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BIOCHAR FROM GASIFICATION IN CULTIVATED SOILS AND RIPARIAN BUFFER ZONES: CHEMICAL CHARACTERIZATION



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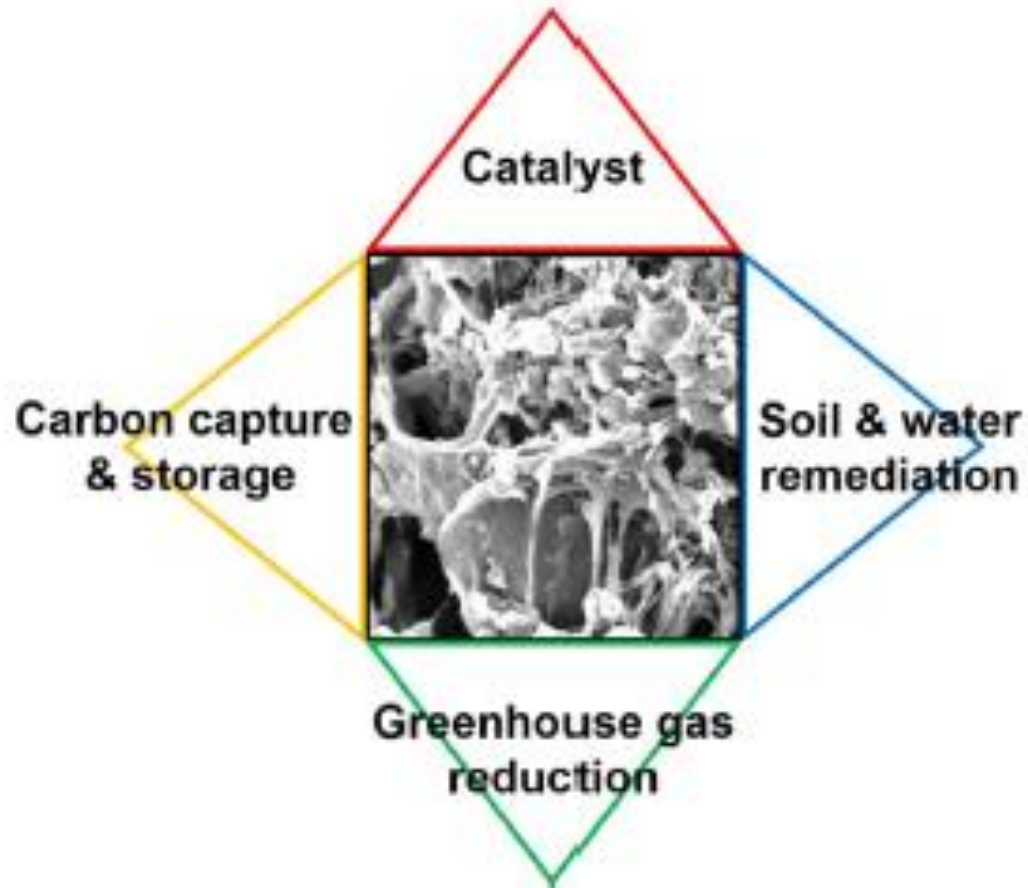
During rain events, pollutants in agricultural soils can be transported from fields to surface and/or groundwater resulting in contamination of streams and rivers.



Ohio Wesleyan University **BISHOPAPPS**

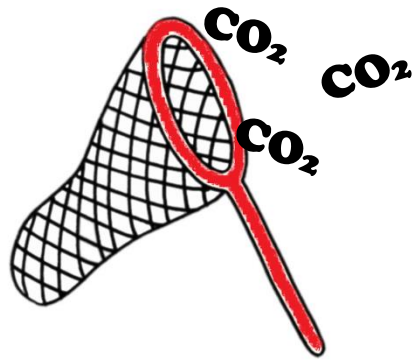
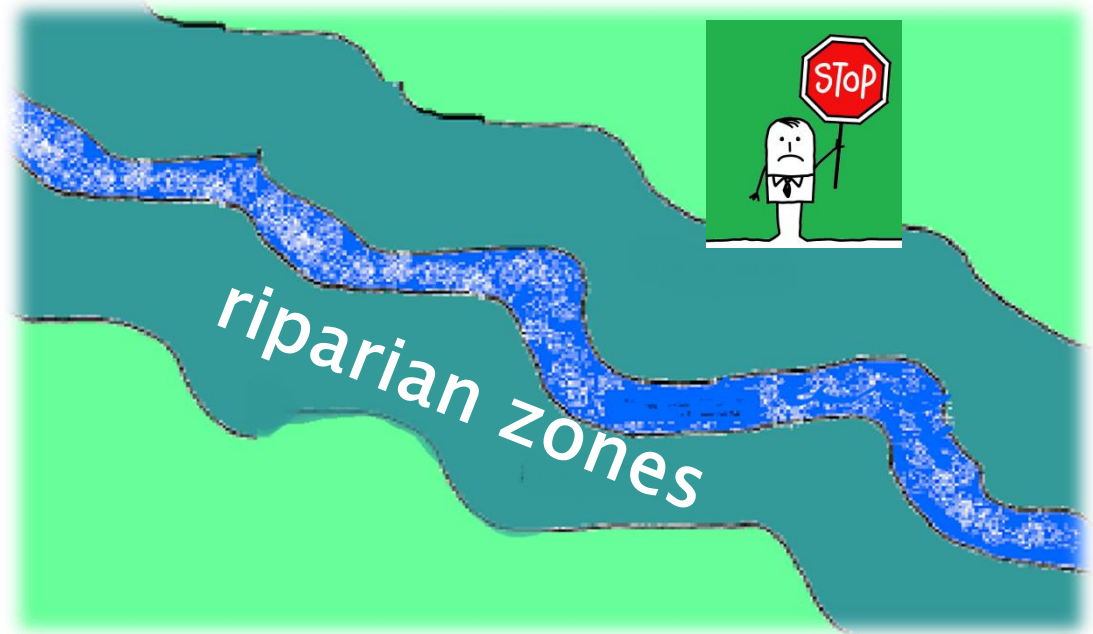
Researchers and farmers should work together to find solutions to ensure the preservation of crop production without modifying water quality or the health of ecosystem.

Versatility of Biochar



Renewable and Sustainable Energy
Reviews 77 (2017) 70–79

The addition of biochar to soils, particularly in a riparian zone, can reduce the mobility of contaminants



....., biochar can concur to climate change mitigation by sequestering soil organic carbon into a form that is more resistant to mineralization than fresh biomass.

Research Projects:



Carbonization of Agricultural Residues: Biochar Precious Solution for Carbon Sequestration in Soil.

(Carbonizzazione dei residui agricoli: Biochar preziosa Soluzione per il Sequestro di Carbonio nel Suolo.)

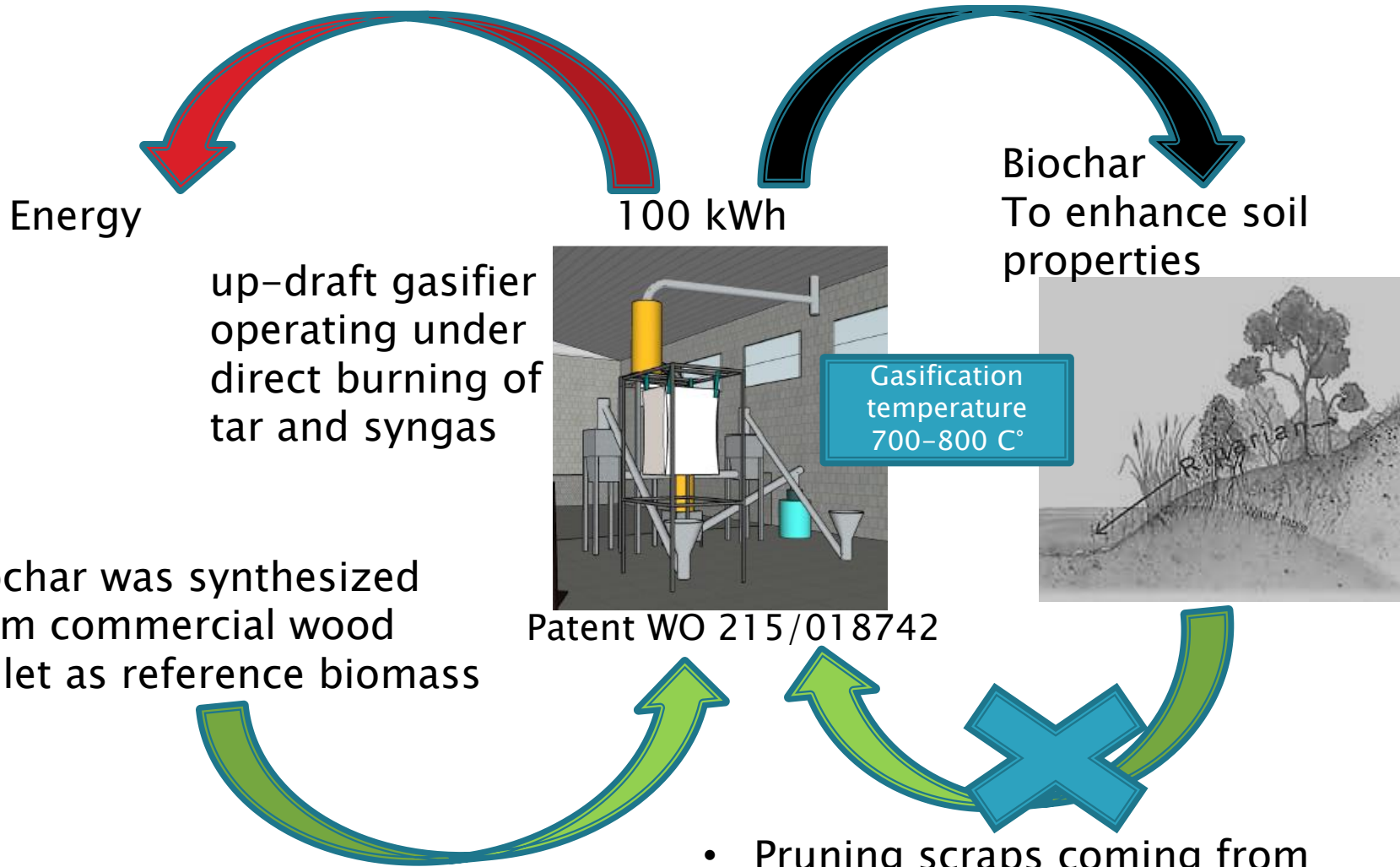
PSR misura 16 Focus Area 5E Regione Emilia Romagna.

The use of biochar as a biological filter for water purification: the Soil amendment that clean the environment

Uso del Biochar come filtro biologico per la depurazione delle acque: l'ammendante che depura l'ambiente

"PSR misura 16 Focus Area 4B Regione Emilia Romagna.

Circular use of biomasses



- Pruning scraps coming from riparian zone management
- Agricultural Waste

Aim

Determination of the quality of biochar obtained from an innovative gasifier prototype

Assessment of pollutant immobilisation capability of biochar

Determination of biochar concentration in soil

Chemical Biological parameters



TOC	% C	> 60	79%
Salinity	mS/cm	≤ 10	1,8
pH (H2O)		4-12	10,1
Ash	%	< 10	<5
H/C (molar)		≤ 0.7	0,3

Fitotoxicity:

Suitable



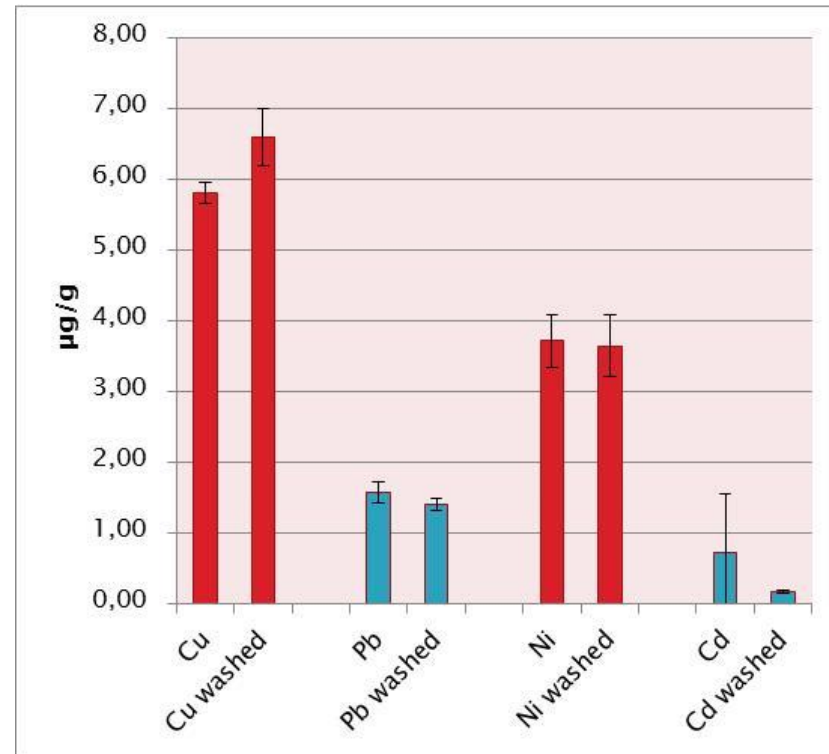
Contaminants



Pb	mg/kg	≤ 140	< 2
Cd	mg/kg	≤ 1.5	< 1.5
Ni	mg/kg	≤ 100	< 4
Zn	mg/kg	≤ 500	< 4
Cu	mg/kg	≤ 230	< 6
Hg	mg/kg	≤ 1,5	nd
Cr(IV)	mg/kg	≤ 0,5	nd
PAH	mg/kg	< 6	1,7
PCB	mg/kg	< 0.5	nd
Dioxine	ng/kg	< 9	nd

PSR is a biochar of high quality

The analyzed metals are not water soluble (1.1 % solubilized)



Elemental and Proximate analysis of PSR Biochar

HCN (Thermo Fisher)

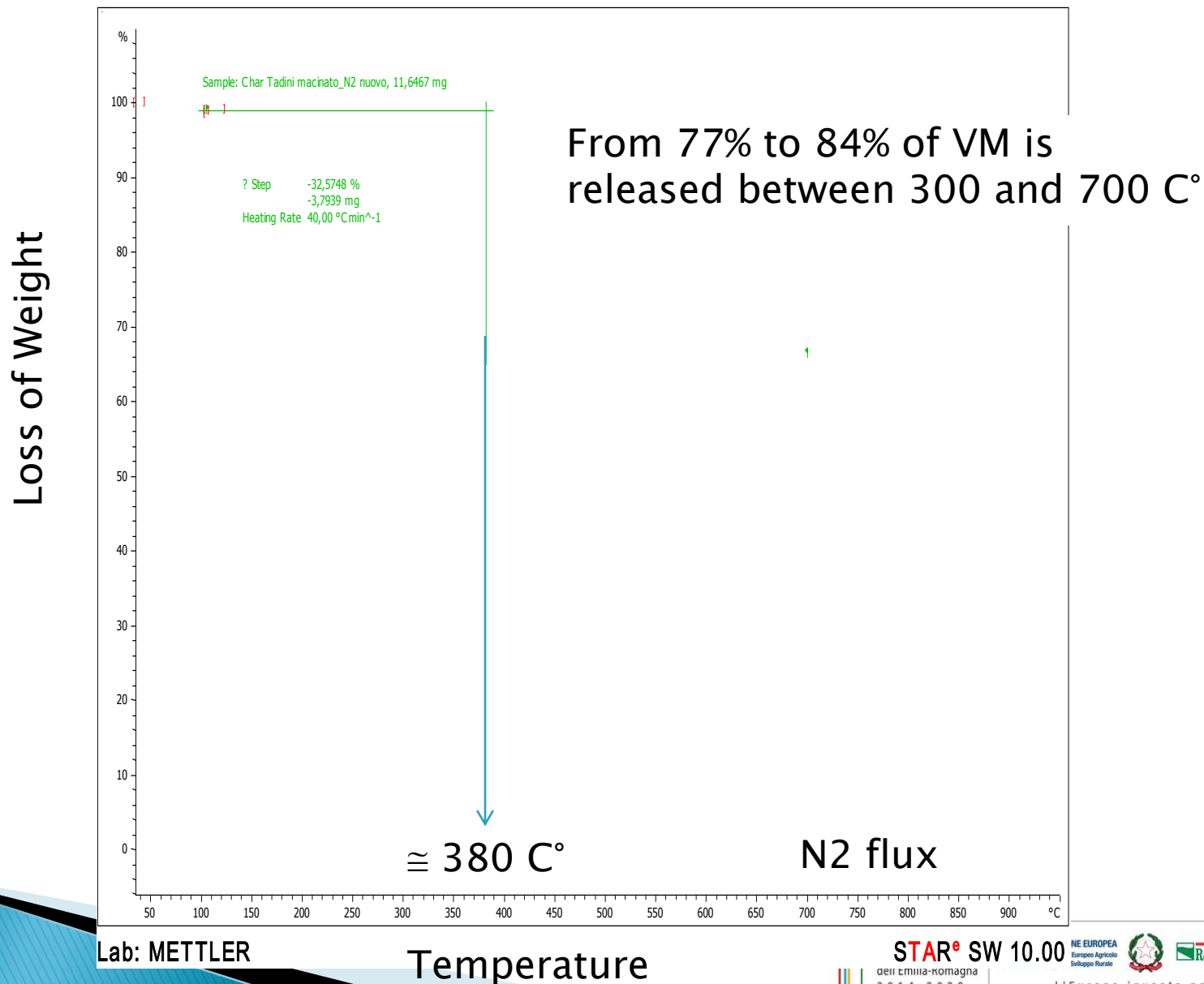
	TC	TOC	N	H	H/C
	% (n=3)				
BIOCHAR	80	79	0,20	1,8	0,27
DEV. ST	4.7	2.1	0.05	0.12	

Proximate analysis (TGA -Metler toledo) ASTM D7582 – 15

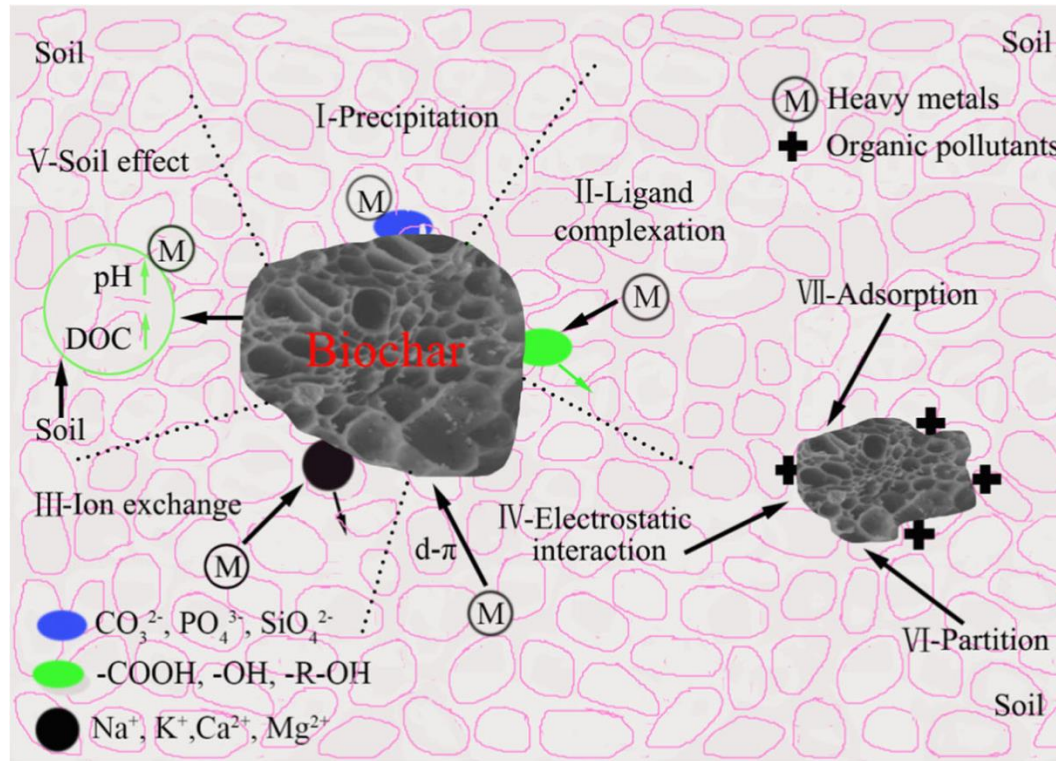
	Moisture	Volatile	Fixed carbon	ASH
	(%) (n=4)			
BIOCHAR	1,2	32	62	4,7
DEV. ST	0,1	6,7	6,5	0,3

	Density	Conductivity EN 13038	pH EN 13037
BIOCHAR	0,4 kg/L	1,8 mS/cm	10,1

Further Thermogram information



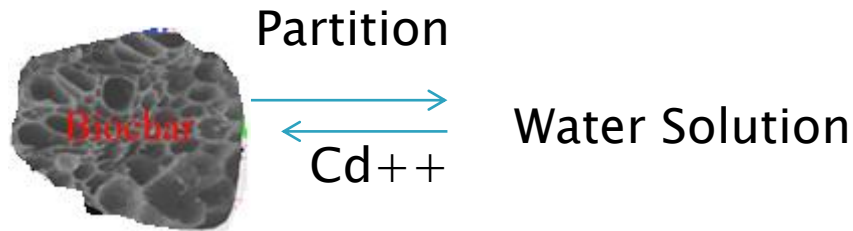
Sorption capacity determination



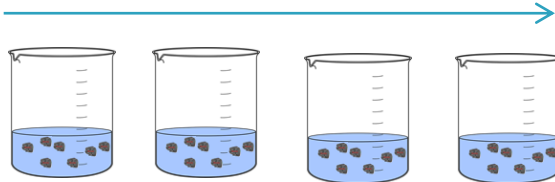
1. electrostatic interactions between metal cations and negatively charged biochar or soil surfaces
2. ligand complexation involving functional groups of biochar in the surface
3. cation exchange with Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , and other cations associated with biochar
4. precipitation or co-precipitation with the formation of oxides, hydroxides, phosphates, carbonates, silicates, and chlorates
5. Sorptive interactions between d-electrons of metals and delocalized π -electrons of biochar
6. increased soil DOC and pH by biochar

Sorption capacity determination: Sorption Isotherm curves

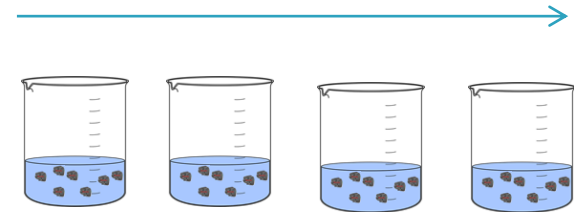
Sorption Isotherm curve of Biochar provides information about the relative sorption capacity



Sorbate
concentration



Sorbent
concentration



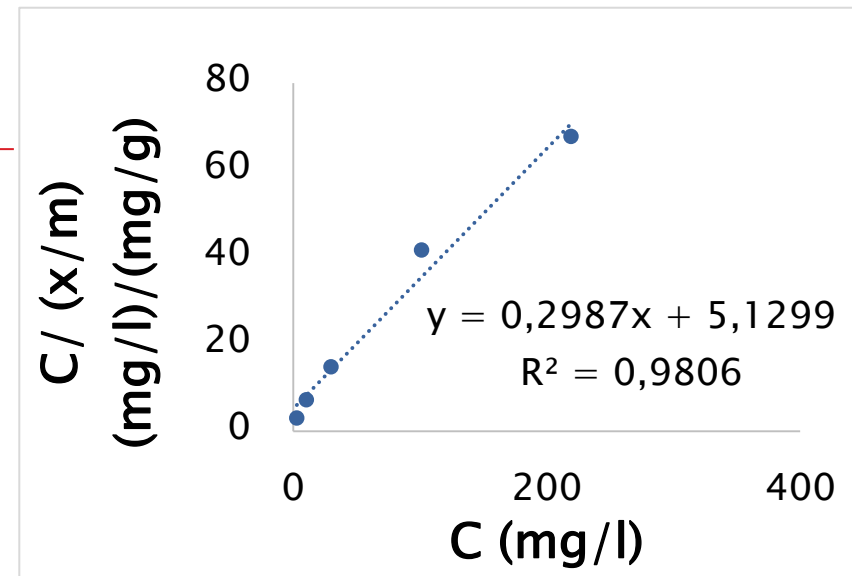
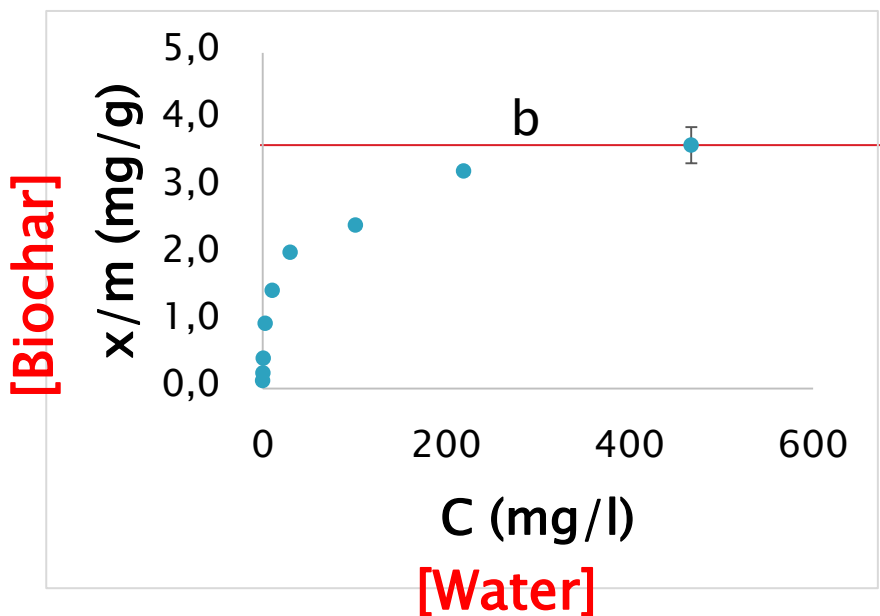
Target metal: Cd

Sorption capacity determination

Sorbate
concentration

- Test n° 1: constant solid liquid ratio, different Cd concentration
1 g of biochar, 100 ml of cadmium solution, Cd concentration 1.25–500 ppm

Langumir equation $\frac{x}{m} = \frac{b \cdot K \cdot C}{1 + KC}$



b = 3.4 mg/g

b = Maximum amount of sorbate which can be retained by the sorbent

Sorption capacity determination

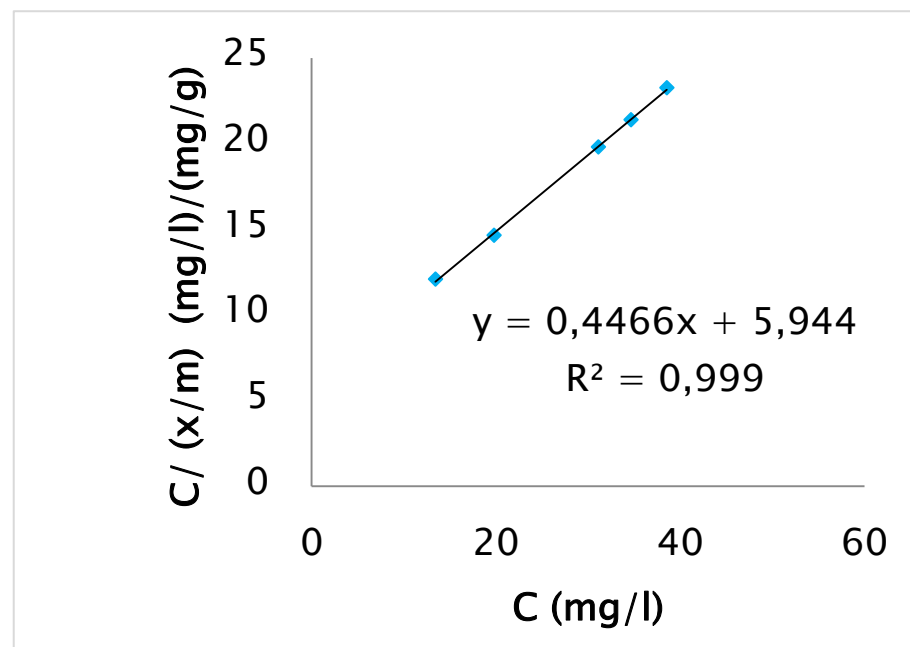
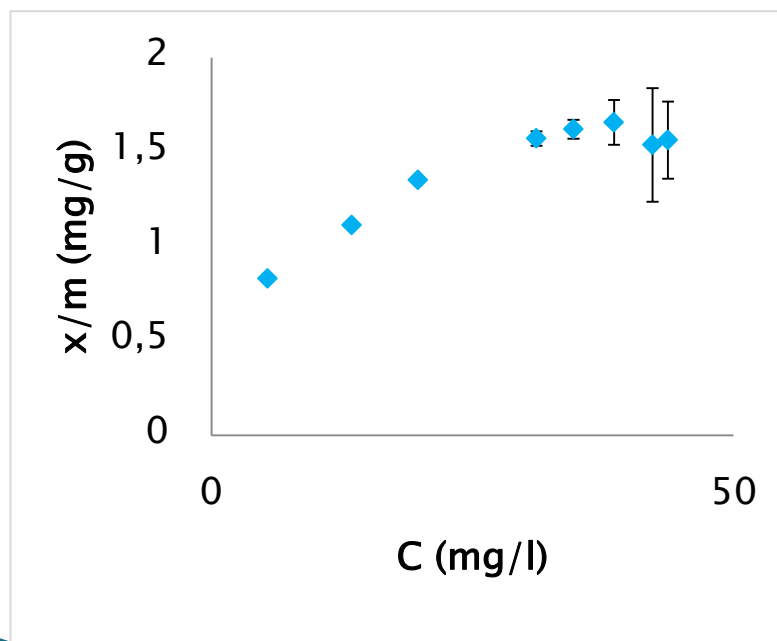
Sorbent
concentration

- Test n° 2: constant Cd concentration (50ppm), different solid liquid ratio

Volume 100 ml

Sorbent amount 0.2–5 g

$$b = 2.2 \text{ mg/g}$$

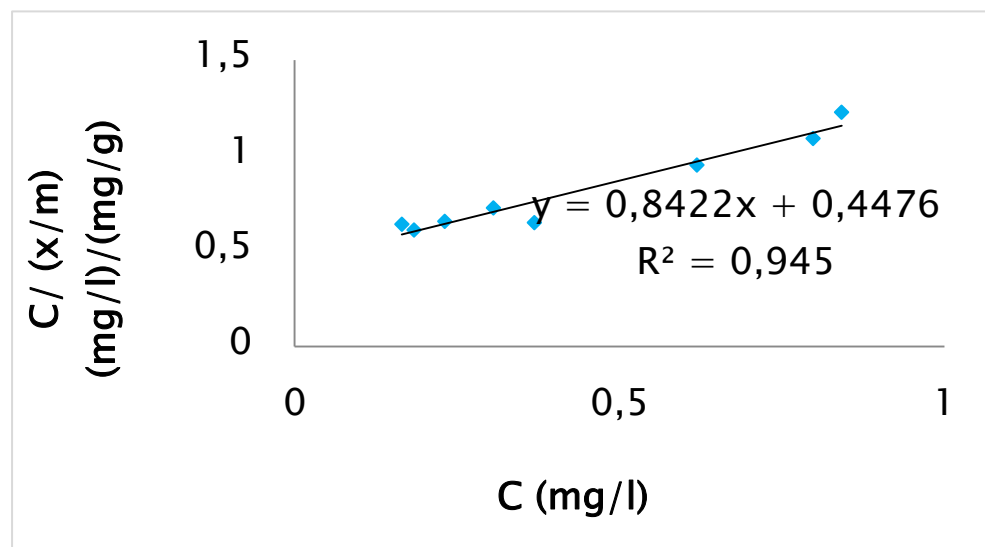
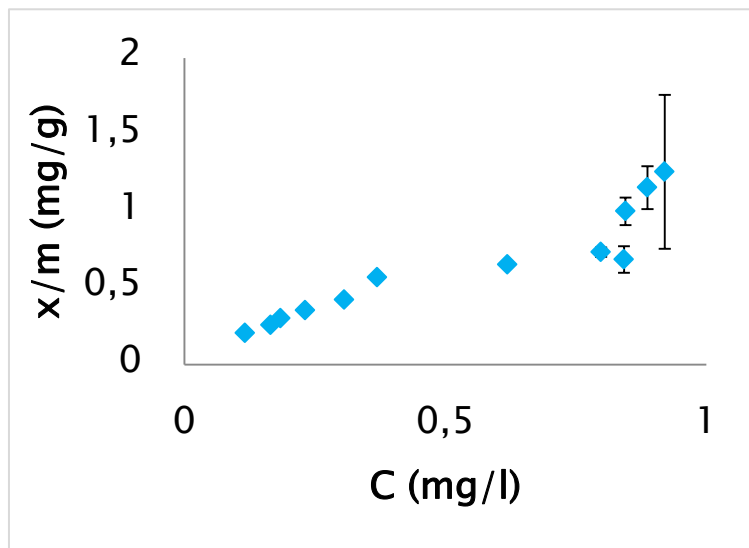


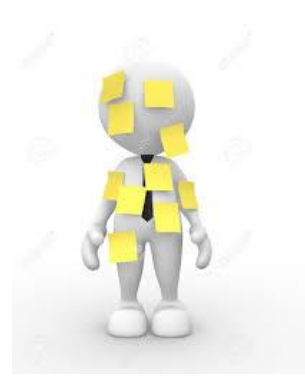
Sorption capacity determination

Sorbent
concentration

- Test n° 3: constant Cd concentration (**1 ppm**), different solid liquid ratio
Volume 500 ml
Sorbent amount 0.01 – 2 g

$$b = 1.2 \text{ mg/g}$$





Conclusion

- **Biochar chemical characterization is useful to give safety information:** biochar compliance has been verified and confirmed
- TGA can give useful information about the **biomass conversion**. Even if the gasification system works at 700–800 C°, it produces a biochar that has an high concentration of volatile matter (30%). **Biomass conversion can be improved.**
- **Sorption Isotherm Curve** could be useful for a relative comparison of biochar adsorption capacity.

Understanding the impact of soil amendment requires the analytical determination of carbon speciation and evaluation of organic matter stability.

Some conclusion...

TOC and HCN Analyzers were both reliable for the determination of carbon in highly carbonized biochars. In biochar/soil systems the values obtained with TOC analyzer were more concordant to the expected values

Potentially, TGA technique could be applied for the quantitative analysis of charred carbon in soils.



ANALYSIS OF TOTAL ORGANIC CARBON IN SOIL TREATED WITH BIOCHAR

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Introduction

Amending agricultural soils with biochar can contribute to negative carbon strategies when the resistance to oxidation of soil carbon is enhanced and plant growth promoted. The sequestration/fertilizing activity is influenced by its physicochemical processes and physical migration out of the cultivated area. Understanding the impact of these processes requires the analytical determination of carbon speciation and evaluation of organic matter stability. Different standard methods can be applied to the determination of carbon [2], but comparative studies on their reliability to biochar treated soils are scant [3].

Aims

Compare dry combustion methods with a TOC analyzer and HCN analyzer total carbon (TC), organic (OC) and IC (inorganic carbon) in model soils with and without biochar.

Validate thermogravimetric analysis (TGA) to determine the contribution of biochar in treated soils.

Samples

Three biochars (Table 1) were utilized to prepare biochar/soil samples

TABLE 1. Biochar samples

Biochar	Origin	Methods	C %	H/C	N/C	Ash %
PSR	Ardente Tasso Super Turco	Wood pellet	80 ± 9	0.27	30	4.7
MSP70E	Gr Biochar S. Cenero (2)	Municipal waste	79.18 ± 0.27	0.19	17	1.2
BC1	COF 1207 (4)	Waste/Industrial waste	82 ± 5	0.22	18	11

Two air-dried tilled agricultural soils with different carbonate content, soil Q (light) and soil T (dark), were mixed with biochar at 5 % w/w level in a molar (Table 2) and biochar MSP at different levels from 0.5% to 10 % w/w

TABLE 2. Biochar/soil samples

Soil	biochar/soil	biochar/soil	
Q	PSR 0.500M	T	PSR 0.500M
Q	MSP 1.024N	T	MSP 1.024N
Q	BC1 1.024N	T	BC1 1.024N

Methods-carbon by dry combustion

CARBON

Two methods were compared:

Method 1 (TC): TOC-L 500M S00EA solid sample module analyzer, CO₂ detection by IR, 150 mg sample.

TC (dry): at 900 °C (standard glucose).

IC at 200 °C after acidification with eq. 42.9M H₂PO₄ (standard sodium carbonate).

OC by difference.

Method 2 (HCN): HCN Titrator Fisher Scientific FUSN 2000 series, CO₂ detection by IR (TC).

TC (dry): standard, 1.5 (mg) sample (dry) 2 (mg) standard 2-(p-tolyl)urea.

OC as in eq. HCl treatment.

IC by difference.

Methods-organic matter by TGA

The organic matter was investigated by thermogravimetric analysis on model components (CaCl₂, glucose, wood) and soils added with different levels of MSP. TGA were performed on 50 mg sample with a TGA Mettler Toledo TGA/DTG5050 with the following program: 40-55 °C/min → 105 °C (3 min), under N₂, 105-10 °C/min → 800 °C, under air. Pyrolytic analysis of biochar was performed by ASTM D7582-05.

References

- 1) Zambelli, D., Vezzani, I., Tomi, C., Romboli, A., Vercesi, E. (2019) Determination of the organic carbon on a series of forest models. *Tracce in Agricoltura*, 2019, 20, 74-76.
- 2) Chapin, F.S., Vitousek, D.M., Matson, P.A. (1986) Nitrogen content of mineral and organic matter in soil. *Soil Science Society of America Journal*, 50, 431-434.
- 3) Zambelli, D., Vezzani, I., Tomi, C., Romboli, A., Vercesi, E. (2019) Determination of the organic carbon on a series of forest models. *Tracce in Agricoltura*, 2019, 20, 74-76.

Results

TABLE 3. TC and OC in biochar samples (5% w/w) with methods 1 and 2.

Method	TC	OC	IC	IC/TC
PSR	80.2 ± 9.2	79.7 ± 9.0	0.2 ± 0.2	79.8 ± 9.2
MSP	80 ± 2.0	80.0 ± 0.8	0.0 ± 2.0	79 ± 0.8
BC1	81.2 ± 0.8	80.9 ± 0.5	0.2 ± 0.4	79.9 ± 0.7

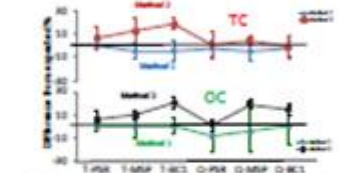


Figure 1. Relative percent difference between the measured and expected carbon content in biochar/soil samples (5 % w/w) with methods 1 and 2. Standard deviations (St. dev.).

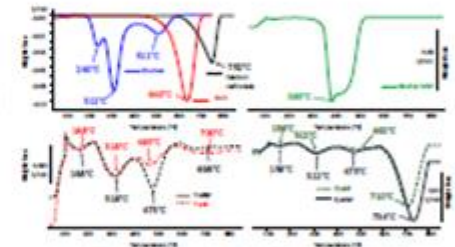


Figure 2. DTG of model components, biochar MSP, soil and biochar 5% soil samples

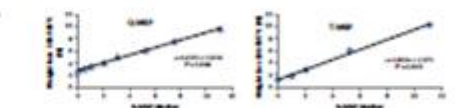


Figure 3. Calibration curves of soils T and Q with different content of MSP biochar.

Conclusions

Analysis of carbon by combustion

Method 1 (TOC) and 2 (HCN) were both reliable for the determination of carbon in highly carbonized biochars (Tab. 4 in Tab. 2) → In biochar/soil systems the values with method 1 were more concordant to expected values (Fig. 1).

Analysis of organic matter by TGA

→ 10% acidified different levels for table (1 → 400 °C), charred (1 → 470 °C), black (1 → 840 °C) organic matter and carbonates (1 → 780 °C) → linear relationships with the weight loss of charred organic matter and biochar content in soil.

Acknowledgments

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Thank you !