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Food safety importance of biophosphate applications in safe food crop productions

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1. Summary

Disrupted nutrient recycling is a problem for Europe and all over the world. Phosphorus and nitrogen, instead of being used for plant nutrition, are lost across environmental media during food production or are wasted. Regarding phosphate fertilisers, the European Union (EU) is currently highly dependent on import of phosphate rock mined outside of the EU. There is no any possibility to substitute Phosphorus in agricultural food crop and animal productions. Therefore, phosphorous recovery and recycling is one of the key priorities of sustainable agricultural systems in the EU and worldwide as well.

The "3R" Recycle-Reduce-Reuse zero emission pyrolysis technology and carbon refinery is specifically designed for the high added value recycling and recovery of BIO-PHOSPHATE, BIO-NPK-C nutrients and bio-materials with different carbon structures, which refined carbon and mineral products can safely be applied in the organic/low input agriculture and adsorber industries.

Animal Bone bioChar "ABC" is a recovered organic phosphorus fertiliser, made from food grade animal bone grist, having high nutrient density (30% P2O5) and pure P-content. The rendering industrial origin food grade category 3 animal bone grist processed ABC is a macro-porous organic fertilizer with as high as 92% pure calcium phosphate and only 8% carbon content. ABC in all agricultural application cases is BIO-NPK-C formulation optimised, enhancing of soil microbiological life, having high water holding and macromolecular organic nutrient retention. The fully safe ABC is used at low doses (100–600 kg/ha) and in cases when justified even up to 1,000 kg/ha.

Therefore the ABC product functionalities are organic fertilizer, soil improver, growing medium and/or fertilising product blend. The substitution of phosphate import by recovered phosphorus is an important goal for the European agriculture already in short term, for which 3R technology processed ABC has over 20% continuous substitution potential in the EU28 before 2030.

2. Introduction

Phosphorus and nitrogen are lost across environmental media during food production or are wasted instead of being used for plant nutrition **[10]**. Reserves of the phosphate rock used to make such fertilizers are finite, and concerns have been raised that they are in danger of exhaustion. For long term global food security the sustainable supply of phosphorus is a key resource for soil fertilisation that cannot be substituted **[7]**. One of the main fertiliser constituents is phosphate rock, which has been identified by the Commission in 2014 as a critical raw material.

The estimated yearly consumption of manufactured phosphorus mineral fertilisers in EU 27 (2014) was

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1.11 Mt P based on data provided by Fertiliser Europe **[12]**. This is the equivalent of **2.55 Mt/year mineral Phosphorus fertiliser expressed in P_2O_5**.

For phosphate fertilisers, the EU is currently highly dependent on import of phosphate rock mined outside of the EU (more than 90% of the phosphate fertilisers used in the EU are imported, mainly from Morocco, Tunisia and Russia) **[9]**. Concerns have been raised that these might be contaminated with cadmium, uranium, thorium and other inorganic contaminants. Concentration of phosphorus mines outside the EU makes the EU fertilising product industry and the European society dependent on imports and vulnerable, due to high prices of raw materials as well as the political situation in supplying countries **[10]**. Therefore, phosphorous recycling is one of the key priorities of the sustainable agricultural systems. Trends and developments on the global phosphate rock market are putting the EU's security of supply of phosphate rock under increasing pressure **[18]**.

The environmental, economic and social implications of food waste are of increasing public concern worldwide **[8]**. In the EU alone, we waste 90 million tonnes of food every year (180 kg per person) **[7]**.

The cattle, fish and poultry industries are the largest source of animal food industry waste **[16]**. Animal-derived food waste contains rather high amounts of protein and cannot be discharged into the environment without proper treatment **[16]**. According to the Eurostat databases more than 51 million tonnes of carcass weight animals (bovine, poultries and pigs) slaughtered in the EU 28 countries **[12]**. Approximately 49% of the live weight of cattle, 44% of the live weight of pigs, 37% of the live weight of broilers are materials not consumed by humans **[17]**. A proportion of each animal is not used for human consumption and rendering is the highest for bovine animals (42%) followed by pig (34%) and poultry (25%) **[5]**. The European rendering industry (35 EFPRA members, 26 EU countries) processed more than 17 million tons raw materials in 2014 from which the category 3 processed products are 12 million tons. EFPRA members processing the majority of the total animal by-products in the EU and additionally, significant amount of material streams produced by non-member organizations **[6]**.

The skeletal system can be up to 20 percent of the carcass weight, which means that over 4 million tons of animal bone biomass produced in the EU annually. Animal bone by-product is characterized by very high phosphorus content compared to other animal waste. The phosphorus content of bone for bovine and poultry bone is about 10.5% on dry weight basis **[2]**; **[14]**. In comparison, the phosphorus content of liquid pig manure widely used in agriculture, with 2-10% dry matter content, is 0.20-1.25% while solid pig manure with 20-30% dry matter content has 1.6-5.08% P content **[1]**.

The conditions for access to the market of fertilising products are only partially harmonised at EU level. The fragmentation of the non-harmonised part of the market is seriously hindering trade opportunities **[5]**. Around 50% of the fertilisers currently on the market, however, are left out of the scope of the Regulation (EC) 2003/2003. This is true for a few inorganic fertilisers and for virtually all fertilisers produced from organic materials, such as animal or other agricultural by products, or recycled bio-waste from the food chain **[9]**.

Biochar is a solid material obtained from the carbonisation of biomass (animal bones or plant residues). Biochar may be added to soils to improve soil functions and soil fertility **[10]**. Biochar is distinguished from charcoal by the fact that biochar is produced with the prior intent to be applied to soil, be it as a means of improving soil productivity, soil fertility, carbon storage or a combination thereof **[19]**.

Since 1870, the age of technological revolution, and through the 21st century, carbon related technologies and products have been one of the most comprehensively researched sectors for energetic, steel industrial, activated carbon adsorbent, pharmaceutical, biotechnological and other wide range of applications. Biochar production is a 2,000 year-old practice to convert agricultural organics into a soil enhancer, and it was originally called Terra Preta "Amazonian dark earth" **[21]**.

However, in modern age the new environmental, climate protection and product safety aspects require new and advanced biochar production technology and quality management systems with significantly improved technology and product quality and safety performances to better protect the environment and human health. In this context the new 3R zero emission pyrolysis technology opens new technical, economical and environmental opportunities for advanced production and use of safe biochar.

Many Member States have detailed, national rules and standards in place for such non-harmonised fertilisers, with environmental requirements (such as potential toxic element (heavy metal) limits) that do not apply to EC-fertilisers (fertilisers of the European Communities) **[9]**. The agricultural use of soil improvers (such as plant based biochar), organic fertilizers (such as ABC Animal Bone bioChar) and other organic products have been regulated by EU Member States for a long time. However EU Member State regulations differ widely and significantly in each EU Member State, so the Mutual Recognition concept is difficult to be applied in practice. Therefore, the new EU Fertilizers Regulation revision under the Circular Economy incentive will soon, hopefully by 2018-2020 open full and EU wide law harmonization opportunity for many agricultural, food industrial by-products and organic material streams, including biochar and its formulated products as well.

The recent initiative on EU fertilising products [COM(2016) 157 final] is expected to create a level playing field for all fertilising products at EU level, thereby increasing the industry's opportunities to have access to the internal market while maintaining the national regulations in place for products limited to national markets, hence avoiding any market disruption **[11]**.

The occurrence of potentially toxic elements (PTEs) and contaminants in biochar may derive either from contaminated feedstocks or from pyrolysis conditions which favour their production [20]. When biochar is irrevocably applied to open and complex soil ecological system, there is also a direct interlink to subsurface water systems, therefore only qualified and safe biochar must be used. Currently there is lack of harmonized quality and safety standards at European level for biochar products. However, the complex and strict criteria for biochar safety and quality, functional application efficiency, environmental and food-safety, full legal conformity under open environmental and ecological conditions according to the European Union, Member States and REACH regulations are already unconditionally valid for all biochar products.

Improved and safe biochar products enhance the environmental, ecological and economical sustainability of the food crop production, while reducing the negative footprint and overall contributing to climate change mitigation. Terra Humana Ltd. has been science and technology coordinator and key technology designer for EU Commission priority supported biochar applied research projects since 2002, with prime specialization on ABC production industrial engineering and economical field applications. The core competence of Terra Humana Ltd. is pyrolysis, carbon refinery and biochar production for added value recycling and recovery of phosphorus and other valuable materials. In this context Hungary is the EU and international center for ABC science, technology and industrial engineering.

The last and recently closed EU project of the Terra Humana Ltd. is the REFERTIL (EU contract number 289785) **[22]**, with complex development works covering the fields from the applied biochar science into economical full scale industrialization and commercialization. The REFERTIL is a biochar policy support specific project since 2011 for conversion of biochar applied science into economical industrial practice, for which a comprehensive biochar law harmonization proposal has been submitted to the Commission. WESSLING Hungary Ltd. was the laboratory partner of the project investigating hundreds of samples (input materials and output products) to determine the quality and safety performance of these materials.

3. Materials and methods

The accredited analysis of the different samples has been done by Wessling Hungary Ltd. The REFERTIL methodology for accredited analysis is based on European Committee for Standardization - Project Committee - horizontal and Member State mutually recognized standards. If no horizontal methods are available, than well recognized and validated accredited methodologies have been used. The concentration of polycyclic aromatic hydrocarbons (PAHs) in biochar was determined according to CEN/TS 16181:2013 standard with a gas chromatography-mass spectrometry (GC-MS) method. GC-MS was also used to determine seven marker polychlorinated biphenyl compounds (PCB7*) according to EN 16167:2013 standard. Following a sample preparation based on EN 13650:2002, potentially toxic elements (PTEs) were analysed by inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) methods according to EPA Method 6020A:2007 and EPA Method 6010C:2007.

4. Results

The rendering industrial origin food grade category 3 animal bone grist processed ABC is a macroporous organic fertilizer with as high as 92% pure calcium phosphate and only 8% carbon content. ABC is NPK formulation optimized for significantly enhancing soil microbiological life, having high water holding and macromolecular organic nutrient retention. The fully safe ABC is used at low doses (100–600 kg/ha) and in cases when justified even up to 1,000 kg/ha. Animal Bone bioChar "ABC" is a recovered organic P-fertiliser, made from food grade animal bone grist, having high nutrient density (30% P_2O_5) and pure P-content. Therefore the ABC product functionalities are organic fertilizer, soil improver, growing medium and/or fertilising product blend. The substitution of phosphate import by recovered Phosphorus is an important goal for the European agriculture already in short term. The imported mineral phosphorus agricultural substitution potential by bio ABC in European dimension is >5% (>125,000 t/y P_2O_5) in short term (<2025) and continuously over >20% (>500,000 t/y P_2O_5) in long term (>2030).

Plant based biochar (PBC) is stabile and high carbon content plant origin micro- and meso porous carboniferous soil improver product, with relatively high water holding, nutrient retention and C-sequestration capacity, but – instead ABC – with no fertilizing effect that is having economic importance.

Most importantly, **the pyrolysis/carbonization processing technology design** quality and efficiency is the critically important **element that will be reflect-**

*PCB 28; PCB 52; PCB 101; PCB 118, PCB 153; PCB 138; PCB 180

ed as unique and recognized fingerprint in the output biochar product quality and safety performance characteristics. In this context, application of inferior biochar production technology will result in inferior biochar products with low quality/safety and low market value, if any at all. Another important factor is the input material characteristics that are also reflected into the output product performance.

The developed new generation "3R" Recycle-Reduce-Reuse pyrolysis is a zero emission thermo-chemical decomposition process. "3R" is highly efficient in carbonizing organic by-product streams of animal and/or plant origin in the absence of oxygen, and between material core temperature ranges from 450 °C up to 850 °C. The "3R" is original solution and specific industrial design for economical recycling, reuse and reduce of organic by-product streams for high added value conversion into refined carbon and mineral products with targeted application functionality and total safe character. It is important, that **there is no one fit for all biochar technology and product.** Different feedstocks for different applications require different pirolysis and formulation conditions.

The EU-funded REFERTIL FP7 project provided advanced applied science and industrial engineering developments to convert local organic by-product streams into safe biochar and compost products produced under market competitive, economical and EU/MS legalization industrial conditions. The REFERTIL project successfully developed, field tested, accredited laboratory evaluated and authority permitted industrial biochar production and safe products.

Several workshop meetings have been organized with EU Commission representatives in 2012-2016 for joint considerations and also a wide range of European biochar science and technology groups have been consulted for knowledge and experience exchange in this new and complex biochar case. The REFERTIL consortium reviewed the respective EU directives, regulations and also the relevant MS national legislations. We concluded that regulations on the use of biochar products are missing. The REFERTIIL biochar research and development on one hand provided EU policy support and, furthermore a proposal for the possible inclusion of the biochar case (as safe organic fertiliser and soil additive) into the EC Fertilizer Regulation No. 2003/2003 revision and law harmonization. As the current EC Fertilizer Regulation covering mineral fertilizers only, there is an ongoing review on it to adopt draft proposals to fully harmonise the market and extend it to mutually recognized fertilizers, including growing media, soil improvers, organic fertilizers, plant biostimulants, organo-mineral and other fertilizers. In this context, the REFERTIL biochar quality criteria are to meet the objectives of the future legislation.

Mandatory maximum level of contaminants was proposed, for which the key quality performance indicator for biochar processing condition and product quality together is the level of PAHs. These priority hazardous substances are toxic, bioaccumulative and persistent in environmental systems. During the project we proposed a maximum 6 mg/kg PAH16[#] ***(Table 1)*** with the possibility for Member States to apply stricter PAH limits, such as the 1 mg/kg PAH16 or PAH19[##] limit which is already applied in Member States since 2006. As an example, the Hungarian legislation is setting up criteria for 1 mg/kg PAH19 [13]. Biochar quality parameters proposed by the consortium is shown in ***Table 2***. ***Table 3*** represents allowable limits for biochar quality from the major biochar standardization groups.

4.1. PAH content of different plant based biochars and animal bone biochar

The production technology performance industrial design is one of the most important factors that is ultimately effecting biochar product quality, where the 1-6 mg/kg maximum allowable limit of PAH19 is a key performance indicator. Manufacturing and application of ABC Animal Bone bioChar organic Phosphorus fertilizer require a far higher technological level than plant based biochar soil improvers. Usually the analytical characteristics of the biochar product quality performance are the fingerprint of the pyrolysis/carbonization processing technology quality performance.

Within the REFERTIL project more than one hundred biochar samples, both PBC and ABC, have been investigated. the analysis were carried out in the Environmental Testing Laboratory of WESSLING Hungary Ltd. Both REFERTIL produced biochar samples and samples from several EU producers have been investigated. The results clearly justified that all the high quality biochars contained less than 1 mg/kg PAH16. 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.

Of the samples, received by the laboratory all together 41 animal bone biochars and 36 plant based biochars (from several countries/producers and different feedstocks) were investigated for PAHs. Of plant based biochars, 83% of the samples complied with the REFERTIL recommended 6 mg/kg PAH16 limit value. This ratio in ABCs is even higher: 88% (***Table 4***). All animal bone biochars have been submitted by the Terra Humana Ltd, as this is the only organization in the EU who is systematically developing advanced ABC technology and high end P recovered products.

With various biochar processing conditions it has been verified that the technology influences the quality of the product. Under appropriate treatment conditions, high quality biochars were made with low PAH content (<1 mg/kg PAH19) (***Figures 1; 2*** and ***Table 4***).

4.2. PCB content of different plant based biochars and animal bone biochars

PCBs were not detected in biochars, but high chlorine content of the input material was also not expected, as the animal by-products contain negligible concentration of chlorine. As in no any case have been dioxins indicated, we have concluded that due to PCBs and dioxins similar genesis and chemical structure PCB presence is a good and under any circumstances safe indicator of these persistent and bioaccumulative chemicals.

4.3. Potentially toxic elements (PTEs) content of different plant based biochar and Animal Bone bioChar

Certain potentially toxic elements (PTEs) such as mercury, cadmium, nickel and lead are included in the list of priority substances. moreover, in the listing of directive 2008/105/EC, cadmium and mercury are identified as priority hazardous substances. Measuring PTEs (metals) in biochars is very important, because of the 3–5 times re-concentration tendencies during phase separated processing (gas, oil and solid products). This results in much higher PTE concentrations in solid output products than the original input average (***Table 5***). 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 depends on the concentration of the given element in the feedstock stream and on the yield of biochar reached with the given pyrolysis condition. All the ABCs and high quality PBCs made from by-products were well below the strict member state regulations and REFERTIL recommended biochar quality and safety parameters (***Table 6***). Even if the biochar product meets PTE limits, the PTE concentration often determines biochar's safe application rate. Higher biochar doses, like 10-20 t/ha, resulting higher PTE impact per area.

5 Conclusions

The food safety significance of bio-phosphate applications in safe food crop productions is critically important. Disrupted nutrient recycling is a problem for Europe and all over the world. Phosphorus and nitrogen, instead of being used for plant nutrition, are lost across environmental media during food production or are wasted. For phosphate fertilisers, the EU is currently highly dependent on import of phosphate rock mined outside of the EU. There is no any possibility to substitute Phosphorus in agricultural food crop and animal productions. Animal Bone bioChar and generally the biochar case is expected to be included in the Fertilizer Regulation revision EU law harmonization, whereas the recent initiative on EU fertilising products [COM(2016) 157] will create a level playing field for all fertilising products at EU level, thereby increasing the industry's opportunities to have access to the internal market while maintaining the national regulations in place for products limited to national markets, hence avoiding any market disruption. The high nutrient dense Animal Bone bioChar, with product functionalities are organic fertilizer, soil improver, growing medium and/or fertilising product blend.

Based on our results it was concluded that biochars produced using the proper technological steps will contain low levels of contaminants, PAHs, dioxins, PCB congeners and toxic metals in particular and, therefore, they will be suitable for agricultural use, as well as for the mitigation of phosphorus scarcity expected in the European Union, in addition to maintaining environmental and food safety. Anaerobic thermal treatment of biowaste contributes to relieving one of the most challenging problems of the 21st century, making it possible to recycle part of the waste streams into industrial production processes.

Animal Bone bioChar is one of the few economical product options that can provide a safe and long term sustainable solution (even in organic farming systems), that is providing as high as over >20% mineral phosphate import continuous substitution potential in the EU28 before 2030.

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