sustainability

Article

Concentrated Phosphorus Recovery from Food Grade Animal Bones

Edward Someus [1,*] and Massimo Pugliese [2]

[1] Terra Humana Ltd., Biofarm Agri Research Station, Kajászó H-2472, Hungary
[2] Università Degli Studi di Torino, Agroinnova and DISAFA, Grugliasco (TO) 10095, Italy; massimo.pugliese@unito.it
* Correspondence: biochar@3ragrocarbon.com

Received: 5 April 2018; Accepted: 4 July 2018; Published: 6 July 2018

Abstract: Disrupted nutrient recycling is a significant problem for Europe, while phosphorus and nitrogen are wasted instead of being used for plant nutrition. Mineral phosphate is a critical raw material, which may contain environmentally hazardous elements such as cadmium and uranium. Therefore, phosphorus recovery from agricultural and food industrial by-product streams is a critically important key priority. Phosphorus recovery from food grade animal bone by-products have been researched since 2002 and a specific zero emission autothermal carbonization system, called 3R, has been developed in economical industrial scale, providing the animal bone char product (ABC) as output. Different animal bone by-products were tested under different conditions at 400 kg/h throughput capacity in the continuously operated 3R system. Different material core treatment temperatures (between >300 °C and <850 °C) were combined with different residence times under industrial productive processing conditions. It was demonstrated that material core treatment temperature <850 °C with 20 min residence time is necessary to achieve high quality ABC with useful agronomic value. The output ABC product has concentrated >30% phosphorus pentoxide (P_2O_5), making it a high quality innovative fertilizer.

Keywords: bio-phosphate; ABC Animal-Bone-Char; 3R pyrolysis; phosphorus recovery; animal by-products; apatite

1. Introduction

Disrupted nutrient recycling is a serious problem for Europe and all over the world. Phosphorus (P) and nitrogen (N) are lost across environmental media during food production or are wasted instead of being used for plant nutrition [1].

Phosphorus occurs in many minerals, of which apatite, $Ca_5(F,Cl,OH)(PO_4)_3$, is the most abundant and by far the most important group [2]. Apatite, a group of phosphate minerals, has two major natural forms with concentrated P-content: mined mineral phosphate and biological origin animal bones. The term of phosphate rock (PR) refers to rock containing phosphate minerals, usually apatite, which can be commercially exploited, either directly or after processing, for commercial applications [2]. Phosphate rocks of sedimentary origin typically have 30–35% phosphorus pentoxide (P_2O_5), whereas those of igneous origin contain marginally higher P_2O_5, typically 35–40% [3].

Phosphate rocks by their geological and mineralogical nature contain a host of environmentally hazardous chemical elements such as cadmium (Cd), uranium (U), lead (Pb), mercury (Hg) and arsenic (As), among others.

Superphosphate fertilizers are particularly abundant in these hazardous elements and they contaminate the agricultural soils when used as fertilizer [4].

U is an accompanying element of PR, particularly that of sedimentary origin. Depending on the geographical and biogenic origin, the uranium concentrations of PR may be as high as 150 mg kg^{-1} in sedimentary and 220 mg kg^{-1} in igneous PR [5]. In Germany, the use of P-fertilizer from 1951 to 2011 has resulted in a cumulative application of approximately 14,000 t of U on agricultural land, corresponding to an average cumulative loading of 1 kg U per hectare [6].

Reserves of PR used to make such fertilizers are finite, especially those ones with low Cd and U content, and concerns have been raised that they are in danger of exhaustion. Long term global food security requires the sustainable supply of P, a key resource for soil fertilization that cannot be substituted [7]. Phosphate rock, which is the main fertilizer constituent, has been identified by the European Commission (EC) as a critical raw material in 2014 and upgraded in 2017 [8].

The estimated yearly consumption of manufactured phosphorus mineral fertilizers in the European Union (EU) 27 member states (MS) was 1.11 Mt P in 2014 based on data provided by Fertiliser Europe [9]. This is equivalent with 2.55 Mt/year mineral phosphorus fertilizer expressed in phosphorus pentoxide (P_2O_5).

For phosphate fertilizers, the EU is currently almost entirely dependent on import of PR mined outside of the EU (more than 90% of the phosphate rock used in the EU are imported, mainly from Morocco, Tunisia and Russia) [10]. Concentration of phosphorus mines and gas fields outside the EU makes the EU fertilizing product industry and the European society dependent on, and vulnerable to, imports, high prices of raw materials and the political situation in supplying countries [1]. Therefore, P recycling is one of the key priorities of the sustainable agricultural systems. Trends and developments on the global PR market are putting the EU's security of supply of PR under increasing pressure [11].

The environmental, economic, and social implications of food waste are of increasing public concern worldwide [12]. The EU alone wastes 90 million tons of food every year or 180 kg per person. Much of this is food that is still suitable for human consumption [7]. Losses from food processing mainly originate from the slaughtering of animals and the subsequent removal of P-rich waste materials (e.g., animal bones) from the biogeochemical P cycles. This loss flow equals 294 kt P $year^{-1}$ [13]. The cattle, fish, and poultry industries are the largest sources of animal food industry waste [14]. Animal-derived food waste contains rather high amounts of protein and cannot be disposed into the environment without proper treatment [14].

According to the Eurostat databases, more than 51 million tons of carcass weight animals (bovine, poultries and pigs) are slaughtered every year in the EU 28 countries [9]. According to Meeker and Hamilton [15], approximately 49% of the live weight of cattle, 44% of the live weight of pigs, and 37% of the live weight of broilers are materials not consumed by humans. According to the European Fat Processors and Renderers Association (EFPRA), the proportion of each animal is not used for human consumption and rendered is the highest for bovine animals (42%), followed by pig (34%) and poultry (25%) [16]. The European rendering industry (35 EFPRA members, 26 EU countries) processed more than 17 million t of raw materials in 2014, from which the category 3 processed products were 12 million t. EFPRA members process the majority of the total animal by-products in the EU and additionally a significant amount of material streams is produced by non-member organizations [17]. The skeletal system can be up to 20% of the carcass weight, which mean that over 4 million tons of animal bone biomass re produced in the EU annually.

Biological apatite is an inorganic calcium phosphate salt. It is also a main inorganic component of biological hard tissues such as bones [18]. The majority of P (85–88%) exists as bone P in the body of vertebrates [19]. Animal bone by-product is characterized by very high P content compared to other animal waste. The P content of bovine and poultry bone is >10.5% on dry weight basis [20,21]. Other animal by-products have far lower phosphorus content than bone grist. For example, the phosphorus content of liquid pig manure, with 2–10% dry matter content, is 0.20–1.25% while the solid pig manure with 20–30% dry matter content has 1.6–5.08% P-content [22].

Since 1870, the age of technological revolution, and through the 21st century, the 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 applications. However, in the modern age, new environmental, climate protection and output product safety aspects require significantly improved and advanced pyrolysis technology performances to better protect the environment and human health. In this context, pyrolysis technology opens new technical, economic, environmental and legal opportunities for advanced production and use of safe Animal Bone Char (ABC) materials.

Pyrolysis (or carbonization process under true value reductive processing conditions) is the chemical decomposition of an organic substance by heating in the absence of oxygen. The process of pyrolysis transforms organic materials into three different components, i.e. solid, gas and liquid, in different proportions depending upon both the feedstock and the pyrolysis conditions used [23].

The key objective of the pyrolysis process is to produce different types of carbon products. The organic carbon content of the pyrolyzed chars fluctuates between 5% and 95% of the dry mass, dependent on the feedstock and process temperature used. For instance, the carbon (C) content of pyrolyzed beech wood is around 85% while that of poultry manure is around 25% and that of bone is less than 10% [24]. Different pyrolysis technology designs have highly variating quality performances to carbonize organic materials with different heat transfer efficiencies under reductive processing conditions, which is directly reflected in the remaining organic residual toxic content in the output char product, most importantly polycyclic aromatic hydrocarbons (PAHs).

Pyrolysis materials are different types of reductive processed stable carbon materials that are specifically made for different functional applications in designed quality, in which a chemically modified substance is produced from eligible input biomass materials via carbonization thermochemical treatment production process that fully meets the EU quality, safety, environmental and climate protection requirements. Biochar products are plant or animal bone biomass originating stable carbon pyrolysis materials with specific quality and safety parameters for explicit soil functional applications. The nutrient content of biochar mainly depends on the source: plant biochar is a high carbon composition soil improver with no or limited nutrient content, while ABC (Animal Bone Char) is a high phosphorus and calcium concentrated innovative organic fertilizer with high agronomic efficiency and low carbon content.

ABC is an innovative phosphorus natural fertilizer made of food grade (category 3) animal bones with concentrated >30% P_2O_5 content and specific quality for agronomical efficient organic and low input farming applications, also known as Bio-Phosphate.

Thus far, bone char has proven to be efficient in the remediation of heavy metal-contaminated soil and water [25,26] and to be suitable for agronomical applications. In previous studies, bone char (15% P, 28% Ca, 0.7% Mg) provided sufficient P and was also able to immobilize Cd in moderately contaminated soils [27]. Meat and bone meal biochar showed potential for soil amendment, as liming agent, and for the remediation of Pb in contaminated waters [28]. In highly Cd-contaminated soil with sufficient P supply, bone char could increase the yields of lettuce, wheat and potatoes, and at the same time decrease Cd contamination of potato [29]. ABC is also suitable as a carrier for microorganisms, mainly P-solubilizing, acting as plant beneficial and biocontrol agents [30,31]. However, these studies used lab-scale pyrolysis processes, while an industrial scale pyrolysis system processing all types of category 3 and category 2 animal bones and converting them into ABC has only been recently developed.

Directive 2008/105/EC [32] lists PAHs as identified priority hazardous substances and persistent organic pollutants which are generated from natural or anthropogenic processes, such as carbonization process. The occurrence of contaminants, such as polycyclic aromatic hydrocarbons (PAHs), Potential toxic elements (PTEs) in pyrolysis may derive either from contaminated feedstocks or from pyrolysis conditions which favor their production [23]. Limits of these contaminants in biochar are under discussion and planned to enter into force in EU regulations and voluntary standards [33]. It has been indicated that low temperatures are unable to remove micro pollutants that were originally present in contaminated feedstocks or created during the thermal process [34–36]. During industrialized pyrolysis process, PAHs are the key target and performance indicator contaminants. Generally, it is considered that adequate pyrolysis methods allow a significant reduction of the PAHs contamination and that high PAHs levels indicate substandard production conditions [37]. For example, if the process conditions do not separate solid residues and volatile tar components during cooling phases, a high PAHs content may eventually result [38].

For slow-pyrolysis processes (at least 20 min reaction time), most of the weight loss in plant based pyrolysis materials derived from contaminated input materials occurs over the temperature range from 250 °C to 550 °C due to burning out of organics [39–41], at least under laboratory conditions. At 500 °C, the pyrolysis reaction time to remove >90% of the organic micro pollutants was less than 5 min [36]. However, animal bone based pyrolysis materials, due to their specific character, require far higher processing temperatures, up to 850 °C material core temperature and longer residence time, under true value industrial production conditions. In all types of pyrolysis materials, it is important to highlight, that there is a significant difference between the processing results from laboratory tests and from true value industrial and market competitive production conditions.

There is a substantial risk for the accumulation of non-volatile pollutants such as inorganic metals and metalloids in the pyrolysis materials as these mostly remain in the solid phase and become concentrated during the production process.

When pyrolysis material is irrevocably applied to open and complex soil ecological systems, there is also a direct interlink to subsurface water systems. Therefore, only qualified and safe biochar products can be applied to avoid both soil and water pollution. Currently, there is lack of harmonized quality and safety standards at European level for pyrolysis material products. However, the complex and strict criteria for safety and quality, functional application efficiency under open environmental and ecological conditions, are already unconditionally valid for all types of biochar products according to the Member State regulations. Nevertheless, since there is not yet a harmonized law on EU level, there are Member State differences. Industrial pyrolysis technology, pyrolysis material production and commercial applications, above 1 tons/year capacity, require Member State Authority permits that conform according to the European Union regulations. Less than 1 ton/year pyrolysis processing capacity is counted as research quantity.

The list of 16 polycyclic aromatic hydrocarbons (PAHs), issued by the U.S. Environmental Protection Agency (EPA) in 1976 with a view to use chemical analysis for assessing risks to human health from drinking water, has gained a tremendous role as a standardized set of compounds to be analyzed, especially in environmental studies [42,43]. Although not mandated by law in most countries, it appears that the list has attained the authority of a legal document and that the 16 priority PAHs compounds are routinely investigated in many environmental situations [43].

The new scientific recognitions and developed analytical methods expanded the list to PAH19, which might be further expanded in the future. As an example, some Member State have required Authority accredited long termed agronomic efficiency tests and maximized potential organic contamination levels <1 mg kg^{-1} for sum of 19 PAHs congeners for soil improvers since 2005, such as Hungary [44], while other Member States do not perform agronomic efficiency testing for novel soil improver products and apply up to <6 mg kg^{-1} for sum of US EPA 16 PAHs congeners. For example, the German Federal Soil Protection and Contaminated Sites Ordinance gives precautionary values for soil with low ($\leq$8%) and high humus content (>8%) regarding the total content of 16 priority PAHs as defined by the Environmental Protection Agency of the United States (EPA 16 PAHs), namely 3 mg kg^{-1} soil and 10 mg kg^{-1}, respectively [33].

The Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) is mandatory for all types of pyrolysis materials for import, manufacturing and placing on the market on its own or in preparation above 1 ton/year capacity, which is to be applied from 1 June 2018 in the EU. REACH is to be applied above 1 ton/year capacity for all types of pyrolysis material cases, i.e. all products that are thermochemically modified substances.

The conditions for access to the fertilizer market are only partially harmonized at EU level. The fragmentation of the non-harmonized part of the market is seriously hindering trade opportunities [45]. Around 50% of the fertilizers currently on the market, however, are left out of the scope of the Regulation. This is true for a few inorganic fertilizers and for virtually all fertilizers produced from organic materials, such as animal or other agricultural by products, or recycled bio-waste from the food chain [10].

Many Member States have detailed national rules and standards in place for such non-harmonized fertilizers, with environmental requirements, such as potential toxic elements (PTEs) contaminant limits, that do not apply to EC-fertilizers [10]. The EU Member States have long regulated the agricultural use of soil improvers and organic fertilizers, such as ABC and other organic products. However, the regulations are different 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 2019–2020, open full and EU wide law harmonization opportunity for many agricultural, food, and industrial by-products and organic material streams, including biochar as well as its formulated products.

The recent initiative on EU fertilizing products (COM (2016) 157 final) is expected to create a level playing field for all fertilizing products at EU level, thereby increase 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 [45].

The improved and safe output pyrolysis material products enhance the environmental, ecological and economic sustainability of the food crop production, while reducing the negative footprint and contributing to climate change mitigation. Terra Humana Ltd. has been the science and technology coordinator and key technology designer for EU Commission co-financed biochar applied research projects since 2002, with prime specialization in ABC recovered bio-phosphate production full industrial engineering, economic field applications and market uptake evaluations. The core competence of Terra Humana Ltd. is zero emission pyrolysis and carbon refinery science and technology developments, objective driven to the added value recycling and recovery of phosphorus and other valuable nutrient materials [46]. In this context, Terra Humana Ltd. is the EU and international knowledge center for ABC Bio-Phosphate matured research, science, technology and industrial engineering.

The recently closed EU project of Terra Humana Ltd. is REFERTIL (EU contract Number 289785 contracted in 2011, www.refertil.info), the complex development works of which cover the fields of applied biochar, most importantly ABC, science, economical full scale industrialization and commercialization. REFERTIL is a biochar policy support specific project for conversion of biochar applied science into economical industrial practice, for which a comprehensive biochar law harmonization proposal has been reported to the Commission.

The objective of the present paper is to describe the Recycle–Reduce–Reuse (3R) zero emission pyrolysis technology designed for phosphorus recovery within the REFERTIL project as a case study for industrial scale production of animal bone char.

2. Materials and Methods

2.1. Origin of the Pyrolysis Materials

All ABC pyrolysis materials were processed by Terra Humana Ltd. Different pyrolysis treatment conditions (treatment temperature and residence time) were used in material treatability tests, considering different food grade animal bone meal and bone grist by-products with 400 kg/h (3200 tons/year) throughput capacity continuously operated 3R zero emission industrial pyrolysis equipment.

The origin of the category 3 food grade bone materials (cattle, chicken and big bones) was from the local animal by-product rendering and fat processing industrial factory. The rendering factory processes fresh raw material animal by-products from the meat and livestock industry into usable materials under heat treatment of 133 °C for 20 min at 3 bars of pressure and operating according to the EU animal by-product regulations 1069/2009 and 142/2011.

Different material core treatment temperatures (300, 450, 600 and 850 °C) were combined with different residence times (15, 20, 30, 40, 50 and 60 min) under industrial productive processing conditions. The temperature instruments were calibrated by accredited calibration laboratory, which is specialized for measuring temperature up to +1200 °C of different solid materials, liquids, gases and air under ISO 17025 standards. Standard Honeywell ceramic thermocouples were used with IP67 head for measurements up to +1200 °C.

Representative plant based pyrolysis material samples were received from the UK, Italy, France and Denmark and comparative tested for PAH16 and PAH19.

Table 1 shows the description of pyrolysis condition (treatment temperature (T), residence time (tres) and samples ID of different EU industrial reference plant based pyrolysis material samples which have been collected and analyzed.

Table 1. List of industrial reference plant based pyrolysis material sample.

Sample ID	Pyrolysis Condition (Provided by the Technology Owner)	Type of Pyrolysis Material	Sample Origin
BCFR2	T = 475 °C, tres = 60 min	Oak chips pyrolysis material	France
BCIT1	T = 450 °C, tres = 60 min	Wood based pyrolysis material	Italy
BCUK1	T = 675 °C, tres = 20 min	Gasification—wood material	United Kingdom
BCDK4	T = 400 °C, tres = 60 min	Wood waste pyrolysis material	Denmark
BCDK5	T = 550 °C, tres = 60 min	Wood waste pyrolysis material	Denmark

Careful material specific consideration is needed for all analytical items, as well as which standards should be applied for investigation of the quality and safety of the pyrolysis materials, especially when open ecological soil applications are targeted. The Environmental Testing Laboratory of WESSLING Group is the first laboratory in Europe to have obtained accredited status for different analyses of the plant based and animal based pyrolysis materials. The accredited analysis of the different samples has been done by WESSLING Hungary Ltd. For sampling, EN-12079 standard was used, while, for sample pre-treatment, Method CEN/TC400—EN 16179:2012 was used.

2.2. Pyrolysis Material Yield

The yield of ABC was calculated as the proportion of the weight of pyrolysis product to the original material.

2.3. Determination of Total Carbon and Total Organic Carbon

Total Carbon was determined according to EN 13137:2001 standard, while the total organic carbon was measured according to EN 13039:2012 standard.

2.4. Determination of Total Nutrient Content of Pyrolysis Material

Total N was measured according to ISO 13878:1998-11 standard. Regarding sample preparation for determination of Total P, K, Ca, Mg, Na and S, the EN 13650:2002 standard was applied, with extraction of aqua regia soluble elements for sample preparation. Total P, K and S were measured by EPA Method 6010C (ICP-OES), while total Mg, Ca, Na were measured by EPA Method 6020A (ICP-MS).

2.5. Calculation of Nutrient Content of Pyrolysis Material Expressed in Oxide Form:

P_2O_5 (Phosphorus pentoxide) was calculated from the directly measured total P. The following chemical conversion factor was applied: P_2O_5 = Total P/0.436.

K_2O was calculated from the directly measured total K. The following chemical conversion factor was applied: K_2O = Total K/0.83.

MgO was calculated from the directly measured total Mg. The following chemical conversion factor was applied: MgO = Total Mg/0.603.

CaO was calculated from the directly measured total Ca. The following chemical conversion factor was applied: CaO = Total Ca/0.715.

SO_3 was calculated from the directly measured total S. The following chemical conversion factor was applied: SO_3 = Total S/0.4.

Na_2O was calculated from the directly measured total Na. The following chemical conversion factor was applied: Na_2O = Total Na/0.742.

2.6. Determination of Phosphorus Soluble in 2% Citric Acid

The EN 15920:2012 standard was used for sample preparation. The Phosphorus soluble in 2% citric acid was measured according to EPA Method 6010C (ICP-OES).

2.7. Determination of Organic Contaminants

PAH16 and PAH19 were measured according to CEN/TS 16181:2013 standard by gas chromatography (GC).

Regarding PCB7, the sum of PCB 28, 52, 101, 118, 138, 153, and 180 was measured according to EN 16167:2013 by gas chromatography with mass selective detection (GC-MS) and gas chromatography with electron-capture detection (GC-ECD).

PCDD/F were measured according to CEN/TS 16190:2012 by gas chromatography with high resolution mass selective detection (HR GC-MS).

2.8. Measurement of Potential Toxic Elements

Regarding Hg, sample preparation was done according to EN 13650:2002 and extraction of aqua regia soluble elements. Analysis was done with EPA Method 6020A using ICP-MS.

Cr (VI) was measured by CEN/TS 16318:2012. The determination was done by ion chromatography with spectrophotometric detection (method B).

As, Cd, Total Cr, Cu, Pb, Ni and Zn were measured according to EN 13650:2002 by extraction of aqua regia soluble elements and ICP-MS: EPA Method 6020A.

3. Results

3.1. ABC Yields

Table 2 shows the percentage amount of ABC product and gas/vapor phase when food grade bone grist (category 3, pig origin) was treated at different (850, 600, 450 and 300 °C) material core temperatures (T), with 20, 50 and 60 min residence time (tres), in continuously operated reductive environment under industrial conditions, when pressure (P) was under -50 Pa. The total processing and residence time was longer than stated residence time (tres) at elevated temperature, such as 850 $°C^{20min}$, which was the final achieved material core temperature with associated tres. All these factors are key performance design quality parameters and specific for each pyrolysis technology designs.

Under industrial production conditions, both the material core temperature of thermal treatment and residence time have been significantly affected the yield of ABC solid products and in parallel the amount of gas/vapor phase. The lowest yield (46 *w*/*w*%) of solid ABC product was achieved at material core treatment temperature of 850 °C with tres 20 min. The highest yield (71 *w*/*w*%) was achieved at low treatment temperature (300 °C), even under as long as 60 min residence time. The yield of solid char phase decreased by the increasing treatment temperature, while the gas/vapor phase increased. As the majority of ABC is produced from cattle bones, having compact and dense character, it is demonstrated, for the animal bone feed stream material case, that high temperature tres, such as material core temperature 850 °C under at least tres 20 min, is needed during industrial conditions.

Table 2. Comparison of ABC (pig bone) yield at 850/600/450/300 °C with different residence time (continuous operation, P = −50 Pa, reductive environment).

ABC Sample	T (°C)	Tres (min)	ABC Yield (%)	Gas/Oil Phase (%)
ABC pig bone	850	20	46	52
ABC pig bone	600	50	47	53
ABC pig bone	450	60	48.7	51.3
ABC pig bone	300	60	71	29

The results indicated that lower material core treatment temperatures (around 450 °C) generally favor ABC production, but were still insufficient to get high quality products. Higher material core temperatures (600 °C–850 °C) produced lower amount of ABC. In other words, ABC yield decreases with increasing pyrolysis temperature. The material core temperature highly affects product quality. Choosing the optimal final material core process temperature under industrial production conditions is highly dependent on the pyrolysis processing design quality and performance, and finally reflected in the economic viability of the commercial production operations.

3.2. Total Carbon and Total Organic Carbon Content

Table 3 shows the total carbon and the total organic carbon content of different ABC materials. The total carbon and total organic carbon content of ABC materials produced from different animal bone feedstock was below 10%.

Table 3. Total carbon and total organic carbon content of different Animal Bone Char samples.

ABC Sample [1]	Total Carbon (%)	Total Organic Carbon (%)
ABC cattle bone [1]	7.5	5.0
ABC chicken bone [1]	10	8.1
ABC pig bone [1]	8.4	6.6

[1] Pyrolysis condition: T = 850 °C, tres = 20 min, P = −50 Pa.

3.3. Total Primary and Secondary Nutrient Content of Different ABC Bio-Phosphate Products

The nutrient contents and its availability from the ABC recovered bio-phosphate products can be used for the evaluation of the agronomic properties. The quality parameters and the agronomic value of all types of ABC products that characterize the usefulness in agricultural applications (such as the nutrient content) should be declared as total. The information concerning nutrient content should also be communicated with the product. In all cases, the nutrient specification should be considered according to the characteristics and the application performance of the product. The mineral nutrient content of the feedstock is largely retained in the resulting ABC, where it concentrates due to the gradual loss of C, hydrogen (H) and oxygen (O) during processing.

Table 4 shows the primary nutrient (N,P,K) content of different category 3 animal by-products and pyrolyzed ABC samples. The phosphorus content of ABC recovered bio-phosphate materials is expressed both in the form of element and in oxide form (phosphorus pentoxide percentage by weight, P_2O_5%). In all cases, the total phosphorus content of output ABC recovered bio-phosphate products were higher compared to the relevant feed materials. The phosphorus content of animal bone varied 19.5–23.9% P_2O_5 content, while the final ABC product was more concentrated, with 28–31.9% P_2O_5 content.

Table 4. Comparison of primary nutrient contents of different animal by-products and ABC samples.

Sample	P mg kg^{-1} Dry Matter	P_2O_5 Percentage by Weight	K mg kg^{-1} Dry Matter	K_2O Percentage by Weight%	N Percentage by Weight
Pig bone grist (cat.3)	93,600	21.5	900	0.11	5.24
Cattle bone grist (cat. 3)	104,000	23.9	191	0.02	3.80
Chicken bone grist (cat. 3)	85,200	19.5	410	0.05	3.85
ABC cattle bone [1]	127,000	29.1	511	0.06	0.897
ABC chicken bone [1]	122,000	28.0	2670	0.32	0.876
ABC pig bone [1]	139,000	31.9	1100	0.13	1.20

[1] Pyrolysis condition: T = 850 °C, tres = 20 min, P = −50 Pa.

The total nitrogen (N) content is expressed in percentages of dry weight. The potassium (K) content of all ABC samples is expressed both in the form of element and in oxide form (potassium oxide percentage by weight, K_2O%). The low nitrogen content of ABC (below 1.5%) results from the nitrogen loss during the pyrolysis process.

Table 5 shows the citric acid soluble P_2O_5 content of different ABC products (pyrolysis condition: T = 850 °C, tres = 20 min, P = −50 Pa) compared to NPK 15:15:15 mineral EC-fertilizer. In the case of ABC products, 39–43% of the total phosphorus content was citric acid soluble, comparing to the rapid release mineral fertilizer where 70% of the total P was citric acid soluble. In this context, the ABC is controlled and/or slow release fertilizer, with a solubility intermediate between phosphate rock and triple superphosphate [47].

Table 5. Comparison of total and P soluble in 2% citric acid content of different ABC samples.

Sample	P mg kg^{-1} Dry Matter	P_2O_5 *w*/*w*%	P Soluble in 2% Citric Acid mg kg^{-1} Dry Matter	P Soluble in 2% Citric Acid *w*/*w*%
ABC cattle bone [1]	127,000	29.1	54,600	12.52
ABC chicken bone [1]	122,000	28.0	64,600	14.82
ABC pig bone [1]	139,000	31.9	51,500	11.81
NPK 15:15:15 mineral EC-fertilizer	77,200	16.55	54,000	12.38

[1] Pyrolysis condition: T = 850 °C, tres = 20 min, P = −50 Pa.

In all cases, the total potassium content of output ABC recovered bio-phosphate products were higher than the relevant feed materials. While the volatile organic compounds were removed during the reductive thermal pyrolysis process under negative pressure conditions, the inorganic elements (having higher boiling point) were enriched in the final ABC products.

Table 6 shows the secondary nutrient content of different ABC samples, such as calcium (Ca), magnesium (Mg), Sodium (Na) and sulfur (S). The results also demonstrated that ABC recovered P also had valuable calcium content, expressed in calcium oxide (CaO) (38.7–43.6% CaO).

Table 6. Comparison of secondary nutrient contents of different Animal Bone Char samples.

Sample	Ca mg kg^{-1} Dry Matter	CaO Percentage by Weight	Mg mg kg^{-1} Dry Matter	MgO Percentage by Weight	Na mg kg^{-1} Dry Matter	Na_2O Percentage by Weight	S mg kg^{-1} Dry Matter	SO_3 Percentage by Weight
ABC cattle bone [1]	312,000	43.6	3700	0.62	6800	0.92	400	0.10
ABC chicken bone [1]	277,000	38.7	5180	0.86	4800	0.65	900	0.23
ABC pig bone [1]	297,000	41.5	5723	0.95	7760	1.05	1000	0.25

[1] Pyrolysis condition: T = 850 °C, tres = 20 min, P = −50 Pa.

3.4. PAHs Content of Animal Bone Chars and Different Industrial Available Plant Based Pyrolysis Material

PAH16 and PAH19 content of 41 different ABC samples were carefully investigated and compared. The most probable components were naphthalenes (all PAHs are naphthalanes in 24% of the samples), including most dominantly naphthalene (present in 95% of the samples at an average concentration of 1.93 mg kg^{-1}). 1- and 2-methylnaphthalenes, which are not listed under US EPA PAH16, were present in 70% of the samples at an average concentration of 0.7–0.8 mg kg^{-1}. Phenanthrene showed similar values. Anthracene, fluoranthene and pyrene were present in 36–38% of the samples (over the benchmark), but only at an average concentration of 3 mg kg^{-1}. A summary of these most probable PAHs is shown in Table 7. Other PAHs were negligible.

Table 7. Average concentration and occurrence of PAHs compounds in ABC (PAH19 components marked with bold).

Name of the PAH Compounds	Average Concentration mg kg^{-1} [1]	Occurrence (%)
Naphthalene	1.93	95.12
Dibenzo[a,h]anthracene	**1.00**	**4.88**
1-Methylnaphthalene	**0.80**	**70.73**
2-Methylnaphthalene	**0.72**	**73.17**
Phenanthrene	0.72	68.29
Chrysene	0.40	19.51
Anthracene	0.30	39.02
Pyrene	0.30	36.59
Fluoranthene	0.29	36.59
Fluorene	0.26	14.63
Benzo[a]anthracene	0.23	17.07
Benzo[e]pyrene	0.16	14.63
Benzo[a]pyrene	0.14	12.20
Acenaphthene	0.14	14.63
Benzo[b]fluoranthene	0.10	9.76
Acenaphthylene	0.10	9.76
Benzo[ghi]perylene	0.06	9.76
Indeno[1,2,3-cd]pyrene	0.04	7.32
Benzo[k]fluoranthene	0.04	2.44

[1] Average concentration of 41 different ABC samples.

Summarizing the PAHs content of all pyrolysis material cases and the results, the scientific evidence fully supports that analysis of PAH19 is a key target for contamination compounds and is very important and justified, as 1- and 2-methylnaphthalenes (measured only under PAH19) are very common. In both the ABCs and the plant based pyrolysis materials cases, naphthalenes were target PAH contaminations. Naphthalanes were present in 83% of the plant based samples at an average concentration of 1.2 mg kg^{-1}, while 1- and 2-methylnaphthalenes probability was 55–66%. Sometimes PAH19 concentration can be double the PAH16 concentration, so it is also an important point to be considered during the definition of limit values, especially in environmentally sensitive areas. The limit value for PAH16 can be exceeded when measuring PAH19. Table 8 shows examples of the different PAH16 and PAH19 results in different industrial available plant based pyrolysis materials.

Table 8. Examples for the difference of PAH16 and PAH19 results in different industrial available plant based pyrolysis material.

Name of Pyrolysis Material Sample	PAH16 mg kg^{-1}	PAH19 mg kg^{-1}
BCFR2 (oak chips, France)	5.27	10.33
BCIT1 (wood, Italy)	8.72	10.12
BCUK1 (wood, UK)	7.73	10.51
BCDK4 (wood, Denmark)	6.71	9.36
BCDK5 (wood, Denmark)	6.09	6.76

Despite the medium temperature processing and the long residence time, the output product PAH content was still too high from these different pyrolysis technologies. The results clearly indicate that industrial production technology performance design is one of the most important and critical factors that ultimately impacts all types of pyrolysis material product quality, including low end product quality, related to biochar soil applications. It is general experience that carbonization of plant materials in industrial scale is faster and less energy transfer demanding than carbonization of animal bone materials, due to the significant character difference of the organic content.

Table 9 shows the sum of EPA PAH16 and of PAH19 contents of the 3R technology produced ABC samples, produced at low, medium and high temperature at equal tres conditions, in industrial scale carbonization process, at 400 kg/h throughput capacity. The results clearly indicate that both the major types of economically interesting animal bone types, but especially cattle bone, require higher processing temperatures down to the material core. The PAH16 and PAH19 concentrations had a decreasing tendency in all ABC samples produced from 300 °C to 850 °C material core temperature at same tres. It is demonstrated that the high heat transfer efficiency and thermodynamics of the 3R pyrolysis process do not support formation of PAHs, while the targeted rapid tres in higher material core temperature is a safe and economically productive solution to process ABC.

Table 9. PAH16, PAH19 and PCB7 contents of different Animal Bone Char samples.

ABC Sample [1]	PAH16 [5] mg kg^{-1} Dry Matter	PAH19 [6] mg kg^{-1} Dry Matter	PCB7 mg kg^{-1} Dry Matter
ABC cattle bone [1]	0.06	0.06	Not detectable
ABC chicken bone [1]	0.42	0.53	Not detectable
ABC pig bone [1]	0.07	0.07	Not detectable
ABC cattle bone [2]	3.39	4.20	Not detectable
ABC pig bone [2]	3.02	3.94	Not detectable
ABC cattle bone [3]	6.35	7.18	Not detectable
ABC pig bone [3]	5.22	6.43	Not detectable
ABC cattle bone [4]	11.15	13.01	Not detectable
ABC pig bone [4]	8.86	9.92	Not detectable

[1] Pyrolysis condition: T = 850 °C, tres = 20 min, P = −50 Pa; [2] Pyrolysis condition: T = 600 °C, tres = 20 min, P = −50 Pa; [3] Pyrolysis condition: T = 450 °C, tres = 20 min, P = −50 Pa; [4] Pyrolysis condition: T = 300 °C, tres = 20 min, P = −50 Pa; [5] Sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene; [6] Sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene, 1-Methylnaphthalene, 2-Methylnaphthalene and Benzo[e]pyrene.

PAHs content of any biochar primarily depends on the carbonization processing technology performance design quality, which ultimately defines the processing conditions. Within the REFERTIL project, 41 ABC recovered P samples were investigated, together with many different types of plant based pyrolysis materials. The results clearly justified that all high quality ABC contains less than 1 mg kg^{-1} PAH19. In this context, it has been demonstrated that the advanced thermodynamics of the modern high quality designed pyrolysis process performance do not support the formation of PAHs and dioxins.

The 1 mg kg^{-1} maximum allowable limit of PAH19 is a key performance indicator, which under commercial production driven industrial processing conditions can be reached only at high material core temperatures, especially in the cattle bone case. The advanced processing condition requirements for plant based pyrolysis materials are far less than for the animal bone case. Therefore, manufacturing and application of ABC Animal Bone Char recovered phosphorus fertilizer require far higher technological level than plant based biochar soil improver. In all pyrolysis materials under industrial production conditions, the analytical characteristic of any biochar products quality performance is the identified fingerprint of the pyrolysis/carbonization processing technology engineering design quality performance and also reflects the feed material characteristics.

3.5. PCBs Content of Different Animal Bone Chars

Table 8 shows the PCB7 content of different ABC samples. PCBs were not detected from any ABC case, but high chlorine content of the input material was also not expected. As in no case have been dioxins detected, we have concluded that PCBs presence is a good and under any circumstances safe indicator of these persistent and bio-accumulative chemicals.

3.6. PTEs Content of Different Animal Bone Chars

Certain Potential Toxic Elements (PTEs) such as mercury, cadmium, nickel, and lead are included in the list of priority substances. The Directive 2008/105/EC lists cadmium and mercury as priority hazardous substance.

Measuring PTEs in pyrolysis materials is very important, because of the 3–5 times re-concentration tendencies during the phase separated processing, thus even higher re-concentration of the PTEs in the final products compared to feed material is common. This results in a much higher PTEs concentration in solid output products than in the original input average.

PTE content of 41 different ABC samples has been carefully investigated. Table 10 shows the potential toxic elements (PTEs) contents of three different ABC samples. All 41 different ABCs samples were well below strict member state regulations and REFERTIL recommended safety limit value.

Table 10. Potential toxic elements (PTEs) contents of different Animal Bone Char samples.

ABC Sample [1]	**As mg kg^{-1} Dry Matter**	**Cd mg kg^{-1} Dry Matter**	**Cr Total mg kg^{-1} Dry Matter**	**Cr (VI) mg kg^{-1} Dry Matter**	**Cu mg kg^{-1} Dry Matter**	**Pb mg kg^{-1} Dry Matter**	**Hg mg kg^{-1} Dry Matter**	**Ni mg kg^{-1} Dry Matter**	**Zn mg kg^{-1} Dry Matter**
ABC cattle bone [1]	<1	<0.3	<1	<0.25	2	<1	<0.02	<1	75
ABC chicken bone [1]	<1	<0.3	2	<0.25	12	2	<0.02	1	310
ABC pig bone [1]	<1	0.03	2	<0.25	2	<1	<0.02	1	198

[1] Pyrolysis condition: T = 850 °C, tres = 20 min, P = −50 Pa.

4. Discussion

For each type of pyrolysis (carbonization) processing technology, at full industrial production scale, the engineering design quality and efficiency performance is a critically important element. The pyrolysis technology design performance and quality will be reflected in all cases as a unique and recognized fingerprint in the output pyrolysis product quality and safety performance characteristics. In this context, the application of low quality pyrolysis production technology under market competitive production conditions result low quality and safety pyrolysis material output products with low market value, if any at all. Another important impact factor is the input material characteristics, which are also reflected in the output product characteristic.

The residence time is an important factor to maintain the economical industrial productivity during a short processing time, while it is also unconditionally important to assure equal quality for the processed carbon products. The Extended Producer Responsibility certification, the product quality and safety labeling documentation as of specified EU regulations, and Customer's "right to know" information, are all important parts for the commercialization of biochar products.

All biological materials might have variations in their natural compositions and character, which is diverse by nature. The advanced carbonization processing must be able to fully compensate these variations and assure equal quality for the output ABC products. The animal by-product rendering pre-processing sterilization ofthe the input material animal bone by-products at 133 $°C^{20min,3bars}$ is upgraded into 3R carbonization final processing 850 $°C^{20min}$ safe performance. This system provides a safe and constant quality ABC product stream, while excluding any biological re- and trans-contamination risks at later agricultural applications, under any variating climatic and soil conditions.

The rendering industrial origin, food grade category 3 and industrial grade category 2 animal bone grist, is processed into ABC Bio-Phosphate. ABC is a macro-porous bio-based fertilizer, having as high as 92% pure calcium phosphate, 8% carbon content, and high nutrient density (30% P).

ABC provides multiple product functionalities in the organic and low input farming sectors, such as organic fertilizer (soil improver, growing medium and/or fertilizing product blends). The substitution of mineral phosphate import by recovered phosphorus is an important goal for European agriculture already in the short term, where ABC is a highly efficient and safe alternative in large extent in European industrial dimension. The fully safe ABC is used at low doses (100–600 kg/ha, on average 300 kg/ha) and in few cases when justified even up to 1000 kg/ha.

ABC bio-phosphate Phosphorus Fertilizer Replacement Value (PFRV) substitution potential in European dimension is estimated already at >5% (>125,000 t/year P) in short term (<2025) for all agricultural applications. The ABC PFRV for the organic farming and low input farming sectors, it is estimated at 100% in medium term (<2030). ABC overall European agriculture PFRV in the long term (>2030) is estimated at over >20% (>500,000 t/year P).

The REFERTIL consortium integrated the pyrolysis applied scientific and high maturity research, the industrial engineering, the legal and market competitive economical aspects and user demands from the horticultural sector. Harmonized and standardized analytical measurements have been developed for the determination of the physico-chemical properties, potential toxic element content and organic pollutants in all types of pyrolysis materials. A proposed quality and safety criterion system has also been set up which sets maximum inorganic and organic pollutant contents for safe application (Tables 10 and 11).

Table 11. Proposed safety criteria for organic pollutants by the ongoing EU Fertilizers Regulation revision law harmonization.

	PAH16 [1] mg kg^{-1} Dry Matter	**PCB7 [2] mg kg^{-1} Dry Matter**	**PCDD/Fs ng WHO Toxicity Equivalents/kg Dry Matter**
Pyrolysis material safety criteria	4	0.2	20

[1] Sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene; [2] sum of PCB 28, 52, 101, 118, 138, 153 and 180.

The most important PTEs are Cd, Cr (Cr total and/or Cr(VI)), Cu, Zn, Hg, Ni, Pb and As, while the key organic parameters are polyclorinated dibenzodioxins and furans (PCDD/Fs), the sum of seven polychlorinated biphenyls (PCB7) and the sum of 16 US EPA priority PAHs (PAH16) congeners.

PCB7 is the sum of seven PCBs, PCB 28, 52, 101, 118, 138, 153 and 180. PAH16 is the sum of the following 16 US EPA congeners: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi] perylene. PAH19, in addition to PAH16, includes 1-Methylnaphthalene, 2-Methylnaphthalene and Benzo[e]pyrene.

All proposed parameters are maximum allowable limits on EU level, which in justified environmental cases may be MS amended to lower limits. PAHs are key performance indicators, while PCDD/F and PCBs are not potential contamination risks. In some MS, 1 mg kg^{-1} for the sum of 19 PAHs congeners is permitted since 2005 as maximum limit for soil improvers. This low limit value requirement is already applied with special concern in environmentally sensitive regions. In general, 4 mg kg^{-1} PAH16 limit value is proposed. With various pyrolysis processing conditions, it has been verified that the technology critically influences the quality of the product.

Extended producers' responsibility and liability for product safety are to be applied for all types of pyrolysis material cases.

Table 11 summarizes the proposed safety criteria for organic pollutants and Table 12 for potential toxic elements by REFERTIL and the ongoing EU Fertilizers Regulation revision law harmonization.

Table 12. Proposed potential toxic elements (PTEs) safety criteria for pyrolysis material by the ongoing EU Fertilizers Regulation revision law harmonization.

	As mg kg^{-1} Dry Matter	**Cd mg kg^{-1} Dry Matter**	**Cr total mg kg^{-1} Dry Matter**	**Cu mg kg^{-1} Dry Matter**	**Pb mg kg^{-1} Dry Matter**	**Hg mg kg^{-1} Dry Matter**	**Ni mg kg^{-1} Dry Matter**	**Zn mg kg^{-1} Dry Matter**
Pyrolysis material safety criteria	10	1.5	100	200	120	1	50	600

5. Conclusions

Disrupted nutrient recycling is a significant problem for Europe, while phosphorus and nitrogen are wasted instead of being used for plant nutrition. Mineral phosphate is a critical raw material, in particular for Europe, which may contain environmentally hazardous elements such as cadmium and uranium. Therefore, phosphorus recovery from agricultural and food industrial by-product streams is a critically important key priority.

A specific zero emission autothermal carbonization system, called 3R, has been developed in economical industrial scale within the EU project REFERTIL, providing animal bone char product (ABC) as output. This system is the first industrial scale pyrolysis process for phosphorus recovery from food grade animal bone by-products. It has been demonstrated that material core treatment temperature <850 °C with 20 min residence time is necessary to achieve high quality and safe ABC with useful agronomic value. At the same time, PAHs have been identified as key performance indicators, and a limit of 1 mg kg^{-1} is recommended for all types of pyrolysis material cases.

Author Contributions: Conceptualization, E.S. and M.P.; Methodology, E.S.; Software, E.S.; Validation, E.S. and M.P.; Formal Analysis, E.S.; Investigation, E.S.; Resources, E.S. and M.P.; Data Curation, E.S. and M.P.; Writing-Original Draft Preparation, E.S.; Writing—Review & Editing, E.S. and M.P.; Visualization, E.S. and M.P.; Supervision, E.S. and M.P.; Project Administration, E.S.; Funding Acquisition, E.S.

Funding: This research was co-funded by the European Commission within the 6th framework programme (PROTECTOR, Contract no. FOOD-CT-2005-514082, 2005-2008) and the 7th framework programme (REFERTIL, Contract no 289785, 2011-2015).

Acknowledgments: The author is solely responsible for the content of this information. The European Community is not responsible for any use that might be made of data appearing therein

Conflicts of Interest: The author Edward Someus declares that this research, technology and ABC products aredeveloped and co-financed by Terra Humana Ltd. since 2002 in which Edward Someus is the original inventor, IPR owner and key technology senior engineer. The author Massimo Pugliese declares no conflict of interest.

References

1. European Commission. *Circular Economy Package, Commission Staff Working Document, Impact Assessment, Accompanying the Document, Proposal for Regulation of the European Parlament and of the Council, Laying Down Rules on the Making Available on the Market of CE Marked Fertilising Products and Amending Regulation EC No 1069/2009 and (EC) No 1107/2009*; SWD(2016)64 Final; European Commission: Brussels, Belgium, 2016.
2. Bartels, J.J.; Gurr, T.M. Phosphate rock. In *Industrial Minerals and Rocks*, 6th ed.; Carr, D.D., Ed.; Society for Mining, Metallurgy, and Exploration, Inc.: Littleton, CO, USA, 1994; pp. 751–764.
3. Schorr, M.; Lin, I.J. Wet process phosphoric acid production problems and solutions. *Ind. Miner.* **1997**, *355*, 61–71.
4. Dissanayake, C.B.; Chandrajith, R. Phosphate mineral fertilizers, trace metals and human health. *J. Natl. Sci. Found. Sri Lanke* **2009**, *37*, 153–165.
5. Kratz, S.; Schnug, E. Rock Phosphates and P Fertilizers as Sources of U Contamination in Agricultural Soils. In *Uranium in the Environment*; Merkel, B.J., Hasche-Berger, A., Eds.; Springer: Berlin/Heidelberg, Germany, 2006.
6. Schnug, E.; Lottermoser, B.G. Fertilizer-derived uranium and its threat to human health. *Environ. Sci. Technol.* **2013**, *47*, 2433–2434. [CrossRef] [PubMed]

7. European Commission. *Communication from the Commission to the European Parliament, the Council, The European Economic and Social Committee and the Committee of the Regions, Roadmap to a Resource Efficient Europe*; COM(2011) 571 Final; European Commission: Brussels, Belgium, 2011.
8. European Commission. *Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, on the 2017 List of Critical Raw Materials for the EU*; COM(2017) 490 Final; European Commission: Brussels, Belgium, 2017.
9. Eurostat, Eurostat—Your Key to European Statistic. 2016. Available online: http://ec.europa.eu/eurostat/data/database (accessed on 18 January 2018).
10. European Commission. *Circular Economy Package, Proposal for Regulation of the European Parlament and of the Council, Laying Down Rules on the Making Available on the Market of CE Marked Fertilising Products and Amending Regulation EC No 1069/2009 and (EC) No 1107/2009*; COM(2016)157 Final; European Commission: Brussels, Belgium, 2016.
11. De Ridder, M.; de Jong, S.; Polchar, J.; Lingemann, S. *Risks and Opportunities in the Global Phosphate Rock Market Robust Strategies in Times of Uncertainty*; The Hague Centre for Strategic Studies No 17/12/12; The Hague Centre for Strategic Studies: The Hague, The Netherlands, 2012.
12. European Commission. *Communication from the Commission to the European Parliament, The Council, The European Economic and Social Committee and the Committee of the Regions, A resource-efficient Europe—Flagship Initiative under the Europe 2020 Strategy*; 26.1.2011 COM(2011) 21; European Commission: Brussels, Belgium, 2011.
13. Van Dijk, K.C.; Lesschen, J.P.; Oenema, O. Phosphorus flows and balances of the 5918 European Union Member States. *Sci. Total Environ.* **2016**, *542*, 1078–1093. [CrossRef] [PubMed]
14. Jayathilakan, K.; Sultana, K.; Radhakrishna, K.; Bawa, A.S. Utilization of byproducts and waste materials from meat, poultry and fish processing industries: A review. *J. Food Sci. Technol.-Mysore* **2012**, *49*, 278–293. [CrossRef] [PubMed]
15. Meeker, D.L.; Hamilton, C.R. *An Overview of the Rendering Industry, Essential Rendering*; Meeker, D.L., Ed.; National Renderers Association: Alexandria, VA, USA, 2006; ISBN 0-9654660-3-5.
16. EFPRA. Rendering in Numbers. Available online: http://www.efpra.eu/Objects/3/Files/EUInfographic.pdf (accessed on 2 February 2018).
17. Dobbelaere, D. Statistical overview of the Animal By-Products Industry in the EU in 2014. In Proceedings of the EFPRA Congress, Cracow, Poland, 5 June 2015.
18. Liu, Q.; Huang, S.; Matinlinna, J.P.; Chen, Z.; Pan, H. Insight into Biological Apatite: Physiochemical Properties and Preparation Approaches. *BioMed Res. Int.* **2013**, *2013*, 929748. [CrossRef] [PubMed]
19. Hua, K.; Liu, L.; Bureau, D.P. Determination of Phosphorus Fractions in Animal 5627 Protein Ingredients. *J. Agric. Food Chem.* **2005**, *53*, 1571–1574. [CrossRef] [PubMed]
20. Beighle, D.E.; Boyazoglu, P.A.; Hemken, R.W.; Serumagazake, P.A. Determination of 3675 calcium, phosphorus, and magnesium values in rib bones from clinically normal cattle. *Am. J. Vet. Res.* **1994**, *55*, 85–89. [PubMed]
21. Hemme, A.; Spark, M.; Wolf, P.; Paschertz, H.; Kamphues, J. Effects of different phosphorus sources in the diet on bone composition and stability (breaking strength) in broilers. *J. Anim. Physiol. Anim. Nutr.* **2005**, *89*, 129–133. [CrossRef] [PubMed]
22. Agrotechnology Atlas. *Livestock Manure*; Agro Business Park: Tjele, Denmark, 2016. Available online: http://AGRO-3651TECHNOLOGY-ATLAS.EU/ (accessed on 8 February 2018).
23. Verheijen, F.G.A.; Jeffery, S.; Bastos, A.C.; van der Velde, M.; Diafas, I. *Biochar Application to Soils. A Critical Scientific Review of Effects on Soil Properties, Processes and Functions*; European Commission: Luxembourg, 2010.
24. EBC. *European Biochar Certificate—Guidelines for a Sustainable Production of Biochar*; European Biochar Foundation (EBC): Arbaz, Switzerland, 2012. Available online: http://www.european-biochar.org/en/download (accessed on 19 June 2015).
25. Hodson, M.; Valsami-Jones, E.; Cotter-Howells, J.D. Bone meal additions as a remediation treatment for metal contaminated soil. *Environ. Sci. Technol.* **2000**, *34*, 3501–3507. [CrossRef]
26. Deydier, E.; Guilet, R.; Scharrock, P. Beneficial use of meat and bone meal combustion residue: An efficient low cost material to remove lead from aqueous effluent. *J Hazard. Mater.* **2003**, *101*, 55–64. [CrossRef]

27. Siebers, N.; Leinweber, P. Bone Char: A clean and renewable phosphorus fertilizer with cadmium immobilization capacity. *J. Environ. Qual.* **2013**, *42*, 405–411. [CrossRef] [PubMed]
28. Vamvuka, D.; Dermitzakis, S.; Pentari, D.; Sfakiotakis, S. Valorization of meat and bone meal through pyrolysis for soil amendment or lead adsorption from wastewaters. *Food Bioprod. Process.* **2018**, *109*, 148–157. [CrossRef]
29. Siebers, N.; Godlinski, F.; Leinweber, P. Bone char as phosphorus fertilizer involved in cadmium immobilization in lettuce, wheat and potato cropping. *J. Plant Nutr. Soil Sci.* **2014**, *177*, 75–83. [CrossRef]
30. Postma, J.; Nijhuis, E.H.; Someus, E. Selection of phosphorus solubilizing bacteria with biocontrol potential for growth in phosphorus rich animal bone charcoal. *Appl. Soil Ecol.* **2010**, *46*, 464–469. [CrossRef]
31. Vassilev, N.; Martos, E.; Mendes, G.; Martos, V.; Vassileva, M. Biochar of animal origin: A sustainable solution to the global problem of high-grade rock phosphate scarcity? *J. Sci. Food. Agric.* **2012**, *93*, 1799–1804. [CrossRef] [PubMed]
32. European Parlament. *Directive 2008/105/EC of the European Parlament and of the Council of 16 December 2008 on Environmental Quality Standards in the Field of Water Policy, Amending and Subsequently Repaling Council Directives 82/176 EEC, 83/513/EEC, 84/156/EEC, 84/491/EEC, 86/280/EEC, and Amending Directive 200/60/EC of the European Parlament and of Council*; European Commission: Brussels, Belgium, 2008.
33. Meyer, S.; Genesio, L.; Vogel, I.; Schmidt, H.P.; Soja, G.; Someus, E.; Shackley, S.; Verheijen, F.G.A.; Glaser, B. Biochar standardization and legislation harmonization. *J. Environ. Eng. Landsc. Manag.* **2017**, *25*, 175–191. [CrossRef]
34. Vom Eyser, C.; Schmidt, T.C.; Tuerk, J. Fate and behaviour of diclofenac during hydrothermal carbonization. *Chemosphere* **2016**, *153*, 280–286. [CrossRef] [PubMed]
35. Weiner, B.; Baskyr, I.; Poerschmann, J.; Kopinke, F.-D. Potential of the hydrothermal carbonization process for the degradation of organic pollutants. *Chemosphere* **2013**, *92*, 674–680. [CrossRef] [PubMed]
36. Ross, J.J.; Zitomer, D.H.; Miller, T.R.; Weirich, C.A.; McNamara, P.J. Emerging investigators series: Pyrolysis removes common microconstituents triclocarban, triclosan, and nonylphenol from biosolids. *Environ. Sci.-Water Res. Technol.* **2016**, *2*, 282–289. [CrossRef]
37. Schmidt, H.P.; Abiven, S.; Kamman, C.; Glaser, B.; Bucheli, T.; Leifeld, J. *Guidelines for a Sustainable Production of Biochar*, 2nd ed.; European Biochar Foundation: Brussels, Belgium, 2013.
38. Schimmelpfennig, S.; Glaser, B. One step forward toward characterization: Some important material properties to distinguish biochars. *J. Environ. Qual.* **2012**, *41*, 1001–1013. [CrossRef] [PubMed]
39. Deydier, E.; Guilet, R.; Sarda, S.; Sharrock, P. Physical and chemical characterisation of crude meat and bone meal combustion residue: “waste or raw material?”. *J. Hazard. Mater.* **2005**, *121*, 141–148. [CrossRef] [PubMed]
40. Koutcheiko, S.; Monreal, C.M.; Kodama, H.; McCracken, T.; Kotlyar, L. Preparation and characterization of activated carbon derived from the thermo-chemical 4633 conversion of chicken manure. *Bioresour. Technol.* **2007**, *98*, 2459–2464. [CrossRef] [PubMed]
41. Ro, K.S.; Cantrell, K.B.; Hunt, P.G. High-Temperature Pyrolysis of Blended Animal Manures for Producing Renewable Energy and Value-Added Biochar. *Ind. Eng. Chem. Res.* **2010**, *49*, 10125–10131. [CrossRef]
42. Wise, S.A.; Sander, L.C.; Schantz, M.M. Analytical Methods for Determination of Polycyclic Aromatic Hydrocarbons (PAHs)—A Historical Perspective on the 16 U.S. EPA Priority Pollutant PAHs. *Polycycl. Aromat. Compd.* **2015**, *35*, 187–247. [CrossRef]
43. Andersson, J.T.; Achten, C. Time to say goodbye to the 16 EPA PAHs? Toward an up-o date use of PACs for environmental purposes. *Polycycl. Aromat. Compd.* **2015**, *35*, 330–354. [CrossRef] [PubMed]
44. Földművelésügyi és Vidékfejlesztési Minisztérium (FVM). *Decree 36/2006 (V. 18.) FVM, Ministry of Agriculture and Rural Development, on the Authorisation, Storage, Marketing and Use of Yield Enhancing Substances*, FVM: Budapest, Hungary, 2006.
45. European Commission. *Commission Staff Working Document, Executive Summary of the Impact Assessment, Accompanying the Document Proposal for Regulation of the European Parlament and of the Council Laying Down Rules on the Making Available on the Market of CE Marked Fertilising Products and Amending Regulation EC No 1069/2009 and (EC) No 1107/2009*; SWD(2016)64 Final; European Commission: Brussels, Belgium, 2016.

46. Someus, E. Towards zero emission solution: 3R pyrolysis process. In *Pyrolysis: Types, Processes, and Industrial Sources and Products*; Donahue, W.S., Brandt, J.C., Eds.; Nova Science Publishers: New York, NY, USA, 2009; pp. 17–29.
47. Warren, G.P.; Robinson, J.S.; Someus, E. Dissolution of phosphorus from animal bone char in 12 soils. *Nutr. Cycl. Agroecosyst.* **2008**, *84*, 167–178. [CrossRef]