PROCESSES OF THE BIODEGRADATION OF BIOCHAR FROM DIGESTATE IN SOIL

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Biochar

- Carbonized organic matter, with a broad spectrum of possible use, such as a soil fertilizer or an element in carbon sequestration (Fisher and Glaser, 2012; Lehman et al., 2011; Lehman and Joseph, 2009).
- Produced by pyrolysis from different substrates (Radawiec et al., 2014).
- Carbonization of matter typically occurs at temperatures from 200 to 600°C (Mohan et al., 2014).

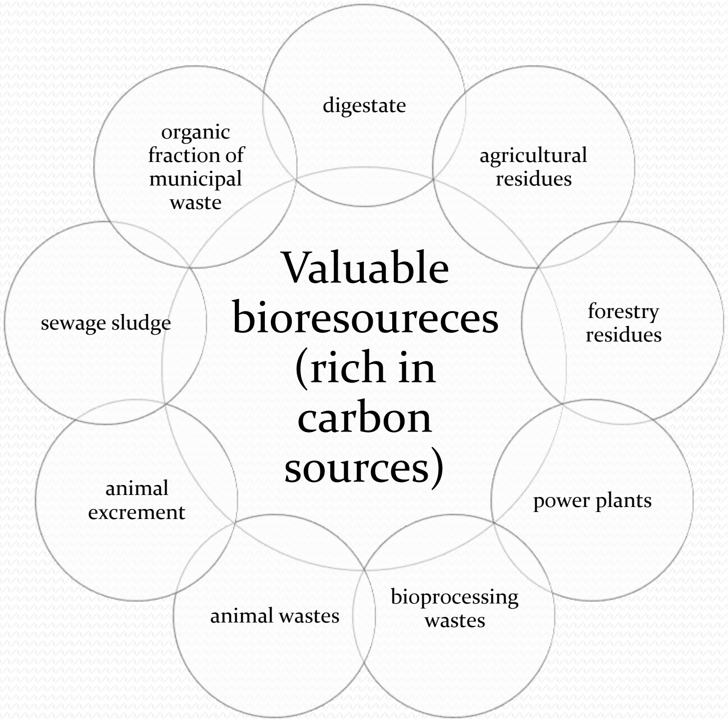


Fig.1. Substrates for the biochar formation (Radawiec et al., 2014).

- Table 1. Specification of digestate and biochar (Troy et al., 2013).

Parameter	Digestate (solid phase)	Biochar from digestate
Water content (g kg^{-1})	85	53 ↓
Volatile substances (g kg^{-1} d.m.)	697	226 ↓
Black carbon (g kg^{-1} d.m.)	81	262 ↑
Ash (g kg^{-1} d.m.)	222	512 ↑
N (g kg^{-1} d.m.)	45	38 ↓
C (g kg^{-1} d.m.)	452	338 ↓
H (g kg^{-1} d.m.)	51	10 ↓
O (g kg^{-1} d.m.)	219	-
H/C mole ratio	1.37	0.34 ↓
HHV (MJ kg^{-1})	19.1	11.3 ↓

Parameters affecting the stability of biochar

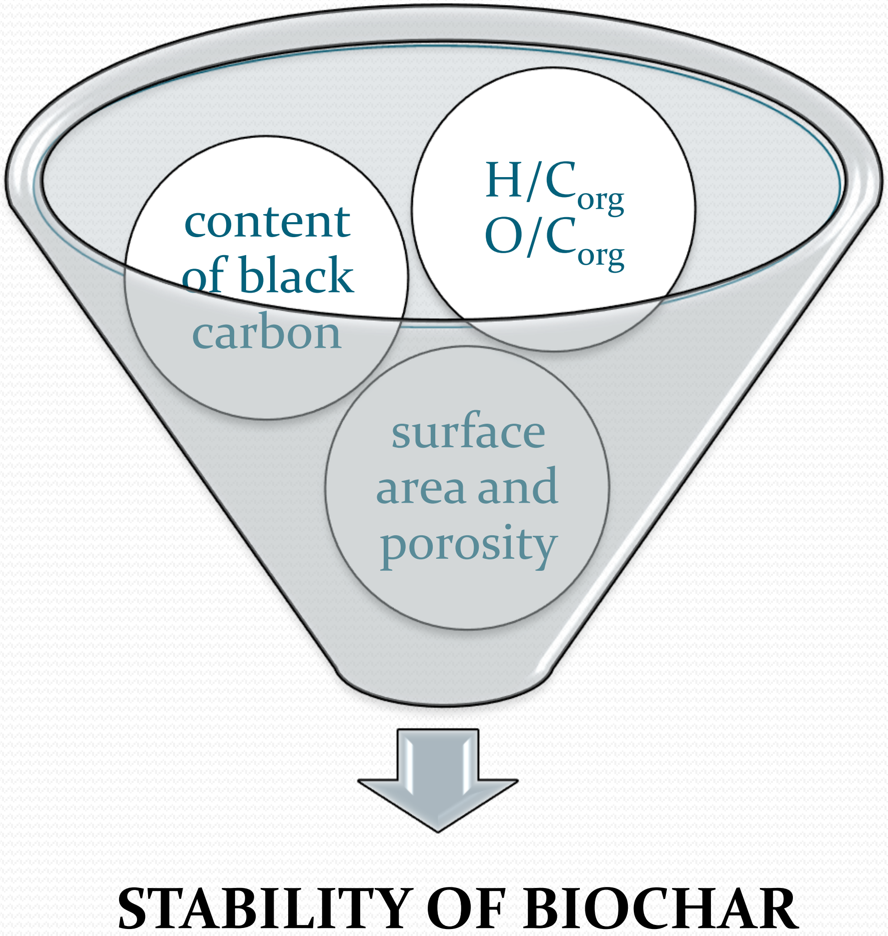


Fig.3 . Parameters affecting the stability of biochar

Content of *black carbon*

- Is fundamental to biocarbon's stability in the soil environment, thus being essential to the process of carbon sequestration in soil (Bai et al., 2014; Spokas, 2010).
- Recalcitrant C stability of its structured, mainly formed by aromatic and heterocyclic C (Wei et al., 2014).
- According to the guidelines of the *European Biochar Certificate* (EBC, 2012), the content of the above fraction should be at least 10% of the total organic carbon.

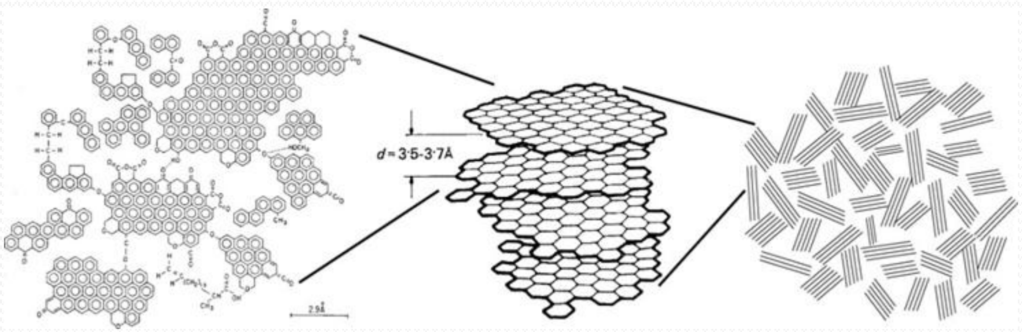


Fig.5 Model for biochar structure being important for environmental properties (Fisher and Glaser, 2012)

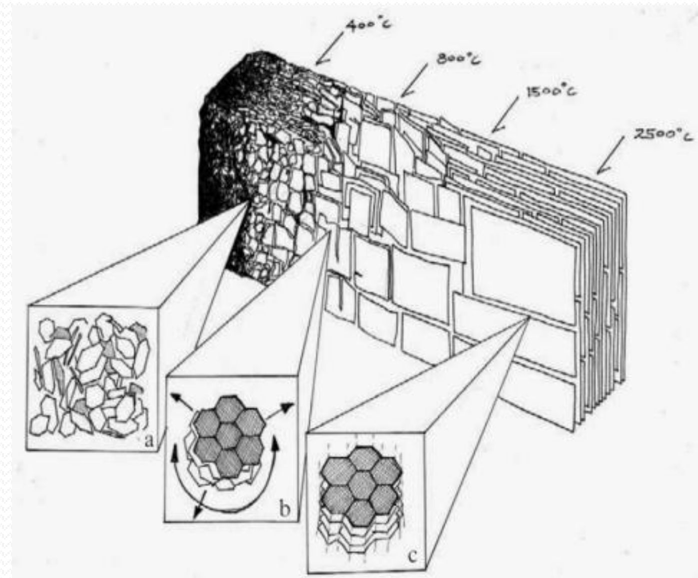


Fig.6 The effect of temperature on the structure of biochar (Lehman and Joseph, 2009)

H/C and O/C molar ratio

- The H/C_{org} mole ratio, which is an indicator of the degree of aromatization, and therefore the stability of biochar, should be less than 0.7;

- The O/C_{org} mole ratio, as an indicator of the degree of carbonization, should be less than 0.4 (EBC, 2012; Fisher and Glaser, 2012; Jinig et al., 2014; Schimmelpfening and Glaser, 2012).

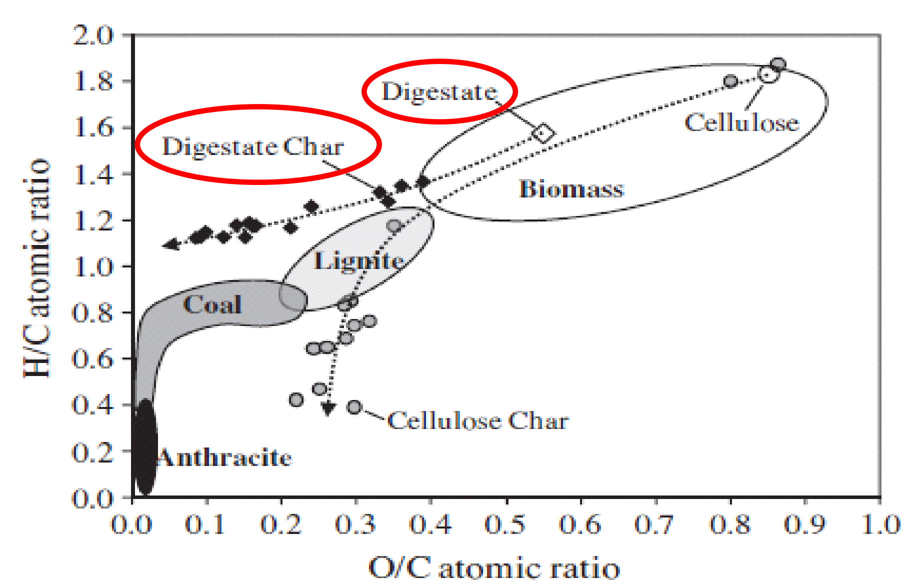


Fig.7. Van Krevelen's diagram illustrating changes in the O/C and H/C atomic ratios in biomass during thermochemical conversion (Mumme et al., 2011).

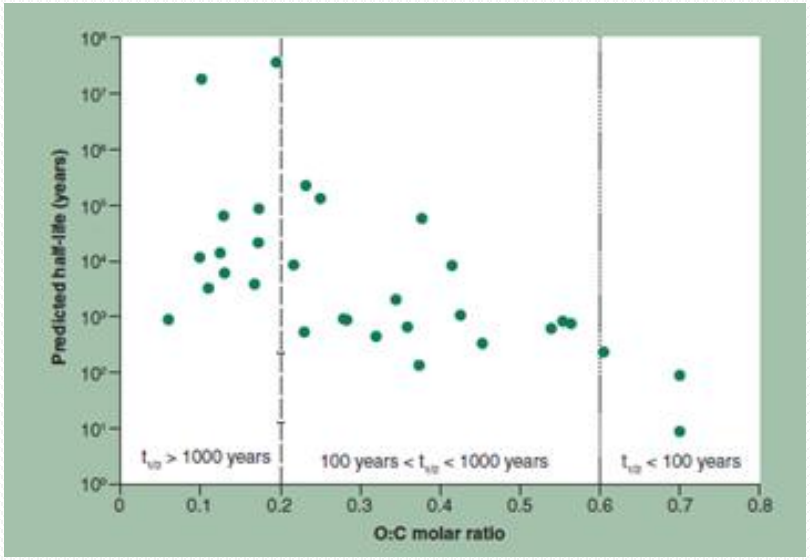


Fig. 8. Correlation of the oxygen to carbon ratio (O:C) molar ratio and predicted half-life of synthetic biochar in various incubations (Spokas, 2010).

The surface area and porosity

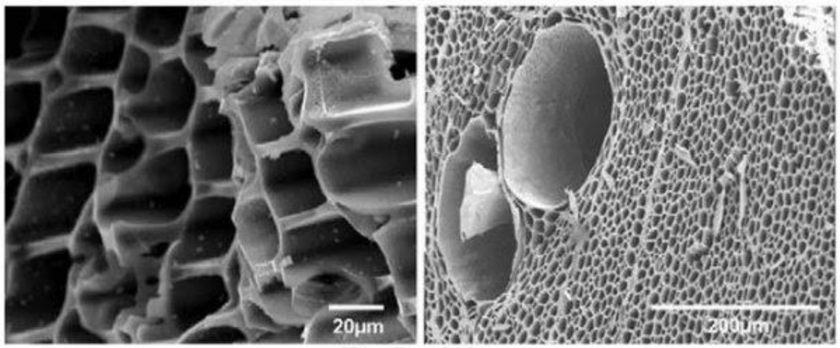


Fig. 9. The porous structure of biochar (Lehman and Joseph, 2009).

Table 3. Average particle size of the biochars detetrmined by microscopy (Bruun et al. 2011).

	Biochar 475 °C	Biochar 500 °C	Biochar 525 °C	Biochar 550 °C	Biochar 575 °C
Average size (µm ± SE)	71 ± 6	50 ± 5	23 ± 1	12 ± 1	12 ± 1
Min–max size	19–490	11–223	3–101	2–56	2–60

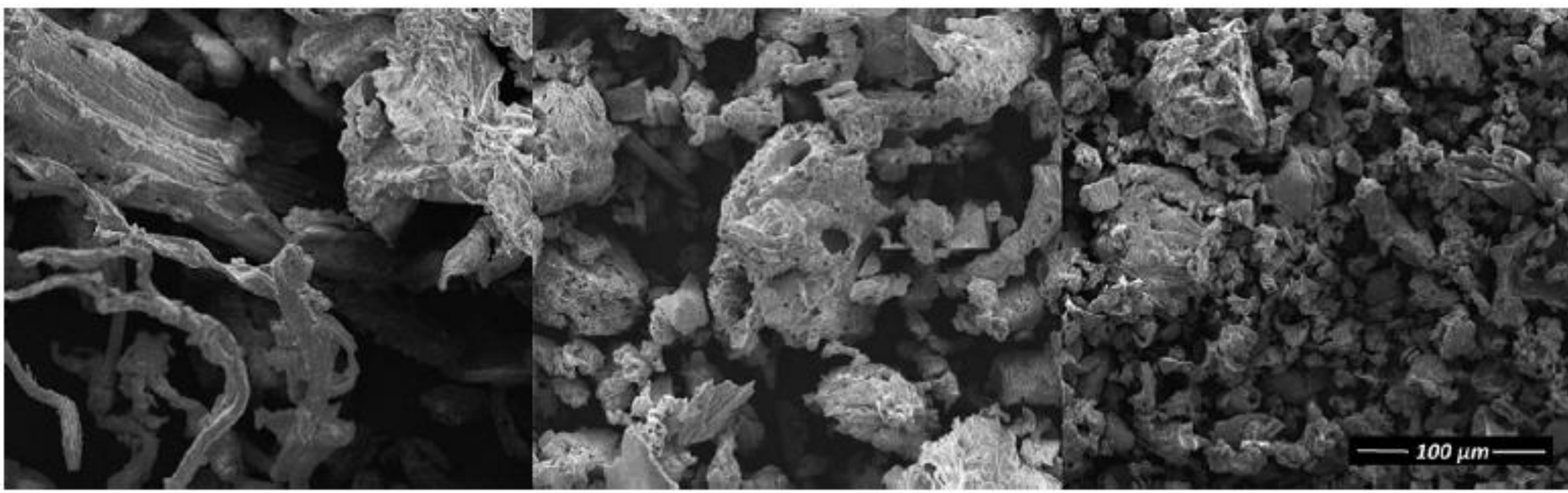
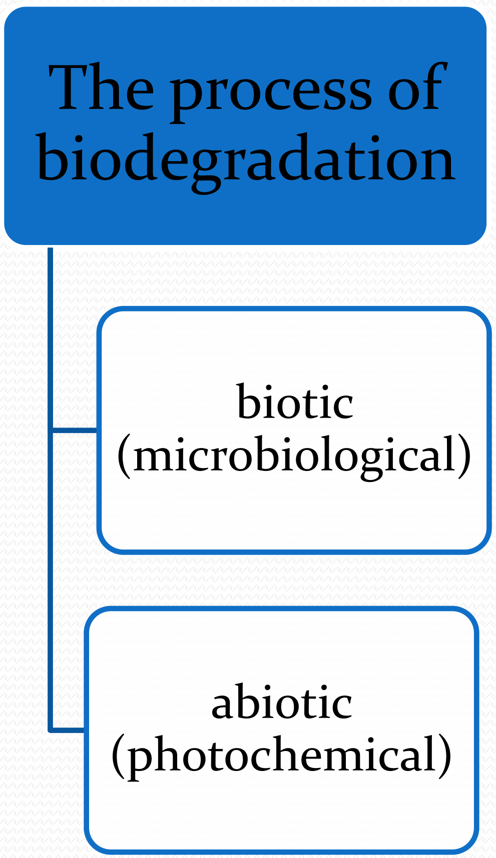


Fig.10. Scanning Electron Misroscope (SEM) images of biochar particles taken at the same magnification. Left ro right: biochar made at 475°C, 525°C and 575°C respectively (Bruun et al. 2011).

Biodegradation as a process of organic matter decomposition



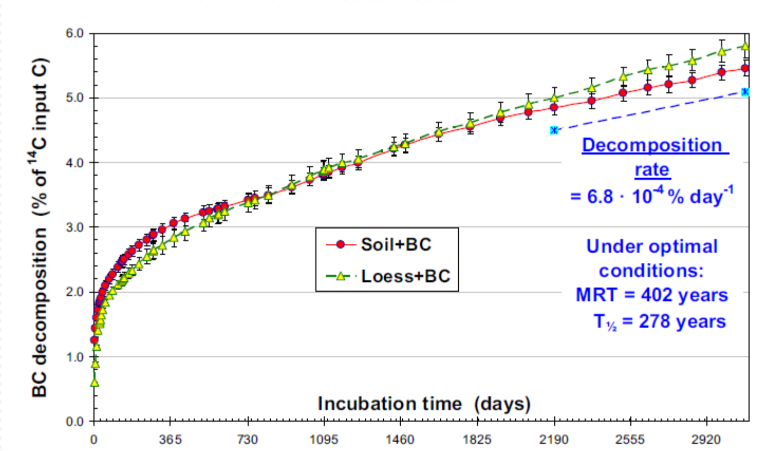
- The relative share of biotic and abiotic processes in the decomposition of biochar, may depend on:
  - the properties of the soil environment (moisture, temperature),
  - the physical and chemical features of the decomposed biochar (Bruun et al. 2011, Sigua et al. 2014).

Abiotic process

- Abiotic process play a more important role in the first stage of organic matter decomposition (Cheng et al., 2006, Bruun et al., 2011).
- Level of CO_2 emission was twice as high when non-sterilized carbon rather than sterilized one was degraded (Zimmerman, 2010).
- According to changes in the composition of a microbial consortium responsible for the process of biodegradation can affect the cycling of nutrients, growth of plants and the cycling of soil organic matter, by stimulating the rate of mineralization of native carbon in soil (Jining et al., 2014).

The rate of biodegradation of biochar

a)



b)

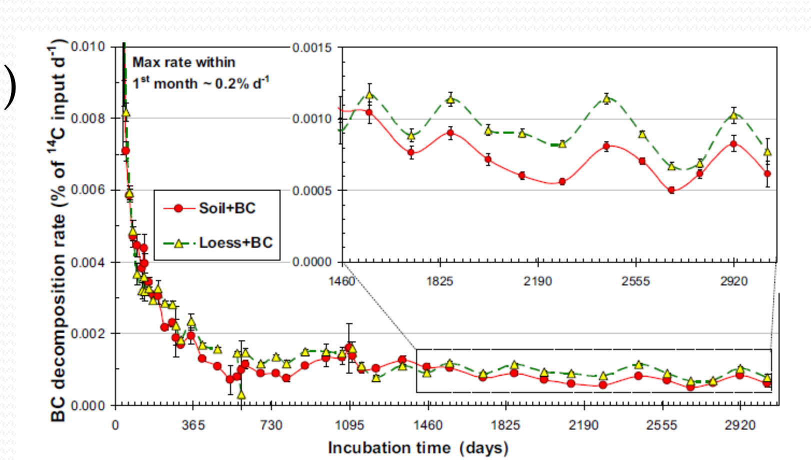


Fig.11. Biochar (BC) mineralization in soil and loess during 8.5 years analyzed based on $^{14}CO_2$ efflux; a) cumulative $^{14}CO_2$, b) biochar mineralization rate (Kuzyakow et al., 2014).

- Less than 6% of the ^{14}C added as biochar were released as $^{14}CO_2$ during 8.5 years, and most of it was released during the first 2 years (Fig.11 a) (Kuzyakow et al., 2014).
- After one year, the biochar mineralization decreased by more than one order of magnitude and amounted to 1.2 x 10^{-3} and 1.6 x 10^{-3} % d^{-1} for soil and loess, respectively (Kuzyakow et al., 2014).
- After five years, the biochar decomposition rate was about 1.4 x 10^{-3} % d^{-1} , and after 8,5 years, was 0.7 x 10^{-3} % d^{-1}(Kuzyakow et al., 2014).

The rate of biodegradation of biochar

- 3-12% of the added biochar was emitted in the form of CO_2 during during 115 days of soil incubation, with 90% of CO_2 loss occurring in the first 20 days of the experiment (Brunn et al., 2011).

- After 115 days of incubation, the cumulative emissions ranged progressively from 11,9 % C loss for the 475 °C treatment, down to 3,1% loss for the 575 °C (Brunn et al., 2011).

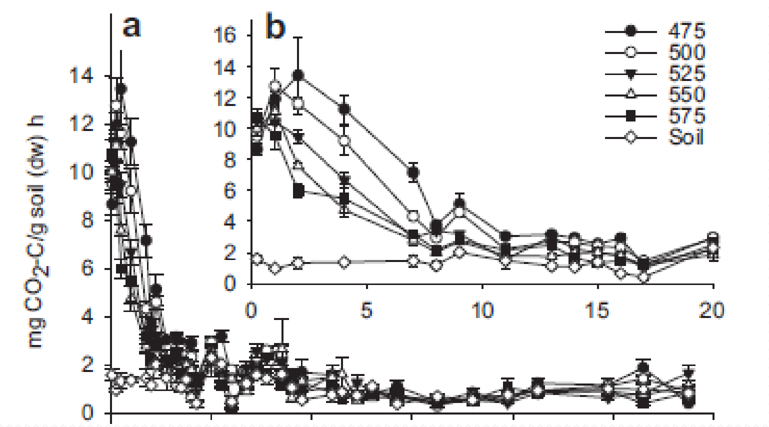


Fig. 12. Measured soil surface CO2-fluxes after incorporation of 40 g soil with biochar produced at 474°C, 500°C, 525°C, 550°C and 575°C, respectively, and no amendment (Bruun et a., 2011).

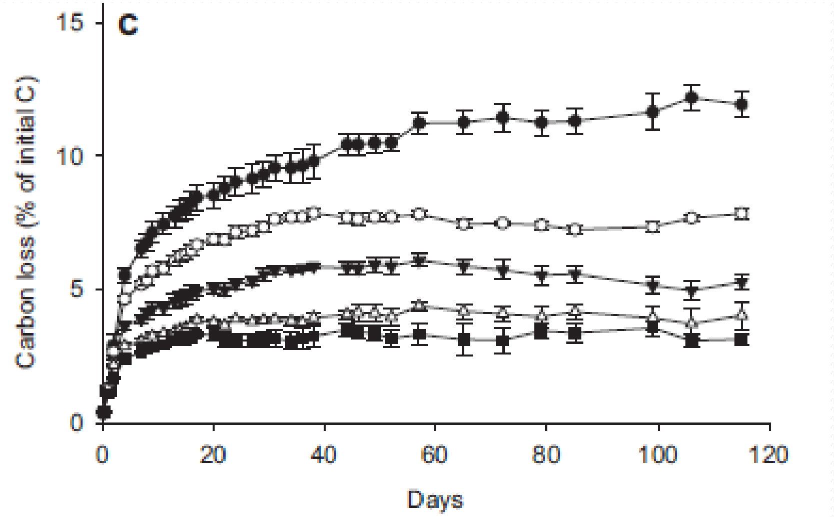


Fig.13. Cumulative biochar decomposition measured as net biochar-C emitted in proportion to biochar-C added (Bruun et al., 2011).

Indicators of the biochar stability in soil

- We lack sufficient in-depth data to understand the global distribution of black carbon (BC) in soil, and to monitor the cycling of recalcitrant carbon in the environment (Bornemann et al., 2008; Bruun et al., 2011).

- According to the *European Biochar Certificate* (EBC, 2012), the content of the black carbon fraction, analyzed by the
  - BPCA (*Benzen Polycarboxylic Acids*) method to mark polycondensed structures (Glaser et al., 1998, modified by Brodowski et al., 2005).
  - FTIR spectroscopic techniques (Bornemann et al., 2008).

Mean residence time (MRT)

Tab.4. The Mean Residence Time of different biochars (Budai et al., 2013).

Publication	Scale of estimated MRT (years)
Masiello andDruffel, 1998	Millennial (2,400 – 13,900)
Schmidt et al., 2002	Millennial (1,160 – 5,040)
Cheng et al., 2006	Millennial (1,000)
Laird et al., 2008	Millennial (1,000's)
Cheng et al., 2008	Millennial (1,335)
Kuzyakov et al., 2009	Millennial (2,000)
Major et al., 2010	Millennial (3,264)
Novak et al., 2010	Millennial (1,400-51,000)
Liang et al., 2008	Centennial to millennial (100-10,000's)
Zimmerman, 2010	Centennial to millennial (100-10,000)
Baldock and Smernik, 2002	Centennial (100-500)
Lehmann et al., 2006	Centennial (100's- 1,000's)
Hammes et al., 2008	Centennial (200 -600)

- Changes in the content of biochar are usually very small, which means they are difficult to capture during experiments lasting from a few months to a few years (Kuzyakow et al., 2014).
- Measurements of the decomposition rate and MRT under laboratory conditions are not fully reliable with respect to the actual MRT in soil because of the excessively large share of organic matter and plant residue in soil in the process of mineralization of black carbon to CO_2 (Kuzyakow et al., 2014).

Sequestration of carbon in soil

Organic carbon in soil:

1) ‘active’ or easily degradable carbon,

2) carbon undergoing slow degradation,

3) ‘passive’ carbon (Favoino and Hogg, 2008; Hermann, 2010).

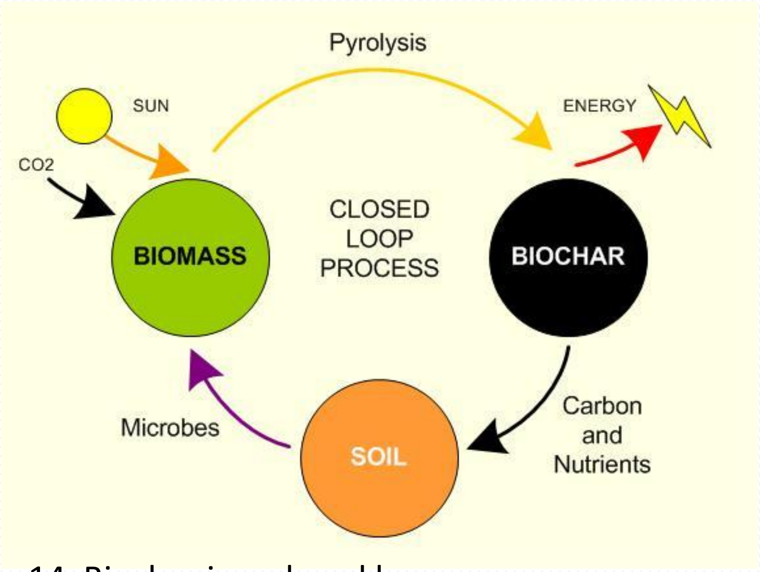


Fig.14. Biochar in a closed loop process.
(http://www.phlush.org/ecological-sanitation/terra-preta/biochar-basics/)

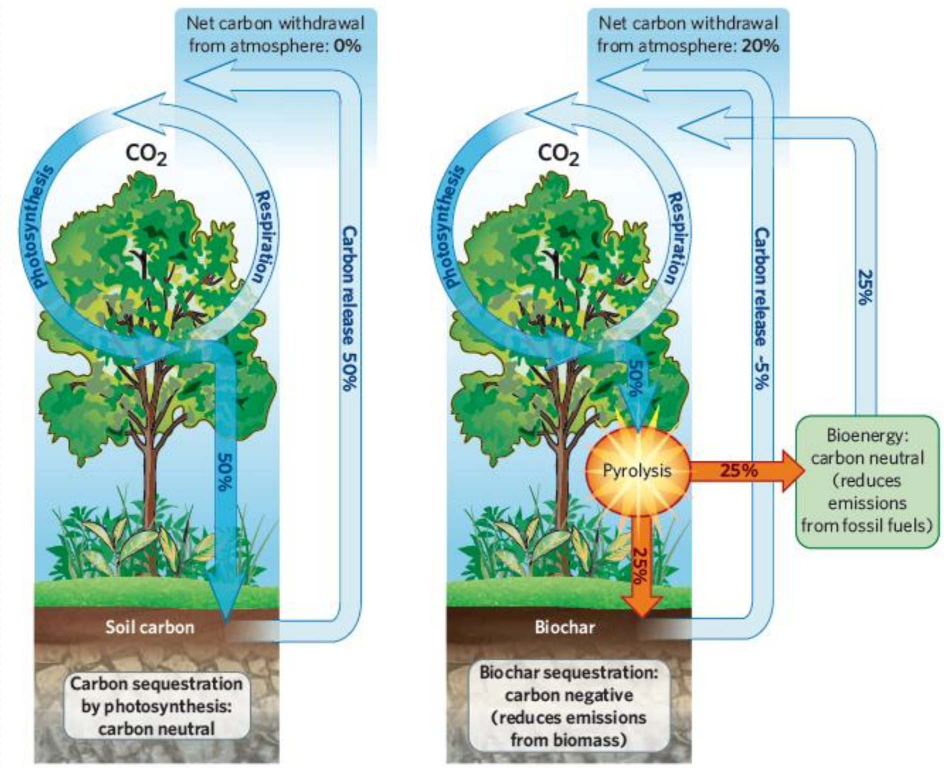


Fig.15. Diagram of biochar sequestration process (Lehman et al., 2006).

Summary

- Digestate is a valuable source of organic matter, which can be added to soil in the form of biochar, where it improves the soil's fertility and contributes to the sequestration of carbon.
- The properties of biochar which determine its stability are: the share of the black carbon fraction and the H/C_{org} oraz O/C_{org} mole ratios.
- It has been underlined that at present we lack sufficient data to be able to fully comprehend the global distribution of black carbon in soil and to monitor its cycling in the environment.
- A review of references has demonstrated that biochar used as a soil amendment has a positive effect on the functions of soil and on the whole natural environment

Biochar: research area in the framework of the doctoral thesis

- It will be studied the biodegradation of organic matter in soils under cultivation of energy crops *Miscanthus x giganteus* and *Sida hermaphrodita* fertilized by various forms of digestate (incl. biochar) derived from agricultural biogas plant.
- In the studies it will be evaluated the biodegradability of various biofertilizers made of digestate in soils and the impact to improvement of soil fertility.
- The biodegradability/bioavailability of soil organic matter will be analyzed using a variety of methods:
  - chemical fractionation, incl. DOM fraction (dissolved organic matter) by sequential cold- and hot-water extraction,
  - biological fractionation, incl.
    - 100-d bioassay for mineralizable C method to estimate the quantities of labile SOM,
    - analysis of bacterial community structure assessed by denaturing gradient gel electrophoresis (PCR- DGGE) (universal bacterial 16S rRNA gene primers PRBa338F and PRUN18R),
    - the respirometric activity

Thank you for your attention!

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