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Issue: September 2015 - Biochar Analytical Newsletter

In This Issue

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REFERTIL in Brief

The REFERTIL project is providing advanced solutions to the added value transformation of the organic biowaste streams from Europe's agriculture and food industries. The targeted **high quality output biochar products** aiming to reduce the use of mineral fertilizers and intensive chemicals in agriculture; enhancing the environmental, ecological and economical sustainability of food crop production. Furthermore reducing the negative footprint of the cities and overall contributing to climate change mitigation, while creating new bioeconomy.

When biochar is irrevocably applied to open and complex soil ecological system, only qualified and safe biochar must be used. Accredited chemical analysis is the only official way to verify the required quality of the product and to maintain high level of quality assurance of processing.

Carbon products; manufactured, imported, applied and placed on the market above 1 t/year capacity; are not classified as biochar product in cases when (1)does not have the mandatory EU/MS/REACH permits for biochar production, product and agricultural applications; (3) does not have Extended Producer Responsibility guarantees; (4)charcoal for energetic applications and/or containing labile carbon.

The input material characteristics and the quality of engineering design performance of the pyrolysis technology with specific process conditions together are the two major critical elements affecting the characteristics, quality and safety of the final carbon product.

The input material characteristics and specific process conditions are individual fingerprints for specific biochar products. An improved and "biochar product specific" pyrolysis industrial design with new generation zero emission reductive thermal treatment processing system, the "3R" technology (Recycle-Reduce-Reuse), has been developed by Edward Someus for high grade and safe biochar production.

What is biochar?

Biochar is plant or animal biomass by-product based stabile carboniferous substance for EU/MS/REACH Authority permitted agricultural applications. Plant BioChar "PBC" is soil improver and produced from agricultural, forest and food industrial by-products, while Animal Bone bioChar "ABC" is organic P fertilizer and made of food grade animal bone meal. There is no one fit for all biochar solution and/or product. However, in all biochar cases above 1 ton/year capacities in the EU, the biochar must meet high safety standards, Extended Producer Responsibility and all the mandatory EU/MS/REACH permits for biochar production, product quality, agricultural applications and placing on the market.

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Accredited biochar analysis at Wessling Hungary Ltd.

The appearance of the ABC and PBC are very similar, although their composition is greatly different. PCB is stabile carbon content plant origin micro- and meso porous material while ABC is high calcium phosphate apatite mineral and low carbon content macroporous material. However, same analytical test methods are suitable for both. In the REFERTIL project, WESSLING Hungary Ltd. is responsible for detailed and accredited analytical characterization of ABC, PBC and all sample streams.

To determine quality & safety performance of biochar, internationally accredited methods and standards are needed. Accreditation of the analytical activities related to the REFERTIL project is an important step to be able to support the research work related to the project with analysis that have a **recognized quality management background**, in addition to the proper professionalism. It is also an important step to **support the legal standardization and mandatory permit process of biochar industrial production**, product application and commercialisation, including producers extended responsibility and liability legal issues for the product.

Most of the standards selected for biochar qualification were chosen from among currently valid CEN/ISO standards. As biochar is a new product, for a number of parameters it was necessary to adopt soil or waste analytical methods, which were validated to assess their analytical performance. Validation methods were developed to check the suitability of not entirely standard methods to be used in laboratory practice. The accreditation procedure was initiated at NAT (National Accreditation Body) after almost two years of continuous work. During this period, WESSLING gained significant experience in this analytical area and maintained the external and internal quality assurance activities as well. **The Environmental Testing Laboratory of WESSLING is the first laboratory in Europe who obtained accredited status, under Wessling-NAT-1-1398/2012 (2014.10.08) for comprehensive analyses of biochar samples.**

According to the mutual recognition agreements[1;2], activities of NAT and organizations accredited by NAT are **recognized internationally** by all other signatories. **According to Regulation EC 765/2008, authorities of the member states of the European Union are obligated to accept the results of organizations accredited by NAT.**

[1] Multilateral Agreement of the European Cooperation for Accreditation (EA MLA) in the areas of analysis, calibration, control, product certification, management system certification and person certification.

[2] Mutual Recognition Arrangement of the International Laboratory Accreditation Cooperation (ILAC MRA) in the areas of analysis and calibration.

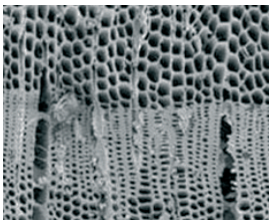
Biochar benefits in soil

Animal Bone bioChar (ABC)
Organic Phosphorus fertiliser, soil improver, growing media

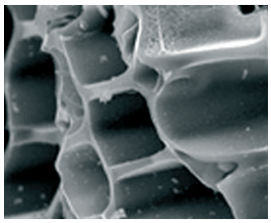
- Made from food grade category 3 bones.
- 90% mineral content and 10% Carbon.
- 30% P_2O_5 and 38 – 42 % CaO + Mg, K.
- Controlled release direct organic fertiliser with different formulation options.
- **Dose: 0.1t/ha - <1 t/ha.**

Plant based biochar (PBC)
Soil improver, growing media

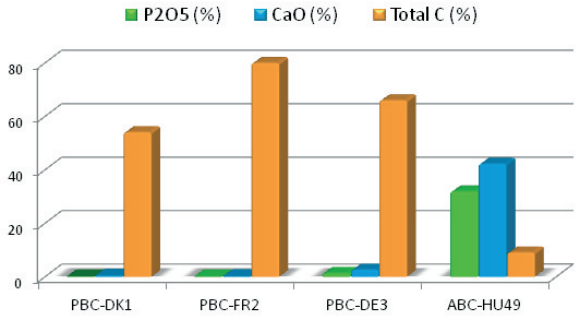
- Made from plant based biomass materials.
- > 90% stabile carbon content.
- High water holding and nutrient retention capacity.
- Neglible P and Ca content - no direct soil fertilization effect with economical value.
- **Dose: 3t/ha - 20 t/ha.**



PBC: micro-mesoporous 1-50 nm



ABC: mactroporous 50-63,000 nm



Nutrient content of different biochars: PBC and ABC

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RISK OF BIOCHAR USE - Organic pollutants: PAHs

What are PAHs ?

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbons many of which are known or suspected carcinogens and their concentrations in the environment are thus of interest. PAHs are toxic, persistent in soil environment and having potential for subsurface water contamination, so it is very important to use only certified, low PAHs concentration biochar in agriculture. Moreover PAHs are included in the list of priority substances. Directive 2008/105/EC listing PAHs as priority hazardous substance.

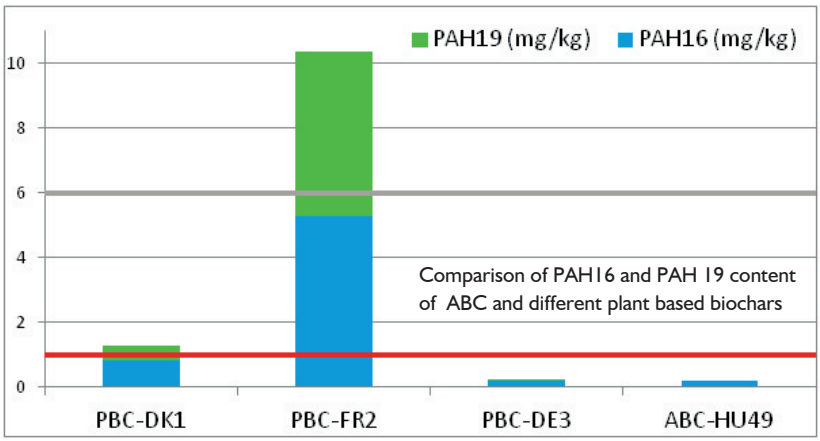
The occurrence of PAHs in biochar primarily derive from obsolete, low grade and inefficient pyrolysis condition, but in the plant based biochar cases also from contaminated and/or improper selected feed stocks as well. The plant biochar material may contribute high levels of PAHs to soil when the total PAHs concentration in the biochar product is high and/or when high application doses are applied to achieve the desired effect requirements.

PAHs can be considered as the key organic pollutants and an indicator of biochar product quality.

Methods for analysis

There are several type of PAHs depending on the number of connecting benzene rings. To get information about specific PAHs represented in biochar, not only 16 priority PAHs (based on US EPA offer) were measured but the 19 most common components.

The **concentration of PAHs in biochar was determined according to CEN/TS 16181:2013 standard with a gas chromathography-mass spectrometry method** after carbon disulfide extraction. The use of carbon disulfide during sample preparation was selected and proved by WESSLING instead of the more traditional hexane, petroleum ether or toluene, because suitable recovery can be achieved even without time-consuming Soxhlet extraction, even in the case of PAHs components with high boiling points.



Rational for stricter limit values

PAH content of biochar is primarily depending on the carbonisation processing technology performance design quality that is defining the processing conditions. Within the REFERTIL project more than one hundred biochar samples, both PBC and ABC, has been investigated. Both REFERTIL produced biochar samples and samples from several EU producers has been investigated. The results clearly justified that all the high quality biochars contained less than 1 mg/kg PAH_{16}. In this context, it has been demonstrated that the advanced thermodynamics of the modern and high quality engineering designed pyrolysis process performance do not support formation of PAHs and dioxins. During REFERTIL project in the Fertiliser Regulation EC 2003/2003 revision supporting document PAH_{16} maximum allowable limit value was defined as 6 mg/kg, but for environmentally justified reasons Member States can describe more strict rules. **As an example the national regulation in Hungary (36/2006 (V.18.) FVM decree) requires PAH_{19} content under 1 mg/kg for soil improvers.**

During the limit value definition it is very important to define how many components are under PAHs. The PAH_{19} concentration can be twice as much as PAH_{16}, because 1- and 2-methylnaphthalenes (measured only under PAH_{19}) are dominant beyond the typical PAH_{16} components in biochar: mostly naphthalene and phenanthere, but in some ABC samples anthracene and phenanthrene are also present. Polycyclic aromatic hydrocarbons can be considered as the key organic pollutants and an indicator of biochar products quality.

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RISK OF BIOCHAR USE - Organic pollutants: PCBs and PCDDs/PCDFs

In **no any cases have Polychlorinated dibenzodioxins (PCDDs) and Polychlorinated dibenzofurans PCDFs been identified as target contamination** as these compounds are predominantly formed at temperatures exceeding 1000°C while the the feed material streams having low chlorine content. Therefore, the risk of dioxins and furans contamination in biochar products is low.

PCB_7 were not detected in the investigated more than one hundred biochar samples (produced in the REFERTIL material treatability test and received industrial reference biochar samples) derived from traditional biomass feedstocks (agri residues, woody biomass, food industrial by-products) and animal and category 3 by-products.

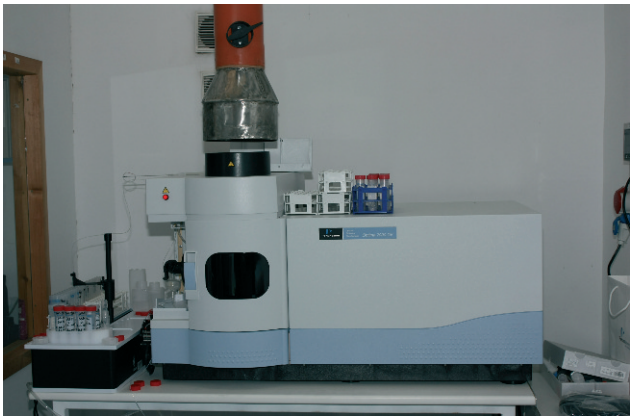
Potentially toxic elements

Certain Potentially Toxic Elements (PTEs) such as Mercury, Cadmium, Nickel, and Lead are included in the list of priority substances. Directive 2008/105/EC **listing Cadmium and Mercury are identified as priority hazardous substance.**
Measuring PTEs (metals) in biochars is very important, because of the 3x – 5x re-concentration tendency during phase separated processing. This results much higher PTE concentration in solid output products than in original input average. **The higher the organic matter content in feedstock, the less the yield of biochar, thus PTE high accumulation occurs especially in PBCs.** The rate of enrichment is depending on the concentration of the given elements in the feedstock stream and on the yield of biochar reached with the given pyrolysis condition. The PTE concentration in the biomass feedstock often determines biochar's safe application rate. All the ABCs and high quality PBCs made from by-products were well below a strict member state regulations and REFERTIL recommended biochar quality and safety parameters.
In the case of pyrolysis of waste material streams with high and/or variating PTE input concentrations there is a high risk that PTEs in final biochar products may reach the recommended safety criteria limits that does not meet the permitted limits and EPR specifications.
Therefore the **concentration of PTEs in input material should be regularly monitored.** Several organic waste streams are known to generally contain high levels of light and heavy metals, which remain and concentrated in the final biochar product following pyrolysis.

PTE content of plant based biochar and ABC

PTE	REFERTIL proposal	MS regulation (Hungary)[1]	PBC-DK1	PBC-FR2	PBC-DE3	ABC-HU49
As	10	10	<1	<1	1	<1
Cd	1,5	2	<0,3	<0,3	0,4	<0,3
Cr	100	100	6	9	15	<1
Cu	200	100	3	9	49	8
Pb	120	100	1	8	14	<1
Hg	1	1	<0,02	0,04	<1	<0,03
Ni	50	50	3	13	14	<1
Zn	600	600	19	150	294	203
Co	-	50	<1	1	3	<1
Se	-	5	<0,3	<0,3	0,5	<0,3

[1](36/2006 (V.18.) FVM decree



Detection of PTEs with ICP-OES

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