HOMEMADE BIOCHAR FROM WOOD BIOMASS

PS.2.2 **Cimò et al.** EFFECT OF HEATING TIME AND TEMPERATURE ON THE CHEMICAL-PHISYCAL CHARACTERISTICS OF CHICKEN MANURE BIOCHAR

PS.2.3 **Cimò et al.** EVALUATION OF INORGANIC CONTAMINANT REMOVAL FROM AQUEOUS SOLUTIONS USING PYROLIZED CHICKEN MANURE, CONIFER AND POPLAR WOOD AS ADSORBENT

PS.2.4 **Marsala et al.** EFFECT OF METALS ON THE DYNAMICS OF WATER AT THE BIOCHAR SOLID-LIQUID INTERFACE

Biochar Effect on Living Systems

PS.3.1 **Palazzolo et al.** EFFECTS ON SEED GERMINATION OF DIFFERENT BIOCHARS FROM INDUSTRIAL THERMO-CHEMICAL PROCESSES

PS.3.2 **Dispenza et al.** USE OF BIOCHAR IN GROWING MEDIA FOR CITRUS ORNAMENTAL PLANT

PS.3.3 **Di Lonardo et al.** BIOCHAR USED AS A PEAT SUBSTITUTE FOR NURSERY PLANTS REDUCES NEGATIVE SALINITY EFFECTS IN SENSITIVE ORNAMENTALS

PS.3.4 **Di Bonito et al.** IMPACT OF THE AMENDMENT WITH BIOCHAR ON SOILLESS SUBSTRATES USED FOR CULTIVATION OF Sedum reflexum FOR GREEN ROOF TECHNOLOGY

PS.3.5 **Baronti et al.** HYDROTHERMAL BIOCHAR PRODUCTION: EFFECT ON PLANT GROWTH AND CARBON DEGRADATION

PS.3.6 **Castellini et al.** EFFECT OF BIOCHAR APPLICATION ON HYDRAULIC CONDUCTIVITY OF A CLAY SOIL

PS.3.7 **Fascella et al.** BIOCHAR AS PEAT SUBSTITUTE FOR GROWING SUBSTRATES OF ORNAMENTAL POTTED PLANTS

PS.3.8 **Conti et al.** EFFECTS OF EXPOSURE OF DIFFERENT BIOCHARS AND A COMMERCIAL SOIL AMENDMENT ON SURVIVAL AND REPRODUCTION RATES OF FOLSOMIA CANDIDA (HEXAPODA: COLLEMBOLA)

Agro-Environmental Effect of Biochar

PS.4.1 **Al-Wabel** CHANGES IN BIOCHEMICAL PROPERTIES OF SANDY CALCAREOUS SOIL AMENDED WITH CONOCARPUS WASTE FEEDSTOCK AND BIOCHAR

PS.4.2 **Caporale et al.** LEAD, CHROMIUM AND COPPER REMOVAL BY ORCHARD PRUNING DERIVED BIOCHAR FROM ACQUOUS MONO AND MULTI-CONTAMINATED SYSTEMS

PS.4.3 **Pusceddu et al.** PARTICULATE EMISSION OF BIOCHAR

PS.4.4 **Seok-Young Oh et al.** SORPTIVE TREATMENT OF METALS AND NITRO EXPLOSIVES IN WATER USING BIOCHAR

PS.4.5 **Conti et al.** PHYTOTOXICOLOGICAL EFFECTS OF DIFFERENT BIOCHARS USING PLANT BIOASSAY

PS.4.6 **Pirelli et al.** CROP PRODUCTION, BIOCHAR AND SOIL FEATURES EVALUATED 5 YEARS AFTER BIOCHAR DISTRIBUTION IN A HIGHLY MANAGED CROPLAND

PS.4.7 **Butera et al.** EFFECT OF TEXTURE ON THE DYNAMICS OF A WATER SATURATED BIOCHAR

PS.4.8 **Lagomarsino et al.** SOIL ADAPTATION TO BIOCHAR: EFFECT OF NEW ADDITION TO SOILS WITH AND WITHOUT BIOCHAR

PS.4.9 **Dell'Abate et al.** BIOCHAR THERMAL STABILITY AND CHEMICAL SOLUBILITY: A DUAL PICTURE OF BIOCHAR FATE IN SOIL

PS.4.10 **Maienza et al.** TRANSIENT EFFECT OF BIOCHAR ON SOIL PROPERTIES AND PROCESSING TOMATO GROWTH

PS.4.11 **Rao et al.** INTERACTION OF BIOCHAR WITH SOIL ORGANIC CONTAMINANTS: REDUCTION OF PHYTOTOXICITY

ORAL PRESENTATIONS

SESSION I

WORLDWIDE BIOCHAR ASSESSMENT

2007-2013: 7 years of biochar research in Italy

L. Genesio

Italian Biochar Association (ICHAR)

The Italian Biochar Association (ICHAR) was born in 2009 to create synergy and collaboration between the research institutions and the private sector in promoting solutions, technologies, advanced studies and demonstration activities related to the use of biochar as a possible strategy to mitigate GHG emissions and simultaneously increase crop productivity.

Starting from 2007 a large number of field and laboratory experiments were made in Italy around biochar, placing the Italian research in preeminent position on this topic. In this period, biochar science has significantly evolved covering a wide range of disciplines from agronomy to ecosystem science, from the physical-chemical characterization of materials to climate modelling. At the same time, following the convincing results brought by research, a wide consensus has grown in Italy about the possibility to operationally introduce the biochar-based strategy in agriculture.

This lecture reports on the state of the art of biochar research in Italy, presents the perspectives for its operational implementation and identifies the research topics that urgently need to be addressed.

Utilization of Charcoal in Japan

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Japan is a sea girt country with 6,852 islands, and the land area is 338,145 km^2 which is the 65th place in the world. About 70% of land is mountain area and ratio of forest is 67%. Japan is dependent on the imports of oil, coal, and natural gas for the majority of its energy supply.

In the other hand, Japan is a long island that is stretched in north and south, also monsoon climate, the condition had made species-rich vegetation. Shortage of fossil energy and rich vegetation made Japanese to invent utilization of forest such as tough paper made from fiber of plant called "Washi", wooden building with high skills like "Houryuji" constructed in 7 AC , painting natural resin from lacquer tree (called japan or Japanese lacquer) which makes hard coating to wooden crafts, and of course charcoal is a part of them.

There is variety of charcoal in Japan as follows;

1. KUROZUMI (Black charcoal)
2. SHIROZUMI (White charcoal)
3. TAKEZUMI (Bamboo charcoal)
4. OGATAN (Pressurized sawdust charcoal)

Physical and Chemical property is different with feedstock or the temperature of carbonization, so JCFA (Japan Charcoal Fuel Association) made a guideline for utilization of charcoal except fuel consumption in 2004. The guideline describes regulation of charcoal for each way to use.

DAILY LIFE	Cooking rice	AGRICULTURE,GREENING, HORTICULTURE	Soil conditioner
	Drinking water		Snow melting
	Deodorization	WATER TREATMENT	Sewage treatment
	Bathing		Purification of land water
	Bedding		Aquatic
	Interior	STOCK FARMING	Feed additive
	Air Purification of indoor		Deodorization
	Freshness retaining	SHIELDING MICROWAVE	
HOUSING	Humidity control of under floor	PAINTING	
	Humidity control of indoor		

AN ECONOMIC ASSESSMENT OF BIOCHAR IN GERMANY

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In the fight against climate change, the incorporation of biochar into soils has gained recent prominence as a possible strategy for carbon-dioxide removal from the atmosphere that does not only sequester carbon in soils but at the same time improves soil quality. This is due to the favorable properties of biochar, most notably its high carbon stability as well as its high nutrient-retention and water-holding capacities. Having ambitious targets for the reduction of its greenhouse-gas (GHG) emissions, biochar could also be an interesting mitigation strategy for Germany. By 2050, for example, Germany aims to reduce its annual GHG emissions by 80% to 95% compared to the 1990 level. It is recognized that a wide variety of measures is necessary to achieve these objectives. In order to select the most efficient ones, however, the mitigation measures must be assessed against both their mitigation potential and the associated costs.

For this reason, the paper provides a scenario-based economic assessment of different biochar options for Germany for the years 2030 and 2050 to figure out whether biochar deployment in soils is a viable mitigation strategy in the German context. Thereby, the biochar options are mainly based on the different feedstocks that might be available for biochar production, different technology scales for the chosen slow-pyrolysis processes and different biochar deployment rates. Due to the strong competition for biomass between food production and energetic uses, we mainly focus on biomass residues, such as cereal straw, forestry residues, industrial wood waste, municipal solid waste, green waste, sewage sludge, manure, and fermentation residues. For the economic assessment, we calculate the GHG mitigation potential of the biochar options, i.e. the amount of GHG emissions that can be avoided compared to a business-as-usual scenario, and their associated costs. Thereby, the paper has a special focus on the means that can help to reduce the costs of carbon sequestration, in particular the energetic use of the biochar by-products and the agricultural co-benefits associated with biochar soil incorporation.

The GHG mitigation potential and costs of the biochar options are illustrated with the help of bottom-up marginal abatement cost curves (MACCs), which rank the abatement options by their costs and then plot the available abatement potential of a given biochar option against the associated abatement costs. For a given abatement level, a resulting MACC allows, thus, to read off the costs that are associated with the next unit of GHG emissions abated, i.e. the marginal abatement costs. Thus, from the pool of technically feasible GHG mitigation options, a bottom-up MACC shows which are viable from an economic perspective. That is, for a given emissions reduction target, it shows which mitigation options are the most efficient to implement.

Turning to the results of the analysis, the mitigation potential of biochar in Germany is ultimately restricted by the availability and amount of suitable feedstocks. Not considering any imports of biomass for biochar production and having a focus on biomass residues, the mitigation potential of biochar in Germany is rather modest. It does not exceed 1% to 2% of the envisaged annual GHG reduction targets. Moreover, GHG mitigation with biochar is usually associated with high costs, often well beyond €30 to €50 per tonne of CO_2e abated.

ECONOMIC PERSPECTIVE OF BIOCHAR APPLICATION TO FORESTRY PLANTATIONS

A. Wrobel-Tobiszewska[1], M. Boersma[2], J. Sargison[3], D. Close[2], P.Adams[4], S.Franks[1]

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3. Rainbow Bee Eater Pty Ltd, Australia
4. Forestry Tasmania, Hobart, Australia

Eucalyptus nitens is a globally significant plantation species and more than 450,000 ha are now planted across southern Australia with more than 50000 ha of E. nitens (app. 53% of the area) and E. globulus plantations within Tasmanian State Forests. The total yield of forestry plantations is partly dependent on the early growth of woody species which is the result of adequate nutrient supply, water capacity, available sunlight and others. During the early years, growth of the plants with relatively high nutrient concentration accounts for a major proportion of net primary productivity. According to available literature biochar could be a promising organic amendment, assisting the growth of young seedlings of Eucalyptus and providing a tool for soil nutrients management and availability for growing seedlings.

Of the currently published research using field trials there is limited information on the effects of biochar on woody plantation species. The possible beneficial effects of biochar on the production of woody biomass may also be very important to the potential biomass supply for renewable energy and biochar production itself.

Forestry harvesting procedures in Tasmania include leaving significant amounts of post-harvesting residues on site. The residues are usually burnt on-site to produce ash which is considered to be soil conditioner. Introducing biochar systems within this structure, both from the residues management and an alternative to incorporating ash into soil point of view, could provide forestry industry with an alternative solution to burn-on-site procedures. The possibility of using post-harvesting residues to make biochar was investigated. A simple cost-benefit analysis model was used to compare the costs of traditional forestry plantation establishment costs with an alternative assuming using woody residues for biochar production in the mobile pyrolyser. Capital and on-going costs were considered as well and environmental benefits; agronomic data from a field experiment was incorporated in the model.

ORAL PRESENTATIONS

SESSION II

BIOCHAR CHARACTERIZATION

ANALYTICAL STANDARDS FOR BIOCHAR CHARACTERIZATION AND CERTIFICATION – LESSONS FROM THE COST BIOCHAR RING TRIAL

Hans-Peter Schmidt[1], Hans Jörg Bachmann[2], Thomas D. Bucheli[2], Daniele Fabbri[3], Heike Knicker[4], Axel Ulbricht[5]

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When biochar took the stage in fields like agronomy, soil science or plant nutrition during the last five to ten years, awareness of the very particular material properties of biochar was low. Instead of using and further developing analytical methods specially adapted for charcoal, most labs and biochar researchers used and still use methods originally adapted for matrices such as plants, soils, compost, etc. for biochar as well. And as collaboration was sparse until quite recently, biochar analysis became rather discordant and comparison of results from different labs and publications got sometimes fortuitous. To address a state of the art in biochar analysis and to eventually develop standard analytical methods for biochar characterization and certification, the EU-COST Action TD1107 organized in 2013 a biochar ring trial. Three biochars from very different feedstocks (woodchip sievings, paper sludge - wheat husks blend, sewage sludge) were produced with the same pyrolysis technology under comparable conditions, though in three different European countries. Following thorough homogenization of 1 m^3 biochar respectively, 25 subsamples were prepared and sent to 23 participating labs in 12 countries. As the objective of the trial was not to evaluate the inter-laboratory reproducibility using the same standard methods, but to estimate the reliability of analytical results obtained by labs using their habitual methods of biochar analyses, no default methods were stipulated. A standard set of characterizing parameters was selected along with some extended parameters that are especially helpful to understand the biochar functionality. The resulting data of the 32 basic parameters then underwent statistical evaluations to check the variability between the used methods and to compare the irrespective reliability. Only three out of the 32 basic parameters featured a robust mean that indicated a sufficient reliability of inter-laboratory values. The variability off all other parameters was too high to be statistically reliable showing the urgent necessity to improve biochar analytical methods and standardization. To verify the performance of the EBC (European Biochar Foundation) accredited methods and to start a qualitative evaluation of the methods data were plotted against the results of Eurofins Labs who have more than forty years experience in analyzing carbonaceous materials. The objective of the not yet finished project is to come up with a set of standard methods for biochar analyses to be used not only for biochar certification but also for the comparability of biochar data in between scientific publications. On the base of this EU-Cost biochar ring trial, the future challenges of biochar characterization, certification and classification will be discussed.

MOLECULAR CHARACTERIZATION OF BIOCHAR BY ANALYTICAL PYROLYSIS-GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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The thermal stability of biochar is associated to the type and extent of polycondensed aromatic structures that affect its environmental persistence and carbon sequestration potential. Several analytical techniques have been applied to establish the degree of carbonisation of biochar, including elemental analysis, thermogravimetric analysis (TGA), ^{13}C-NMR and analytical pyrolysis (Py-GC-MS). Typically, Py-GC-MS of biochar afford pyrolysates characterized by the presence of oxygenated organic compounds preserving the chemical functionality of cellulose (e.g. anhydrosugars, pyrans, furans) and lignin (methoxyphenols), and by aromatic hydrocarbons (benzenes, naphthalenes) not specific of biopolymer precursors, but indicative of the carbonaceous matrix. Thus, the relative abundance of aromatic hydrocarbons in the pyrograms could be a measure of the charring intensity in biochar production. We present a comprehensive study aimed at comparing the results produced by Py-GC-MS with the data obtained from elemental, proximate and others analyses (HCNS, ash, volatile matter (VM), fixed carbon, pH, PAHs, etc.) on a large set of biochar samples of different origins (feedstock, process units, synthesis conditions). A subset of samples was subjected to CO2 respiration experiments in soil. Biochars from herbaceous biomass (switchgrass, corn stalk) were obtained at different pyrolysis temperatures (400-700 °C) and residence times (1-20 min) with a fixed bed pyrolyser. Data comparison was also conducted on biochar samples within the EU COST Action TD1107. The quantity of evolved pyrolysis products (yields) and their molecular distribution depended on biochar synthesis conditions and were strictly related to indices of the extent of carbonization (e.g. H/C, O/C, pH, VM). In particular, the yields decreased and the relative content of aromatic hydrocarbons increased with decreasing H/C ratios. Comparing Py-GC-MS and TGA of corn derived biochars a good correlation was found between the relative content of pyrolytic markers of cellulose/lignin and VM. Additional information could be gathered on the molecular distribution of the pyrolysable matter, in particular about the occurrence of nitrogen-containing compounds. Short term respiration experiments in soil containing switchgrass biochars characterized by different thermal alteration and pyrograms suggested that the presence of partially degraded cellulose may play the key role in the rate of CO_2 production. In general, the pyrolytic molecular pattern was consistent with bulk parameters and provided structural information potentially useful to predict the environmental behavior of biochar.

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POROSITY CHARACTERIZATION OF BIOCHAR SAMPLES WITHIN THE FRAMEWORK OF THEBIOCHAR COST ACTION TD1107

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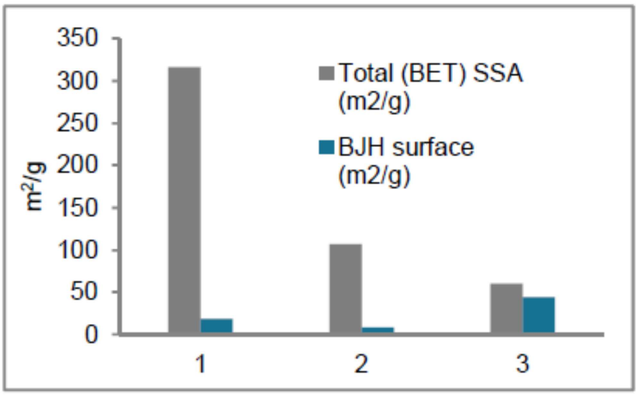
The specific surface area (SSA) of biochar is considered as a main characterizing parameter of biochar (European Biochar Certificate, International Biochar Initiative), however without knowing the pore size distribution, the simple value of surface area might mislead the interpretation of the properties and functionality of a biochar. In the present work, the pore size distribution and specific surface area for three different samples from the Ring Trial, developed by the Working Group 1 from the Biochar Cost Action TD1107, are measured using N_2 adsorption. For the characterization of SSAs the BET method is the most commonly used. However, it gives no information about which kind of pores are contributing to this surface area. For example, the low or medium SSA of a biochar can be due both to high macroporosity with low microporosity or to mesoporosity with e.g. collapsed micropores. This would make a significant difference in the application of the biochar, since micropores and mesopores would contribute more to the adsorption of nutrients or to increase the soil-water retention while macropores would have other possible functions more related to aeration or life or microorganisms. For this reason, more information which complements the BET surface area is needed. In this case, the whole adsorption and desorption isotherms (for partial pressures 0 <p/p0 < 1) are measured. From these isotherms, the total specific pore volume can be calculated (p/po≈1), assuming that all the pores are filled with liquid adsorbate. Comparing the total pore volume with the SSA, a relative pore size distribution can be established between samples, i.e. lower SSAs with higher total pore volumes would mean bigger pores. The BJH (Barrett, Joyner and Halenda) method is also applied to determine the pore size distribution for pores bigger than 3 nm. In the figure, the total SSA (BET method) and the SSA for pores bigger than 3 nm (BJH method) are compared, showing that the SSA of samples 1 and 2 would come mostly from pores smaller than 3 nm while the SSA in sample 3 would show mostly mesoporosity. It must be taken into account that the BET and BJH measurements never provide absolute values as results depend very much on the gas used as adsorbate. In principle with N_2 adsorption pores smaller than 0.4 nm cannot be measured due to the molecule size and the low measuring temperature (77 K), leading to diffusion limitations and lower SSAs in microporous materials. This can be improved with other gases, such as CO_2, but with the disadvantage that it's not an inert gas as N_2 and there may be some kind of interactions with the surface that potentially falsify the results. The sample pretreatment may also affect the results. As it can be seen, there is no method that gives a true absolute value. Therefore the combination of several methods, giving complementary information, is necessary to be able to interpret the results. The measuring conditions are highly relevant and should be always specified.



WATER DYNAMICS AT THE SOLID-LIQUID INTERFACE OF DIFFERENT BIOCHARS

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In the last ten years, knowledge about the characteristics of biochar and its agronomic effects on soil – plant – microbial systems improved tremendously. However, the electro-chemical function of biochar in these systems as well as what actually occurs on the surfaces of the biochar porous labyrinth is only poorly understood. In the present study, water dynamics on the surface of three biochars produced from wood, paper- and sewage sludge (B1, B2, and B3, respectively) have been subjected to solid-state ^{13}C nuclear magnetic (NMR) spectroscopy and fast field cycling (FFC) NMR relaxometry in order to investigate the relationship between their chemical composition, porosity and the impact of their surface properties on the mobility of water. The latter is of high interest in particular if biochar is amended to soils, since the accessibility into and translocation of water within their pore system determines the availability of nutrients adsorbed to their solid surfaces for plant growth. The cross polarization magic angle spinning (CPMAS) ^{13}C NMR spectra of B2 and B3 evidenced high but varying aromaticity, which is explained by the fact that the high content of proteinaceous material in the feedstock of B3 increased the contribution of alkyl C in the charred product. Also in agreement with the variation of the feedstocks, the three biochars contain different amounts of ashes rich in paramagnetic species (i.e. Fe^{3+}). In particular, whereas B1 and B2 show comparable contents of iron, Fe amount in B3 is approximately one order larger. Specific surface area (S) and total pore volume (V) investigations by BET and BJH methods revealed that the S/V ratios were in the order B1>B2>B3. After water saturation, the three biochars were analyzed by FFC NMR relaxometry. The technique allowed monitoring the dynamics of water on the solid surfaces through measurements of the longitudinal proton relaxation times (T_{1H}). It is well recognized that longitudinal relaxation time values are affected by both molecular mobility and presence of paramagnetic species. In fact, as water moves in large pores, it is subjected to motions that are faster than those occurring in small sized pores. For this reason, inter and intra molecular dipolar interactions are weaker in the former than in the latter case. As a consequence, the longitudinal relaxation times (T_{1H}) measured for fast moving water are longer than the T_{1H} measured for slow moving water. Presence of unpaired electrons in paramagnetic species (either organic or inorganic in nature) generate additional magnetic fields which fasten proton relaxation, thereby allowing shorter T_{1H} values. FFC NMR results discussed here surprisingly showed starting from a certain S/V the biochar porosity had a higher impact on T_{1H} than the paramagnetism of the biochar surfaces. In our study, B3 showed the longest relaxation times suggesting that this material has higher contribution of larger pores than B1 and B2. According to relaxometry, two hydration spheres have been recognized. The inner hydration sphere consists of a layer of H_2O molecules that are strongly bound to the surface of the biochar. The inner hydration sphere is coated with an outer sphere of one or several layers of water that is hooked to the biochar surfaces through bridges formed by the H_2O molecules of the inner sphere. Changes of the surface biochar properties - for example by prior adsorption of nutrients - is expected to alter the mobility of the water. Based on the results obtained in the present investigation, such alterations should be detectable by FCC NMR relaxometry, which turns this technique into a promising tool for obtaining a better understanding of how biochar is performing in soils and how it can improve soil productivity.

ORAL PRESENTATIONS

SESSION III

BIOCHAR EFFECT ON LIVING SYSTEMS

MINERALIZATION KINETICS OF BIOCHAR SERIES AND ASSOCIATED CHANGES IN SOIL MICROBIAL COMMUNITIES

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Biochar technology has received a lot of attention recently, notably for its capacity for long-term C storage in soils. The mineralization rate of biochars as a function of production conditions remains a key question. The kinetics of biochar mineralization may be influenced by changes in microbial communities. Ours study is based on corncob and miscanthus biochars prepared through hydrothermal carbonization (HTC), flash carbonization, and slow pyrolysis at multiple temperatures between 250 and 800 °C. Biochars were incubated in soils for a period of one year. Mineralization rates of C4-based biochars and soil organic matter (SOM) were measured with 13C natural abundance. The microbial communities of both bacteria and fungi were investigated by using terminal restriction fragment length polymorphism (T-RFLP) analysis of amplified 16S rRNA genes (bacteria) and ITS region of the fungi.

HTC exhibited a high initial mineralization rate as compared to other biochars, which displayed a fairly constant mineralization rate throughout the experiment. This suggests that HTC contained a substantial labile fraction, as did the feedstock. After 50 days of incubation, the labile fraction of the HTC appeared exhausted, and after 1 year of incubation, the HTC had not mineralized more than the 250C biochar did, i.e. 10-15%. This was higher than the mineralization rate of SOC estimated at ~5%. All >300°C biochars displayed constant mineralization kinetics and reached between 0.3 and 0.6% mineralization after 1 year. The mineralization rate of these high-temperature slow pyrolysis and flash carbonization biochars was two orders of magnitude lower than that of non-pyrolyzed biomass. The overall microbial community composition changed with time in all incubation treatments inclusive of soil control. After 1 year, fungal communities in all >300C slow pyrolysis biochars appear to have evolved in a similar way which deviated from that of the soil treatment. This suggests that all >300°C slow pyrolysis biochars displayed similar response, both in terms of mineralization rates and changes in microbial community composition.

ANTS AND BIOCHAR: A FIELD EXPERIMENT STUDY

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Ants, by nest building, bioturbation of soils, food storing behavior and interactions with many other organisms, are important “ecosystems engineers” and “keystone species” in many ecosystems. These insects might have a direct impact on physical and chemical structure of soils, by construction of subterranean galleries that induce modification of soil profile, aeration, drainage and density or by food storing behavior that influences the transformation of organic matter. Ants might play an important role in maintaining or restoring soil quality and fertility in rural environments.

Little is known about the effect of biochar application on soil biota and the study of ant communities might be a suitable approach to investigate the potential impact of biochar application in soil ecology. In our work, we used ants as biological model to study the effect of biochar on a field scale irrigated processing tomato crop in northern Italy.

The effect of three biochars (different for feedstock type and production process) on abundance and composition of ant community was assessed against a control in a field experiment. Biotic data (ants sampling) were collected during the season of plant growing (May-August) and they were correlated to abiotic factors (e.g. fertilizations, irrigation rate, temperature, soil moisture and pH and biochars chemical properties). We outlined the trend of ant community during the crop-growing season.

More than 10 different species of Formicidae (with Tapinoma madeirense, T. nigerrimum, Tetramorium caespitum, Solenopsis fugax and Messor structor within the most abundant ones) were found. Results showed no difference in species abundances and richness between biochar treatments and their controls. Diversity indices, that provide important information about rarity and commonness of species in a community, demonstrate how the soil application of the biochar, also at rate of 20 t ha-1 did not affect the ant distribution, suggesting a null interference of biochar..

Further data are needed to employ ants as bio-indicators for the evaluation of efficient agricultural managements and proper ecological practices that involve the use of biochar in Mediterranean environments.

BIOCHAR APPLICATION AFFECTS PLANT-WATER RELATIONS IN *Vitis vinifera* (L).

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In the Mediterranean area water scarcity is a major limiting factor for agriculture that currently accounts for the consumption of roughly 65% of available freshwater. According to the IPCC (2007), the vulnerability of Mediterranean systems to water scarcity is predicted to increase in the near future as a consequence of larger inter-annual rainfall variability and higher frequency and intensity of extreme events such as droughts and heat waves. In this context, the identification and implementation of adaptation measures aimed at enhancing the resilience of the agroecosystems to water scarcity is a key priority to maintain both the quality and quantity of crop productions and protect water resources. Crop management strategies play an important role in the capability of soils to hold nutrients and water. The depletion of soil organic matter in agricultural soils over the last century due to the management intensification, the sustained removal of crop residues and the use of chemical fertilizers has had dramatic effects on the water holding capacity of soils, and on the capacity of plants to adapt to a changing climate.

Soil water status plays an important role on the growth-yield response and on the grape quality of Vitis vinifera (L.). Moderate water stress periods are in some cases needed to ensure high quality productions, but especially in dry Mediterranean environment, water stress may lead to an unbalance of the sugar/acidity ratio due to berry dehydration.

Biochar is a co-product of thermochemical conversion of biomass and it is well recognized to exert a soil amendment action and to increase the soil water retention. In this work we investigated the effect of biochar application on plant water relations of V. vinifera in a field experiment made in Central Italy. Biochar was applied at a rate of 22 t ha^{-1} in two consecutive growing seasons (2009 and 2010). Soil samples analysis and ecophysiological measurements clearly indicated a substantial increase in soil available water content (from 3.2 to 45 % respect to the control) and a significant improvement of plant water status (from 24% to 37 respect to the control) in biochar amended plots in key periods for vine crop cycle.

BIOCHAR IMPROVES PHYSIOLOGY AND BIOCHEMISTRY OF POTATO IN RESPONSE TO SALINITY STRESS

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Salinity is a major threat to global food security. Up to 20% of the world's irrigated land, which produces one third of the world's food, is salt affected. Salinity depresses plant growth by activating stress hormones (like ABA) after immediate exposure of roots to salt which in turn affects plant physiology and ultimately reduces yield. A pot experiment was conducted in a climate-controlled greenhouse to investigate the physiological and biochemical changes of potato in response to salinity stress under biochar amendment. It was hypothesized that biochar may improve physiology and biochemistry of plants by mitigating drastic effect of salinity through its high sorption ability. From tuber bulking to harvesting, plant were exposed to three saline irrigations i.e. normal water (Tap water), 25 mM and 50 mM NaCl solutions, respectively and two levels of biochar (0 and 5 % W/W) treatments. An adsorption study was also conducted in order to confirm the Na+ adsorption capability of biochar. The results indicated that biochar was capable to ameliorate salinity stress by adsorbing Na^+ on its exchange sites. Increasing salinity level resulted significant reduction in photosynthetic rate, stomatal conductance, leaf water potential (Ψ leaf) but increased ABA concentration in both leaf and xylem sap. At each salinity level, incorporation of biochar increased A, gs, Ψ leaf and decreased ABA concentration in leaf and xylem sap as compared with the respective non-biochar control. Decreased Na^+, Na^+/K^+ ratio and increased K^+ content in xylem with biochar amendment also indicated its ameliorative effects in response to salinity stress. Therefore, incorporation of biochar might be a good approach in reclaiming salt affected soil for sustainable crop production.

Key words: salinity, ABA, Na^+, K^+, physiology

ORAL PRESENTATIONS

SESSION IV

AGRO-ENVIRONMENTAL EFFECT OF BIOCHAR

BIOCHAR FOR DESERT RECLAMATION AND CARBON DIOXIDE SEQUESTRATION

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Egypt as a southern Mediterranean countries lays on the Desert belt and enjoys arid climate at the northern part and hyper arid in the south. Egypt receives an average rainfall of 150 mm/year along the Mediterranean then decreases toward south to be almost zero at Asuit. The soils outside the Nile Delta and Valley are of mainly sandy or sandy loam or lighter textures. Egyptian desert soils have very low organic matter contents and extremely low water holding capacity as well as very low soil fertility.

Biochar, a soft by-product from the pyrolysis of biomass, for producing charcoal, appears to have remarkable agronomic values when used at the early eighties as a source of potassium and micro nutrients in organic agriculture. Although Biochar is not yet considered as a fertilizer or desert soil enhancer, however practical data, expertise and many applied researches which were performed in the desert soils of Egypt using Biochar proved remarkable success in reclamation, organic vegetable, fruit production and super gardening in desert. In the meantime Biochar production play a major role in environmental agricultural wastes and carbon dioxide sequestration all over the country rather than the direct burning.

In the meantime organic agriculture activities were quite difficult in the desert particularly soil fertility conservation for organic vegetables. For the sake of encouraging the small farmers, several trials of establishing small super gardens of vegetables in desert of Ismaillya, 100 Km east of Cairo were implemented using soil enhancer including mainly compost and Biochar in addition to pulverised rocks. Tomatoes, Green Beans, cucumber and Squash, were grown in a sandy soils of Ismaillya desert following the normal Organic Agricultural practices in comparison with the same treatments plus appreciable amount of Biochar and super gardening applications for two growing seasons within the same crop rotation. Crop yield and water saving were the main criteria for comparison in addition to water holding capacity of the soil. Data revealed that Biochar increased the organic yield with 17.7 % and 16 % water saving for Tomato, 14.3 % yield increase and 21% water saving for Green Beans and 27.0% yield increase and 15% water saving for Melon and 23 % yield increase and 16.6% water saving for Squash, 13 % yield increase and 15% water saving in cucumber. The soil water holding capacity of the sandy soil increased by 3.4 % after the second growing season.

Meanwhile carbon dioxide sequestration with an average of about 25 tones of Biochar per hectare in addition to avoiding the direct burning of the none economic agricultural wastes which protect the farm environment and help mitigating the global warming. This induces the sequestration of carbon from atmospheric CO_2, (one ton of biochar being the equivalent of 3 tons of CO_2), thus mitigating long-term climate change.

BIOCHAR IN GREEN ROOFS

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Green roofs in urban infrastructures are able to positively affect the urban climate, the energy consumption and runoff of buildings. Compared to the Nordic habitat, where green roof technology has established positively, Mediterranean climate is characterized by hot summers with long days without rain, cold winters and springs and autumns with intensive and concentrated rainfall events. All these aspects lead to rethink the construction methods of green roofs, in all its layers, in particular for growing media and species of plant that can be used. In Italy there is a official standard (UNI 11235:2007) about the criteria for design, execution, testing and maintenance of green roof. This standard, currently under revision, mainly deals with the performance that each layer of the green roof must ensure, including the reference standards for laboratory testing. About growing media, a critical layer to maintaining green our roof, the UNI standard provides strict guidelines about the properties that it must possess in terms of bulk density, water retention, permeability, organic matter content (low), pH, salinity, phytotoxicity; moreover it must guarantee an effect of filtration of waste water for containing of potential pollutants. Research on biochar has provided excellent results in terms of the fertilizer effect in soil of some types of biochar: high carbon content in a stable form, high porosity, water retention, low bulk density, stimulation of microbial life. The purpose of this work is to evaluate the use of certain types of biochar as a component of the growing media for green roofs, verifying the respect of UNI standard and evaluating the effects on plant growth, permeability, water retention, runoff, stability and water filtration. In this work, the first results for "biochar growing media" characterization compared to green roofs UNI standard.

CHANGES IN MORPHOLOGICAL AND PHYSICAL CHARACTERISTICS OF BIOCHAR AFTER LONG-AGING IN SOIL

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There is increasing attention on the potentials of using biochar as a climate mitigation strategy. The mitigation potential of biochar is associated to the fact that carbon is not easily returned back to the atmosphere, even after very long incubation time into the soil. In a recent study, Woolf et al. (2010) quantified the theoretical carbon sequestration potential of biochar following its incorporation into agricultural soils as 1.8 Gt of carbon per year. Nevertheless much remains to be understood on the effective long-term decomposition rate of biochar: is the carbon contained in biochar lasting for decades, centuries or millenia? In this study, fragments of biochar were extracted from the soil of a charcoal burning site in the Eastern Alps (Trentino, Val di Pejo), exactly dated at 1859 by dendroanthracological approach and identified as Larix decidua from the morphological structure. We investigated biochar decomposition in those soils and reliably calculated the fraction of carbon that was lost over 155 years. Then, we focused the morphological and physical characterization of several fragments, using scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray fluorescence (XRF). Such study enabled the identification of peculiar morphological features of tracheids, which were tentatively associated to a differential oxidation of the structures that were created during carbonization from lignine and cellulose. In order to assess the effect of soil-aging we compared the old-biochar with a modern one obtained from the same feedstock and with similar carbonization process. XRD and XRF analysis were performed on both old and modern biochar, in order to study the multiphase crystalline structure and chemical elements found. We observed mineralization and a fossilization of old biochar samples respect to the modern ones, with accumulation of several mineral oxides and a substantial presence of quartz. A graphene structure was also found, indicating weak bonds in the carbon structures, explained by inter-molecular Van der Waals forces. Furthermore, we have detected a graphite oxide structure responsible of the bending effect in the tracheid, revealed in SEM images. We consider that those results may contribute to the ongoing debate on the best, most suitable geo-engineering strategies that can potentially enable effective and sustainable carbon sequestration in agricultural soils, using biochar.

AGRONOMIC EFFECTS OF THE ADDITION OF BIOCHAR FROM DIFFERENT FEEDSTOCKS TO A TYPICAL MEDITERRANEAN AGRICULTURAL SOIL IN RELATION TO THE APPLICATION RATE.

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Biochar has been proposed as a new ecological amendment and its capability to enhance agronomic productivity has been demonstrated (Sohi et al., 2010). Biochar may improve the retention of nutrients and provides refuge for beneficial soil micro-organisms. In addition, it can increase the pH, electrical conductivity and cation exchange capacity of soil. All of this makes biochar a suitable product for agricultural purposes. Additionally, the benefits of this product also vary according to the kind of soil and crop under consideration as well as the application rate.

The main goal of this study was to evaluate the application effect of four contrasting biochars on the agricultural productivity of a typical calcareous Mediterranean agricultural soil. Each biochar was produced from different feedstocks. Three of them were supplied by the European Biochar Research Network & COST Action TD1107 and consisted of 1) wood biochar, 2) paper-sludge biochar and 3) sewage-sludge biochar. The fourth was provided by a Spanish winery and consisted of 4) grapevine wood biochar.

A greenhouse incubation study was carried out, lasting for 79 days. Pots contained 150 g of soil and an amount of biochar equivalent to 10, 20 and 40 t ha^{-1} were prepared in quadruplicate for each biochar using grass as test plant (40 seeds per pot). Control pots, without biochar amendment, were also settled for comparison purposes (n=6). After adjusting the soil humidity to 60% of the maximum WHC, the pots were placed into a greenhouse under similar conditions than those reported by De la Rosa et al 2013. Briefly they consisted of 25 °C, 14 h light day^{-1} and water supply equivalent to 760 L m^{-2} per year. In this experiment, germination and survival rates were measured by accounting the number of shoots per pot each week. Additionally, biomass production was calculated by cutting, drying (48 h at 40 ºC) and weighing the shoots each 15 days until the end of the experiment.

This experiment confirmed that the benefits of biochar in agriculture vary according to the kind of biochar used and its application rates. Germination and plant-survival increased significantly in all biochars except for grapevine wood biochar (biochar 4). In this case, it resulted in similar germination rates than un-amended pots. In addition, biomass production raised significantly in presence of all biochars, being the response in presence of biochars 1, 2 and 3 significantly higher than the response in presence of biochar 4. Regarding the application rates, the biomass production was significantly increased for all doses when comparing to the control pots. Excepting biochar 3, the application rates of 10 and 20 t ha^{-1} produced a major agronomic effect than 40 t ha^{-1}, which suggests a possibly harmfulness effect of biochar at high application doses.

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ANALYTICAL CHARACTERISATION AND PAH ASESSMENT OF FOUR BIOCHARS AND A BIOCHAR AMENDED CAMBISOL FROM SOUTHERN SPAIN

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Producing biochar from a waste material can be classified as a waste recovery operation, but more intense research in the fields has only recently started. Therefore, biochar products are at a very early stage of development and their regulatory and testing requirements are liable to change. In April 2013, Switzerland has become the first country of Europe to officially approve the use of certified biochar in agriculture. Hungary also approved its use in 2012, however, the certification rules are still in progress in this case. Other nations are developing policies and strengthen the standing and potential funding for biochar projects (special mention in this particular case to New Zealand, Australia, USA and UK). Presently, the EU COST Action 'Biochar as option for sustainable resource management' is performing several experiments devoted to discern the properties and characteristics of a biochar before being officially approved as soil ameliorant. On the other hand, it is well known that polycyclic aromatic hydrocarbons (PAHs) are formed during combustion and pyrolysis processes, and as a consequence are likely to be components within biochar. PAHs form adducts with DNA and have, as a consequence, been prioritized by the US EPA and EU on account of their carcinogenetic, mutagenic and teratogenic properties. Consequently, their presence in biochars and biochar amended soils need to be assessed.

In this study, we present an in-detail characterization of four biochars produced from different feedstock under different conditions. Biochar 1 to 3 (1-wood, 2-paper-sludge, 3-sewage sludge) were provided within a ring trail of the EU Biochar COST Action (http://www.cost.eu/domains_actions/fa/Actions/TD1107). Biochar 4 was produced by traditional char production method from grapevine wood by a Spanish winery.

Characterization was performed by elemental analysis, microscopy and the determination of chemical and physical properties such as, pH, electrical conductivity (EC), ash content and water holding capacity (WHC). Fourier-Transform Infrared Spectroscopy (FT-IR) and ^{13}C solid-state NMR techniques were also applied to elucidate the molecular structure and main chemical groups, whereas field emission scanning electron microscopy (FE-SEM) is a valuable research tool that was used to investigate the surface topography and chemical composition of biochars. Finally, the abundance of PAHs was determined in the biochar and in a Cambisol from SW Spain amended with 10, 20 and 40 t ha^{-1} biochar and subjected to plant growth pot experiments for 80 days.

Biochar 1, 2 and 4 revealed comparable elemental composition (C, H, N). In addition, values of pH, WHC and ash content were analogous (10.3-10.4, 178-266 and 7-25% respectively). Biochar 3, exhibited the lowest C (18%) and highest N (2%) contents, whereas physical properties were drastically different (pH= 6.7; WHC= 26.7; ash content~70%). The H/C and O/C atomic ratios suggested a generally high aromaticity for all the biochars, which was confirmed by the ^{13}C solid-state NMR spectroscopy. However, Biochar 1 could not be elucidated by NMR most likely due to its graphenic properites, the latter were confirmed by IR spectroscopy. For wood-derived biochars, the IR spectra indicated the presence of lignin structures. The FE-SEM allowed distinguishing not only compositional but structural differences of the studied biochars. For instance, it showed the presence of metal rich crystals on the surface of wood biochar (biochar 1), collapsed structures for paper sludge biochar (biochar 2), mineral phases (rich in Al, Si, Ca and Fe) and organic residues for sewage sludge biochar (biochar 3) and etched surfaces for vineyard wood biochar (biochar 4) respectively.

Biochars 1, 2 and 3, revealed PAH concentrations of approximately 2900, 1600 and 650 µg kg dw^{-1} respectively, whereas biochar 4 contained the highest amount of PAHs (Σ16 EPA PAH), reaching about 16000 µg $kgdw^{-1}$, which is considerably above the maximum allowed threshold for PAHs (6000 µg kg dw^{-1} for the 16 EPA PAHs according to the International Biochar Initiative). Thus biochar 4 should not be used for agricultural purposes. Taking into account that biochar 4 was the only sample produced by the traditional kiln methods, the biochar production process seemed to affect significantly the PAHs levels.

The Andalusian Cambisol used for the biochar amendment experiment showed values for the 16 EPA PAHs which are typically reported for non-polluted soils from rural areas. The biochar addition resulted in a significant increase of the amounts of PAHs. However, preliminary results indicated that the increase did not correlate with the biochar loads applied.

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POSTER PRESENTATIONS

SESSION PS.2

BIOCHAR CHARACTERIZATION

CHARACTERIZATION OF A HOMEMADE BIOCHAR FROM WOOD BIOMASS

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It is well known that biochar properties depend strongly on original biomass and on conditions of thermal treatment (temperature and residence time). Hence, understanding mechanism of thermal degradation is important to evaluate biochar characteristics before addressing it to any specific use.

This study reports about the chemical-physical properties of a biochar obtained from a wood biomass (fir sawdust).

Biochar homemade samples have been prepared at 400°C for 10 and 30 minutes and at 600°C for 120 minutes in a muffle furnace.

Original biomass and derived biochars have been analysed with different techniques in order to evaluate influence of temperature and charring time on the chemical changes occurring during the thermal treatments.

By applying thermogravimetry it was possible to notice a higher thermal stability of biochar samples compared to raw biomass. The same technique revealed differences in degradation mechanisms dues to their different structure. DTG graphs showed two peaks corresponding to degradation of labile material and aromatic compounds for biomass and biochar obtained after 10 minutes at 400°C. For other samples just one peak corresponding to aromatic fraction appeared.

IR spectra showed that OH and NH_2 groups disappear as biomass is thermally treated to obtain the biochars. Intensity of OH and NH_2 decrement depends on the charring temperature, being larger as temperature is increased. During the thermal treatment, disappearing of labile groups is associated also to disappearing of linear chains and appearance of aromatic groups (CPMAS ^{13}C NMR spectra).

This study confirms heterogeneity of biochar stucture due to different conditions of pyrolysis process. Moreover, it brings out useful informations about steps of thermal degradation to direct biochar production.

EFFECT OF HEATING TIME AND TEMPERATURE ON THE CHEMICAL-PHISYCAL CHARACTERISTICS OF CHICKEN MANURE BIOCHAR

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Biochar is a fine-grained and highly porous carbonaceous substance, arising from the pyrolitic decomposition of natural or synthetic organic materials. It is lately applied to soils to favorably affect soil physico-chemical properties, such as water and nutrient retention and cation exchange capacity (CEC). The extent of the effect of biochar on crop productivity is very variable due to the different biophysical interactions and processes that occur when it is applied to soils. Char properties are greatly influenced by both natures of feedstock and process conditions. An accurate characterization of biochar is crucial to evaluate the possibility to amend soil with such material by avoiding environmental damages.

The aim of this work was the chemical-physical characterization of biochar from chicken manure (CM) in order to investigate its potentiality either as fertilizer or as metal bio-sorbent in soil remediation procedures.Biochars were produced at different temperatures (350, 450 and 600°C) and residence times (30 and 120min) into a heating muffle. Chemical-physical characterization of the different CM chars was conducted by cross polarization magic angle spinning (CPMAS) ^{13}C NMR spectroscopy and NMR relaxometry.^{13}C NMR spectroscopy results revealed that char chemical nature is affected more by production temperature than by production time. In particular, CM chars obtained at 350 and 450°C contained both aromatic and alkyl domains whereas only aromatic systems were present after charring at 600°C. Conversely, CM char composition at each temperature remained more or less unchanged as heating time was gradually switched from 30 to 120 min. Unlike char chemical nature, its physical properties were found to be produced both by pyrolysis temperature and residence time. In general, residence time has a major effect at the lowest charring temperature used (350°C). Vice versa, above 450°C, the pyrolysis temperature has a major influence in char structuring. Moreover, NMR results suggest a reduction of biochar affinity for water as pyrolysis temperature or charring time increases. This reduction could be explained by: 1) the loss of acidic functional groups on poultry manure biochar surface (such as phenolic, lactone and carboxylic group) able to interact with water protons, 2) the increase in biochar hydrophobicity (due to their reduced organic matter content) or 3) the increase in the pores size with charring temperature or muffle residence time. According to our results, the chemical composition and the physical structure of chicken manure biochar vary mainly depending on process temperature. But, below 450°C, residence time also influences char physical properties. In conclusion, biochar formation can be described as an aromatic growth and polymerization process, resulting in carbon enrichment. In addition, porosity development is achieved as volatile matter is removed. The combination of several analytic techniques provided good basis for the comprehension of complex systems making it essential for the complete characterization of the char as a porous medium.

EVALUATION OF INORGANIC CONTAMINANT REMOVAL FROM AQUEOUS SOLUTIONS USING PYROLIZED CHICKEN MANURE, CONIFER AND POPLAR WOOD AS ADSORBENT

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Anthropogenic activities alter the natural flow of materials and introduce novel chemicals into the environment thereby causing serious soil and water pollution. Indeed, many industries produce aqueous effluents containing toxic substances, especially heavy metals. The presence of these contaminants in the environment is a great issue because of their toxicity and bioaccumulation ability which affect human life and the environment. Various physicochemical and biological techniques have been used to remove the heavy metals from waste waters, including chemical precipitation, ion exchange, chemical coagulation, electrolytic methods, membrane processes, and adsorption.

Biochar is a carbonaceous material obtained from the pyrolysis of plant and animal biomasses. Due to its high porosity, it could be a potential alternative to the existing conventional technologies for the removal and/or recovery of metal ions from aqueous solutions.

The aim of this work was the chemical-physical characterization of biochar produced from chicken manure (CM), conifers and poplar wood wastes in order to assess their ability in the removal of heavy metal from aqueous solutions.

Chemical-physical characterization of the different CM chars was conducted by cross polarization magic angle spinning (CPMAS) ^{13}C NMR spectroscopy and NMR relaxometry together with a comparative study between the removal efficiencies of Cu(II), Ni(II) and Pb(II) from synthetic wastewater by using adsorption onto biochars surfaces.

From adsorption studies, it was observed that conifer biochar did not significantly adsorbed metals. This behavior is probably due to his own chemical characteristics, since it's quite hydrophobic and probably its surface lacks functional groups able to bind ions.

Conversely, chicken manure biochar proved to have the highest removal efficiencies for all the metals considered, in the order Pb(II)>Cu(II)>Ni(II) ions.

In conclusion, different chars have different physicochemical characteristics so they should be addressed to different uses. For example, conifer char should not be used for remediation since it's not effective in removing inorganic metals from aqueous solutions.

The most effective in remediation was chicken manure biochar, probably thanks to the presence of nitrogen on its surface. In fact, nitrogen has a free electronic doublet/pair able to interact with cation.

Finally, char metals absorption involves both a physical and a chemical mechanism and further studies should be addressed to explain it.

EFFECT OF METALS ON THE DYNAMICS OF WATER AT THE BIOCHAR SOLID-LIQUID INTERFACE

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Previous studies revealed that water molecules are hooked to biochar surfaces through unconventional hydrogen bonds (De Pasquale et al., 2012; Conte et al., 2013). Next question to answer is how metals can affect water mobility as they are adsorbed on biochar surface. To this aim, an orchard pruning char obtained by pyrolysis at 500°C was treated with solutions of Cu(II), Cr(VI) and Cu(II)+Cr(VI). Atomic adsorption investigations revealed that the amount of each metal after adsorption was as reported in Table 1.

Table 1. Amount of copper and chromium adsorbed on biochar (BC)

Sample	Cu (II) (mg/g)	Cr (VI) (mg/g
BC	1.9	0.6
BC + Cu (II)	20	--
BC + Cr (VI)	--	43
BC + Cu (II) + Cr (VI)	17	38

After water saturation, biochar (BC) and metal-treated-biochar (MTBC) samples were analyzed by fast field cycling NMR relaxometry (Fig.1).

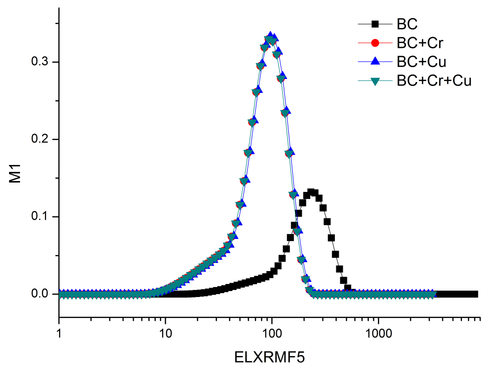

Fig. 1. ^{1}H T_1 relaxograms of biochar (red curves) and the metal-treated-biochar samples (the remaining curves). All the relaxograms have been deconvoluted (curves below the relaxograms) in order to recognize the different water components

Two different types of water can be recognized in BC. Namely, a fast relaxing water (T_1 = 99 ms) is differentiated by a slow relaxing one (T_1 = 233 ms). The former is made by molecules interacting with biochar surface through formation of the unconventional H-bonds previously identified (De Pasquale et al., 2012; Conte et al., 2013). The latter is made by water molecules freely slipping on the immobilized water layer. After metal adsorption, no changes were observed in MTBC relaxogram shapes as compared to BC relaxogram (Fig. 1). Moreover, all the MTBC relaxograms were similar to each other, regardless of the metal adsorbed on the carbonaceous material. Nature of the metal appears not to affect water dynamics on the porous material.

The shortening of the T_1 values in MTBC as compared to BC sample (from 99 to 42 ms, and from 23 to 95 ms, respectively) has been interpreted by two different molecular models. In the first case, a water layer may be immobilized on the metals directly adsorbed on MTBC surface (Fig. 2A). Since metal-water interactions can be stronger than those in the untreated BC, the result is a shortening of the T_1 values from 99 to 40 ms. As a consequence, also the H-bonds between the immobilized water and the freely moving one can be strengthened, thereby leading to shorter T_1 value.

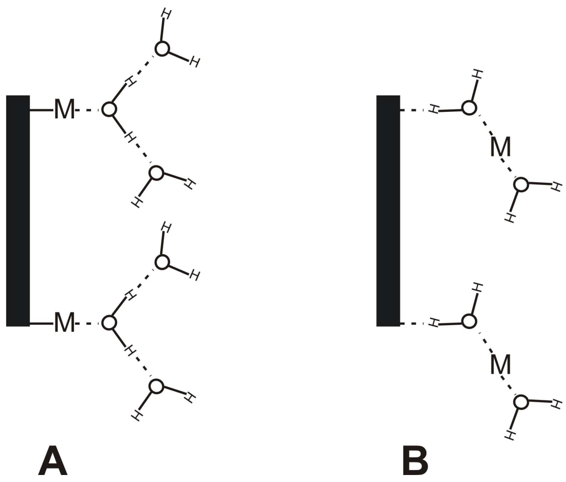

Fig. 2. Molecular models representing water behavior of porous surface after adsorption of metals. **A**. Metals are adsorbed directly on the surface and are connected to two different water layers. The closer one contains fast relaxing water. **B**. Metals are bridging two water layers. The inner one is more immobilized than the outer layer due to the interaction with the surface of the porous material.

The second molecular model considers metal ions bridging two water layers (Fig. 2B). The first water layer is immobilized directly on the surface of the porous material and it is bridged to the second water layer through the metal cation.

Further investigations are needed in order to differentiate among the different models accounting for water dynamics on the surface of biochar treated with metal cations.

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POSTER PRESENTATIONS

SESSION PS.3

BIOCHAR EFFECT ON LIVING SYSTEMS

EFFECTS ON SEED GERMINATION OF DIFFERENT BIOCHARS FROM INDUSTRIAL THERMO-CHEMICAL PROCESSES

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Char or biochar is a type of charcoal obtained from gasification/pyrolysis of biomasses. Instead of burning standing biomass from cleared forest, the resource is charred. The result is a highly porous, carbon-rich solid residue, really similar in appearance to the coal produced by natural burning. First considered an industrial waste, in recent years, the interest in this material has grown enormously given its ability to improve physical, chemical, biological and mechanical properties of soils, when used as amendment. However, its effects are highly variable depending on its chemical-physical properties which in turn depend greatly on the starting feedstock.

The present study reports about the effects of different chars obtained from industrial thermo-chemical processes (gasification for energy production) on soil quality. In particular, radish germination was monitored using conifer, poplar and marc biochar as amendment. Results revealed that radish roots had different lengths depending on the nature of biomasses used to produce the different chars. Actually, the char produced from marc completely inhibited seeds germination.

Moreover, to investigate the effect of the genotype, a study is going on regarding the influence of different biochars on seed germination of Troyer citrange [Citrus sinensis (L.) Osb. x Poncirus trifoliata (L.) Raf.]. High resolution solid state NMR spectroscopy revealed no differences among the chemical nature of the different chars. Conversely, low resolution 1H fast field cycling NMR relaxometry showed that porosity of chars was directly related to the nature of the biomasses used for the thermo-chemical transformations. We can conclude that not all the chars can be applied to soil to improve its quality, thus a careful characterization must be carried out prior to field application in order to avoid counter-effects which can damage soil productivity.

USE OF BIOCHAR IN GROWING MEDIA FOR CITRUS ORNAMENTAL PLANT

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In the last decade, floriculture sector, both in greenhouse and field, has been oriented towards the development of cultivation technologies that combine production efficiency to environmental sustainability.

Biochar is a fine-grained and porous medium that can be useful in improving physical, chemical, biological and mechanical properties of soils as well as greenhouse substrates. The purpose of the present study was the evaluation of the effects of biochar as an alternative substrate in field experiments.

Biochar was used as a peat substitute for container-grown Citrus ornamental plants at 4 different concentrations (10, 30, 50, and 100 %, w/w). Results showed that root biological activity, which is directly related to the aeration conditions, water content, and availability of nutritional elements, is strongly related to the presence of biochar in soils. In particular, commercial qualities of the investigated potted plants appeared increased.

BIOCHAR USED AS A PEAT SUBSTITUTE FOR NURSERY PLANTS REDUCES NEGATIVE SALINITY EFFECTS IN SENSITIVE ORNAMENTALS

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Biochar is a fine-grained material with a high porosity (10-15 times higher than soil), primarily composed of organic carbon. As reported by many studies, its water and nutrient retention capacity could make it a good amendment for plants. Therefore, few data are reported in the literature for biochar addition to ornamental sector substrates. The utilization of biochar could open up interesting possibilities for the ornamental sector by reducing peat volumes used in the substrates and amounts of good water for irrigation. An experiment was done on potted cherry laurel (Prunus laurocerasus L.), a salinity sensitive species, and phillyrea (Phillyrea latifolia L.), a resistant one, using substrates with different percentages of biochar to replace peat. Irrigation waters at two different salinity concentrations were applied and the results showed that the addition of biochar to the medium had no effect on plant growth but limited the damage due to salinity in cherry laurel, the sensitive species. The observed tolerance was related to lower Na+ retention in the substrates with biochar. Consequently biochar could allow not only the reduction of peat percentage in the substrates commonly used for ornamental species cultivation but also the utilization of low quality water for irrigation reducing also the leaching of nutrients such as K^+ and N-$NH4^+$.

IMPACT OF THE AMENDMENT WITH BIOCHAR ON SOILLESS SUBSTRATES USED FOR CULTIVATION OF Sedum reflexum FOR GREEN ROOF TECHNOLOGY

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The installation of green roofs and green facades (greenery) on urban buildings has received a growing interest for the potential environmental benefits. One of the beneficial effects of the greenery is the reduction of the temperature on the building surfaces covered by the canopy through plant transpiration. This results in the mitigation of the “heat island” effect on urban developments, with consequent reduction of energy consumption. The application of the greenery technology has required a research focused on the development of substrates characterized by waterholding capacity and low density, able to support the plant growth without affecting the building structure in different climatic conditions. In addition, the greenery technology requires the selection of plant species characterized by drought resistance, tolerant to the cold and able to develop a dense canopy in a limited substrate depth. The aim of this work is to test the use of biochar in the substrates used for extensive green roofs under the climatic conditions of the Central Italy. The physical characteristics of biochar (porosity, low density and ability to retain water and nutrients) indicated its potential as amendant in soilless cultures for green roofs. The biochar used was obtained by pyrolysis of wood, and presented particles of 1-10 mm diameter. It was added in the ratio of 10% V/V to a blend of perlite and a commercial substrate made of lapil, pumice, peat and a slow release fertilizer. A second treatment tested the effect of biochar in combination with compost (5% V/V each) and compost alone. The blends of substrates were tested in pots for the cultivation of plants of Sedum reflexum during the summer-fall season under the conditions of the green roofs. This work has evaluated the structure of the microbial communities of the substrates in relation to the presence of biochar using molecular profiling methods based on amplification of 16S rRNA genes. The effect of the treatments on the parameters of plant growth and physical characteristics of the substrates was evaluated and discussed.

HYDROTHERMAL BIOCHAR PRODUCTION: EFFECT ON PLANT GROWTH AND CARBON DEGRADATION

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Greenhouse gas mitigation options include the production of carbonized materials and their addition to soils for longer term storage. One mitigation option that has been recently discussed is the production of biochar, for example from organic waste material, and its addition to soil.

Usually, biochar is produced by pyrolisis of biomass (biochar). In recent years an alternative procedure (hydrothermal carbonization, HTC) has been developed to transform labile biomass into a more stable end product (hydrochar). A clear scientific definition of the products of hydrothermal carbonization does not exist. From a chemical point of view, hydrochars are similar to brown coal. HTC is a process of heating wet biomass with a suitable water content above 50 mass % at a temperature between 160 °C and 250 °C in a pressure vessel for several hours. Hydrothermal carbonization (HTC) is a novel way to produce carbonized materials. The goal here was to test if HTC material, in our case derived from maize silage, has adverse effects on plant growth and Carbon degradation on soil. We carried out a box experiment in which we examined the effects of HTC-material on poplar plant (vr.Villafranca) for two consecutive years. HTC was applied before transplanting at a rate of 200 kg of HTC for plots corresponding to 10 kg of C per box. Plant growth was periodically assessed and the contribution of HTC degradation to total CO2 efflux was measured using a Picarro G2131-i δ 13C High-precision Isotopic CO_2 Cavity Ring Down Spectrometer (CRDS) and Keeling plot method.

An overall increase in wood biomass was achieved after HTC application to soil (+30%) while significant differences in total CO2 efflux were detected only during the first two months after application showing an initial degradation of HTC. In fact, during this period, the contribution of HTC degradation to total flux was between 17 and 50%.

EFFECT OF BIOCHAR APPLICATION ON HYDRAULIC CONDUCTIVITY OF A CLAY SOIL

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Biochar has been reported to improve soil physical properties, such as bulk density, water retention, porosity and penetration resistance. However, compared to these properties, little is known about the impact of biochar addition on soil hydraulic conductivity, especially for fine-textured soils. In this study we evaluated the impact of biochar amendments (0, 5, 10, 20 and 30 g kg^{-1}) on both field saturated, K_{fs} (Simplified Falling Head technique, SFH) and near-saturated, K(*h*) (Mini-disk Tension Infiltrometer method, MTI) hydraulic conductivity, as measured on repacked clay soil columns (25 cm in diameter by 28 cm in height), that remained in field (about 30 month), exposed to weather conditions until the soil bulk density was nearly constant. Soil water content was continuously monitored by TDR probes. Biochar was obtained through a traditional method of slow pyrolysis (at approximately 500°C) from a mixed feedstock of pruning wood from fruit trees. Its effects on K_{fs} measurements were evaluated in four different times (between July and September2013) and considering two initial conditions of soil water content, qi (high, $\theta_{i,H,}$ = 0.30 cm^3cm^{-3} and low, $\theta_{i,L,}$ 0.20 = cm^3cm^{-3}). A comparison between K_{fs} and K(*h*), corresponding to a pressure head, h= –1 cm, was also carried out for a single date of measurement, and the relative change (RC%) was adopted to calculate the percentage difference of hydraulic conductivity between amended and unamended (control) soils. No effect of biochar on bulk density measurements was detected for the studied clay soil. Our results highlighted an increasing with time for all soil columns, but the differences between amended and un-amended soils were always no significant. The measurements showed significantly higher, and less variable, K_{fs} values when the infiltration experiments started from relatively low qi values. In general, the observed differences between K_{fsL} and K_{fsH} decreased as the concentration of biochar increased, ranging respectively from 258-325 cm d-1 to 105-145 cmd^{-1}. However, compared to the control, biochar addition produced no significant differences in terms of K_{fs}. These discrepancies were equal to a factor 0.8-1.1 and 1.0-1.3, depending to the qi value(low and high, respectively). The higher differences are linked to the biochar concentration of 30 gkg^{-1}. The comparison between K_{fs} and K(*h*) showed no significant difference, ranging from a factor1.3 to a factor 1.0. These discrepancies decreased with increasing of biochar concentration. The relative change of hydraulic conductivity always increased as the biochar concentration increased.

This improvement was more evident in terms of K(*h*) (RC% = +10%, +18 and +31%) than K_{fs} (RC% = +2, +15% and +16%), respectively for 10, 20 and 30 g kg^{-1} of biochar addition. However, the different representativeness of the infiltration surface of the adopted methods (about 490 and 16cm^2, respectively for SFH and MTI) may have affected this result. Our investigation suggests that biochar addition, at the least equal to 20 g kg^{-1}, has the potential to improve appreciably the hydraulic conductivity of fine-textured soils.

BIOCHAR AS PEAT SUBSTITUTE FOR GROWING SUBSTRATES OF ORNAMENTAL POTTED PLANTS

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A greenhouse experiment was conducted with the aim to evaluate the performance of conifers wood biochar as peat substitute for growing substrate of flowered pot plants. Micropropagated plants of Euphorbia x lomi Rauh cv. 'Ilaria' were grown in an unheated greenhouse on plastic pots filled with different mixtures of brown peat and biochar (60% peat-40% biochar, 40% peat-60% biochar, 20% peat-80% biochar,100% biochar, respectively). Plant growth (plant height, stem diameter, leaf area, chlorophyll content, root length, dry biomass) and ornamental characteristics (number of shoots, leaves and flowers) were observed throughout the experiment.

Plant growth and ornamental traits were significantly affected by biochar content of growing substrates as best results, in terms of plant height, stem diameter, number of shoots and leaves, leaf area, leaf dry weight, were recorded in plants grown in 40% peat-60% biochar. Lowest values of the same parameters were measured in plants cultivated in 100% biochar. Chlorophyll content and stem dry weight were higher in plants grown in 40%-60% and 20%-80% peat-biochar. No differences were observed among treatments as regards flower yield.

Hence, a growing substrate containing 40% brown peat and 60% conifer wood biochar allow to have a high-quality production of flowering potted plants of *Euphorbia x lomi*.

EFFECTS OF EXPOSURE OF DIFFERENT BIOCHARS AND A COMMERCIAL SOIL AMENDMENT ON SURVIVAL AND REPRODUCTION RATES OF FOLSOMIA CANDIDA (HEXAPODA: COLLEMBOLA)

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Biochar application to soil is currently regarded as one of the most promising strategies to climate change mitigation associated with improved agricultural productivity; nevertheless few data are available about the potential negative effects of biochar on soil biota. High salinity and possible presence of contaminants such as PAH and heavy metals, derived either from contaminated feedstocks or the use of processing conditions that may favour their production, may induce detrimental effects on environment when biochar is intended to be applied to soil as amendment.

The aim of this study has been to assess the ecotoxicological effects of two different biochars (derived from wheat straw and grape marc respectively) on the survival and reproduction of the collembolan Folsomia candida (Willem, 1902), according to standard protocols ISO 11267-1999. The obtained results have been compared to a standard soil and a commercial vegetable soil amendment. The biochars tested were obtained by a fixed-bed gasifier producing fine-grained, highly porous charcoals that may significantly vary in their chemical and physical properties depending on originating material. The biochars and the amendment have been pulverized and mixed to soil standard (composed by 70% of quartz sand, 20% of kaolinite clay, 10% finely ground Sphagnum peat) at 8 different percentages (w/w): 0.5%, 1%, 2%, 5%, 10%, 20%, 50%, 100%. For each percentage, five replicates have been prepared: 15 g of mixture were put in 90 mm disposable Petri dish, wetted in order to reach a soil moisture content of 55% of the water holding capacity. Then 10 springtails, 10-12 days old, obtained from synchronous egg hatchings, have been disposed in each Petri dish. As control, the test had been carried out on standard soil without any addition of biochar or vegetable amendment. The test took four weeks to complete. A pulverized mix of wheat, oats, rye, soy, and rice has been added weekly to feed the collembolans (2-3 mg in each Petri dish). After 28 days, adult and juvenile springtails have been counted after flotation.

The results obtained have showed that adult survival was heavily affected by the higher percentages (20-100%) for either biochars, but some differences between the toxicological effects of the two biochars have been observed too. On the contrary, adults were able to survive even at the highest percentages of the amendment. The reproduction was greatly reduced compared to the control also at the intermediate percentages of biochars in which the adults survived, while was significantly lower compared to the control but only at higher percentages in the amendment.

POSTER PRESENTATIONS

SESSION PS.4

AGRO-ENVIRONMENTAL EFFECT OF BIOCHAR

CHANGES IN BIOCHEMICAL PROPERTIES OF SANDY CALCAREOUS SOIL AMENDED WITH CONOCARPUS WASTE FEEDSTOCK AND BIOCHAR.

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The application effects of conocarpus waste (CW) feedstock and biochar (BC) at four rates (0, 1%, 3% and 5%) on soil pH, dissolved organic carbon (DOC), organic carbon mineralization, microbial biomass C (MBC), and metabolic quotient (qCO_2) of sandy calcareous soil were studied in an incubation experiment lasting 60 days. The biochar used was produced from conocarpus wastes by pyrolysis at 400 ^oC. The results showed that the addition of CW led to a significant lower soil pH than the control and biochar additives. The rate of CO_2-C was highest in the first few days of incubation than the progressed periods. Applying CW and BC gave significantly higher CO_2-C rates than the control, especially with increasing application rate. However, the added BC showed lower and non-significant increases in cumulative CO_2-C evolution after 60 days incubation. Overall incubation periods, applying CW showed significant higher cumulative CO_2-C, microbial biomass C and DOC than the control and BC treatments. With the exception of 0 day (after 1 h of incubation), both CW and BC led to lower values of qCO_2 as compared to the control. Power function kinetic model satisfactorily described the cumulative CO_2-C evolution, especially in the control and the BC amended soil. Generally, the lowest values of organic carbon mineralization were pronounced for BC, indicating that the contribution of BC to CO_2-C efflux is too small compared to soil amended with CW.

Keywords: Conocarpus waste, Biochar, CO_2 evolution, Microbial biomass; Metabolic quotient

LEAD, CHROMIUM AND COPPER REMOVAL BY ORCHARD PRUNING DERIVED BIOCHAR FROM AQUEOUS MONO- AND MULTI-CONTAMINATED SYSTEMS

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Biochar is a carbonaceous solid residue of thermal treatment of carbon-rich biomass under O_2-limited and low temperatures (<700°C), a process known as low temperature pyrolysis. It has received considerable interest as a soil amendment to improve soil fertility, crop production, and nutrient retention and to serve as a recalcitrant carbon stock. The complex structure of its polycyclic aromatic carbonaceous fraction allows biochar to persist in the environment and not be degraded by microorganisms. Biochar derived from waste biomass is now gaining much attention for its function as a biosorbent for environmental remediation; given that it is highly recalcitrant, the beneficial effects of its eventual application may be prolonged over a long period of time. The sorption capacity of the biochar is linked to the nature of its original biomass, the pyrolysis temperature, the physico-chemical properties of its surfaces and the capacity to form π-backdative bonds with the metals.

The aim of this study was to determine the effectiveness of an orchard pruning derived biochar in removing heavy metals, such as lead (Pb), chromium (Cr) and copper (Cu), from aqueous solutions. The sorption of the contaminants was studied at pH 4.5 and 20°C in single, binary and ternary systems, in order to evaluate the Pb, Cr and Cu sorption capacities of this biochar, in both mono- and multi-contaminated environments.

Lead and Cr showed a good affinity for the surfaces of the biochar (Pb > Cr), while the Cu resulted to be less affine; accordingly, larger amounts of Pb and Cr have been sorbed by biochar compared to those of Cu, in the single systems. Certainly, the different metals sorption capacities shown by biochar have been strongly affected by the radii of the hydrated ions, electric charge, metal electronegativity, ionization potential, hydrolysis constant, etc.

In binary systems, the Pb showed the greatest capacity to inhibit the sorption of the other two metals on the biochar surfaces, whereas the opposite was true for Cu. In ternary systems, even in the presence of large amounts of Pb and Cr, considerable extent of Cu sorption still occurred, indicating that some sorption sites of the orchard pruning derived biochar were highly specific for each metal.

The implementation of decontamination systems of heavy metals-enriched environments by providing biochar as sorbent, would be able to combine an effective removal of the contaminants with low costs of remediation. Further studies are currently being developed to understand the mechanisms by which these metals are sorbed and identify the nature of biochar-metal bonds at the solid-liquid interface.

Keywords: biochar, heavy metals, lead, chromium, copper, orchard pruning, sorption.

PARTICULATE EMISSION OF BIOCHAR

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The application of biochar as soil amendment in agriculture is widely recognized. This carbon-based material is characterized by several positive aspects in agriculture, however, few information about its fine particles dispersed during its application in the field are known. In this study a quantification of the particulate emissions of the biochar is assessed, using aerosol spectrometer. We measured the particles size distribution of PM10, PM2.5 up to ultrafine UFP of several biochar types came from pelletized and no-pelletized feedstocks. Furthermore, we measured the particulate emissions of biochars related to dry and wet condition. Our results show that the biochar pelletized produces less particulate emission (-77%) than to no-pelletized ones and a markedly decrease (-86.7%) in PM2.5 and UFP in wet biochar compared to those dry. These preliminary results contribute to suggest a safe use of the biochar in agriculture sector.

SORPTIVE TREATMENT OF METALS AND NITRO EXPLOSIVES IN WATER USING BIOCHAR

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Biochar, a solid byproduct of a pyrolysis process was investigated as a sorbent to remove toxic metals and nitro explosives from natural water and wastewater. It was hypothesized that biochar can sorb dissolved metals and nitro explosives due to its high surface area and strong sorption affinity of aromatic organic compounds. Using a tube furnace under N_2, various types biochar were synthesized by changing biomass (poultry litter, sludge, fallen leaves, corn stalk, rice straw, and coffee grounds) and temperature (250, 400, 550, and 700 oC). The physical, chemical, and engineering properties of the biochar were characterized. Through batch experiments, the extent of removal of dissolved metals (Cd, Cu, Pb, Zn, and As) and nitro explosives [2,4-dinitrotoluene (DNT), 2,4,6-trinitrotoluene (TNT), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)] was evaluated using sorption isotherm models. The removal of metals and nitro explosives was as effective as granular activated carbon, widely used as a typical sorbent in remediation processes. Considering the properties of biochar and maximum sorption capacity for each contaminant, factors affecting the sorption of contaminants to biochar were discussed. Our results suggest that biochar may be applied as a sorbent to decrease the concentrations of metals and nitro explosives in natural and engineered systems.

PHYTOTOXICOLOGICAL EFFECTS OF DIFFERENT BIOCHARS USING PLANT BIOASSAY

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The application of biochar to soil as amendment is proposed as a novel approach to improve soil fertility, soil properties and functions, and carbon sequestration. Despite the benefits that biochar seems to give to the soil, a sufficient knowledge of the soil-biochar interactions is still lacking. In particular, it is important evaluate eventually toxicological effects of biochar that may be caused by its polycyclic aromatic hydrocarbons (PAHs) content, deriving from the process of production, and metals that can be different linked to biomass feedstock origins.

The aim of this study was to assess toxicological effects of four types of biochars, deriving from gasification of conifer, grape marc, poplar, wheat straw, on germination and root elongation of tree plant species routinely used in bioassay tests (Cucumis sativus L., Lepidium sativum L., Sorghum saccharatum Moench) compared to commonly used commercial vegetable soil amendment. The biochars tested were obtained by a fixed-bed gasifier producing fine-grained, highly porous charcoals that may significantly vary in their chemical and physical properties depending on originating material. The biochars and the amendment were pulverized and mixed to a standard soil (ISO11267:99) at the following percentages (w/w): 0.5%, 1%, 2%, 5%, 10%, 20% and 50%. For each percentage, four replicates were prepared: 15 g of mixture were put in 90 mm disposable Petri dish, covered with a Whatman #1 filter paper and wetted with 5 ml of deionised water. 10 undamaged and plump seeds were then added on the surface. The dishes were closed into polyethylene bags and incubated at 25 ±1° C in the dark for 72 hours. The procedure was repeated for each plant species. As control, the test was carried out for each plant on standard soil. Germination rate, germination index and ECx (EC10, EC30, EC50) values, using a log-logistic model, were determined.

The results obtained showed a reduction in germination depending on the plant species (sorghum showed lower germination rate compared to cucumber and watercress) and the types of biochar. Root elongation was considerably inhibited at higher concentrations in all the biochars tested, and starting from 1% there were significant differences ($p<0.01$) between the root lengths from the control and some biochars, grape marc in particular. EC50 values were ranged from 3 to 7 % depending on the types of vegetable matrices. At the higher concentrations tested, significant differences were also found between all the types of biochars and the vegetal amendment.

CROP PRODUCTION, BIOCHAR AND SOIL FEATURES EVALUATED 5 YEARS AFTER BIOCHAR DISTRIBUTION IN A HIGHLY MANAGED CROPLAND

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Biochar is an organic material produced via pyrolysis from several different possible feedstocks and its application to soil has been suggested as a viable option for carbon sequestration, crop production increase and soil properties amelioration. However, most of the studies carried out up to date were short term experiments and evaluated biochar agronomical effects in controlled environment such as pots or lysimeters, using acid and nutrients-poor soil. On the contrary, the present work aimed to evaluate the effects of biochar on crop production in a field experiment and the associated changes in biochar and soil properties in the long term (5 years).The trial started in 2008 on a highly managed agricultural silty-loam soil, with a pH of 7.8 and optimal P and K plant availability. Two treatments were compared in three times replicated plots (20 m^2 $plot^{-1}$): control (C) and biochar (B) applied before winter tillage in two consecutive years (10 t ha^{-1} y^{-1}). The crop planted was maize in 2008, 2009 and 2010, soybean in 2011 and again maize in 2012. Grain yield and above ground total biomass were measured at harvest and harvest-index was calculated for each plot. Moreover, in 2013 soil enzyme activities were determined and biochar acidic functional groups were assessed by comparing original biochar with the 5 years aged one collected from the soil. In 2008 and 2009, biochar improved significantly grain yield (+24% and +21%, respectively) and total biomass (+47% and +16%, respectively), but no differences with control were detected in the following three years and harvest index was never significantly affected by biochar. A significant increase in acid functional groups was observed in the chars that were aged in the soil, mainly in terms of carboxylic and lactonic acid groups, while first analytical results indicated that biochar did not affect the enzymatic activities in the soil at the end of the experiment. In conclusion, these preliminary results indicate a positive effect of biochar on productivity soon after its application and a declining effect in the medium-long term at least in a highly managed and nutrient rich soil even though aged biochar showed an increase in acid functional groups thus improving nutrients' retention capacity.

EFFECT OF TEXTURE ON THE DYNAMICS OF A WATER SATURATED BIOCHAR

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Biochar is defined as charred organic matter applied to soil in a deliberate manner, with the intent to improve soil properties (Lehmann et al., 2009). Biomass-derived char can be used as energy carrier, as adsorber and as material for the improvement of soil properties. Carbonized organic matter can have different physical and chemical properties depending on the technology used for its production. Moreover char texture influences deeply physical and chemical properties. In this work effect of texture on the dynamics of a water saturated biochar was analyzed by FFC NMR.

An industrial biochar derived from gasification of poplar wood was sieved to determine influence of texture on water dynamic on particles surface.

Sieves with 2, 1 and 0.3 mm have been used to separate three different texture fractions.

Each sample has been saturated with water and then analysed by FFC NMR relaxometry by applying a range of magnetic field from 40MHz to 0.01MHz.

Three profiles with different longitudinal relaxation rate have been carried out. Sample with texture 1-2mm has a profile with the lowest longitudinal relaxation rate (R1). Profile of sample with textures <0.3mm has the profile with highest R1.

Behavior of water can be explained associating an increment of longitudinal relaxation rate with an increment of porosity.

Surface area reduction is achieved when the sizes of the pores increase. As water molecules flow through larger sized pores, their motion occurs at a frequency that is broader than that of water molecules constrained in smaller sized pores. For this reason quickly moving water can not efficaciously interact with either neighboring molecules or with the molecular sites on the surface at the liquid-solid interface. As a consequence intermolecular dipolar interactions are weakened and a reduction of the proton longitudinal relaxation rate (shorter R1 values) can be observed compared with the R1 values for slowly moving or immobilized water systems.

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SOIL ADAPTATION TO BIOCHAR: EFFECT OF NEW ADDITION TO SOILS WITH AND WITHOUT BIOCHAR

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It is not clear whether adaptation by microbes responsible for decomposing biomass will have a significant effect on biochar stability in the long term. To answer this issue we tested the effect of biochar history on the mineralization of new biochar (NB). Biochar history was developed through a one-year soil incubation with and without miscanthus straw (MS), hydrochar (MSHTC), and low- and high-temperature slow pyrolysis biochars (MS300 and MS700). We further incubated these soils with and without the addition of a mid-temperature slow pyrolysis biochar prepared from MS at 450 °C (NB). This allowed for assessing the effects of previous biochar incorporation on the mineralization of NB. The evolution of CO2 and its 13C signature was monitored for 2 months, and natural abundance stable isotopes were used to calculate substrate mineralization rates and priming of soil carbon.

Cumulative CO2 emitted during the incubation was higher in soils with new biochar addition, with a percentage effect of NB varying from 21 % (for soil), to 45 % (for MS700), suggesting a larger response of soils already containing biochar to NB addition.

Considering the mineralization rate of NB only, the proportion of newly added C4 mineralized showed a similar pattern, showing the rank MS700 > MS > MS300 >= MSHTC >= soil, confirming that biochar mineralization may be higher in soil having been previously exposed to high-temperature biochar.

The priming effects on soil organic matter mineralization due to previous biochar amendments are slightly altered by NB addition: negative priming from MS is augmented and negative priming from MSHTC is diminished.

In conclusion, biochar history affected mineralization of NB, suggesting a microbial adaptation favoring mineralization processes, in particular with high-temperature biochar.

BIOCHAR THERMAL STABILITY AND CHEMICAL SOLUBILITY: A DUAL PICTURE OF BIOCHAR FATE IN SOIL

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Peculiar characteristics of biochar as potential C sink are the relative stability in soil together with high C content, being these the major advantages of its use as soil amendments with respect to fresh or composted organic biomasses. However, the term "biochar" refers to a wide class of products greatly varying in composition, due to both chemical composition of original biomasses and production technology used. Often comparison of results of different investigations carried out on agronomical and environmental effects of biochar are controversial, due to the lack of a common set of reliable methodologies in assessing biochar stability.

In the present study we compared two biochars, obtained by the same technology (gasification) from biomasses of different origin (maize and conifer), and two natural organic matter rich materials (peat and leonardite). Biochar samples were produced by gasification technology and were kindly furnished by AGT s.r.l. as materials with contrasting composition, whereas peat and leonardite were chosen among standard materials from International Humic Substances Society, as characterized by different degree of polymerization.

The methodological approach we used to characterize these materials included the determination of C content and its fraction soluble in cold water together with a set of thermal stability indices deduced by Differential Scanning Calorimetry (DSC), Thermogravimetry (TG) and elemental analysis. The specific aim was to furnish an in depth and direct characterization of some chemical-physical characteristics of the investigated products on a scale of differing stability.

Potential environmental impact of biochar incorporation in soil on target organisms, such as soil micro-biota and plants, was also investigated by using both solid samples and aqueous extracts. Specific bio-assays previously set up for fertilizers and amendments were used in order to assess short term effects on soil ecosystem functions, directly related to soil fertility and elements cycling.

Main results showed that the two biochar samples differed in thermal stability, as well as they were contrasting in both C content and chemical solubility in water. Similar differences were found also between peat and leonardite. Bioassays showed differences according to the different soluble C content in the aqueous extracts. In conclusion, the integrated approach to biochar stability assessment according to both thermochemical and biological assays may represent a realistic modelling of biochar fate in soil.

TRANSIENT EFFECT OF BIOCHAR ON SOIL PROPERTIES AND PROCESSING TOMATO GROWTH

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Biochar application to soil has been reported to improve soil fertility and decrease nutrient leaching, under laboratory and field conditions and consequently increasing crops productivity. These positive effects may be related either to a direct addition of nutrient, which are present in biochar from biomass feedstock, or to chemical-physical and biological changes of the soil environment that biochar can induce. Biochar with high specific surface area amplify the cation exchange capacity of soil and play a role in soil hydrophobicity and due to its high porosity may influence the soil water holding capacity and offer a suitable habitat for bacteria and fungi.

In our study, we investigated the impact of two different biochars type (same biomass feedstock but different pyrolysis process) on plant growth of processing tomato, nitrogen availability and uptake, soil bulk density, water retention, hydrophobicity and soil microbial communities composition, in a field experiment. Biochar treatments positively enhanced plant height and the dry matter at the beginning of the experiment, but this priming effect disappeared after 60 days of biochar application and disappear at the end of the experiment. This priming effect of the biochar at the beginning of the experiment was consistent with an increase of leaf N content in plants treated with biochar during the first months, which however was similar to control values at the end of the experiment.

Soil chemical, physical and biological properties were investigated to analyze thoroughly these changes. In particular, nitrate (NO_3) and ammonium (NH_4) availability showed an initial higher N availability due to biochar addition, suggesting a positive effect on nutrients retention and exchange. The bulk density measurements did not show significant differences between the treatments. Biochar did not influence soil hydrophobicity, while induced a slight increase of soil water holding capacity. No significant effects of biochar incorporation was detected with the Denaturing Gradient Gel Electrophoresis (DGGE) analysis on soil eubacterial population during the vegetative cycle: the similarity level of the pattern profiles belonging to the eubacterial populations inhabiting the treated and control plot soil were extremely high all along the vegetative cycle, although profiles from the same sampling time clustered together and, mainly in the last samples, were grouped accordingly to their different management.

Our results suggest that the initial growth effect on processing tomato could be linked to a direct effect of biochar on N retention and bioavailability that boosted plants growth and leaf N content, which was lost after the first two months.

INTERACTION OF BIOCHAR WITH SOIL ORGANIC CONTAMINANTS: REDUCTION OF PHYTOTOXICITY

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Among the most dangerous pollutants released by human activities into the environment every year, polycyclic aromatic hydrocarbons (PAHs) and chlorophenols are also listed because they can cause serious effects, such as disease, birth defects and death in humans and animals.

New remediation systems and technologies, always more efficient and low cost, are used to recover polluted soil. Recently, biochar arises particular interest due to high porosity and remarkable capacity to adsorb pollutants.

The purpose of this study was to evaluate the ability of biochar, derived from poplar and conifers, in the absorption of a polycyclic aromatic hydrocarbon, phenanthrene (Phe), and a chlorophenol, pentachlorophenol (PCP). The effect on the extractable fraction of contaminants and phytotoxicity was evaluated after different remediation times. The coexistence of biochar and organic matter in form of compost was also tested in order to individuate an enhancement of the remediation process.

The remediation process was influenced by contaminant and biochar nature. In fact, hydrophobicity influenced interactions between contaminants and biochar: biochar from conifers, due to higher specific surface, porosity and hydrophobic sites, was much more efficient in the contaminant adsorption of the than that from poplar. In addition the amount of biochar added in remediation test affected the treatment efficiency, especially for PCP.

Organic matter, in terms of compost addition, led to reduce the contaminant extractable fraction because of sequestration process in organic and organo-mineral aggregates.

All these factors as well as remediation time favoured the immobilization of contaminants on carbonaceous matrices thus limiting their bioavailability. Phytotoxicity of PCP was strongly reduced by biochar addition, though only at higher rates (20 and 50 mg g^{-1}); conversely Phe phytotoxicity was not affected by biochar treatment since this contaminant was not phytotoxic in itself.

Even if further investigations need to be carried out to confirm these interesting results, the use of biochar can be considered a valid in situ remediation technique.

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