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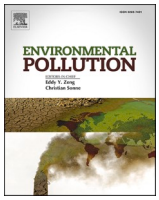

Current analytical methods to quantify PAHs in activated carbon and vegetable carbon (E153) are not fit for purpose☆

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ABSTRACT

Pyrogenic carbonaceous materials (PCM) are increasingly used in a wide variety of consumer products, ranging from medicine, personal care products, food and feed additives, as well as drinking water purification. Depending on the product category and corresponding legislation, several terms are commonly used for PCM, such as *Carbo activatus, C. medicinalis,* vegetable carbon (E153), (activated) charcoal, (activated) biochar, or activated carbon. All PCM contain polycyclic aromatic hydrocarbons (PAHs) co-produced during pyrolysis. However, the actual PAH-content of PCM may range from negligibly low to alarmingly high depending on pyrolysis conditions and, if any, subsequent activation. Because of their health risk, PAHs need to be determined in many such PCM containing products, and concentrations are regulated by respective legally binding documents. Several such documents even specify the analytical method to be used. In this paper, we first argue that based on existing literature, currently legally binding methods to quantify PAHs in such products might not be fit for purpose. Secondly, we exemplarily determined PAH concentrations with a method previously optimized for biochar in a selection of 15 PCM or PCM-containing commercial products, illustrating that concentrations up to 30 mg kg^{-1} can be found. Consumer safety is of concern according to Swiss norms for drinking water and EU regulations for food additives for some of the investigated samples. In fact, some products would not have been allowed to be put on the market, if regulations with fit for purpose analytical methods existed. As PAHs were detected in considerable concentrations when extracted with toluene for 36 h, the authors suggest a corresponding adaption of existing methods and harmonization of the legislation.

1. Introduction

Pyrogenic carbonaceous material (PCM) is an umbrella term for (activated) charcoal and biochar produced from organic precursors such as wood or other plant materials, and activated carbon, often made from fossil carbon like coal or peat (Hagemann et al., 2018; Pignatello et al., 2017). Pyrolysis is a thermochemical process that converts carbonaceous feedstock such as oil, waste or renewable biogenic material into PCM (Hagemann et al., 2018). Thermal activation to produce activated charcoal, activated biochar, or activated carbon uses, e.g., carbon dioxide or water vapour during pyrolysis to maximize their adsorption potential (Marsh and Rodríguez-Reinoso, 2006c). Activated charcoal or carbon is mainly applied for purification of water and air, or separation of gas mixtures (Marsh and Rodríguez-Reinoso, 2006a) and for remediation of sediments (Hilber and Bucheli, 2010) or soil (Hagemann et al., 2018). For certain products, activated carbon has been increasingly replaced over the last 10–15 years by the eco-friendlier biochar produced from locally available biomass (Lehmann, 2007). Numerous medical, personal care, food, and feed products consist of, or contain biochar (Schmidt, 2012).

However, PCM in general can contain pollutants that are of potential risk to consumers, such as polycyclic aromatic hydrocarbons (PAHs). During pyrolysis, PAHs are predominantly formed by gas phase pyrosynthesis of volatilized organic compounds which then condense on residual carbon particles during cool down (Bucheli et al., 2015). More generally, PAHs are formed by incomplete combustion of fossil fuel or biomass burning used for transportation, heating or cooking (i.e., grilling, smoking). Consequently, PAHs are widely distributed in the environment, as well as in correspondingly produced food. A summary of exposure to PAHs in the environment, including food, is given by Menzie

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et al. (1992).

1.1. PCM categories, major uses and regulations

The use and quality of PCM as an industrial, medical or consumer (by-)product is regulated by (inter-)national legislation. It is beyond the scope of this study to compile all aspects of PCM regulations for all applications systematically. Instead, Table 1 categorizes the major types of PCM addressed in this paper, lists synonyms, the production protocol, uses, and the most relevant ordinances of the European Union (EU) and Switzerland concerning PAH content and quantification in the main product categories food and feed additive, medical, and personal care products (PCP). Note that we do not cover PCM applications such as material enforcements, construction materials, industrial applications, etc. (Schmidt, 2012).

The European Pharmacopoeia (EPh) 10.0 (EPh, 2020) lists PCM as activated charcoal or *Carbo activatus* "obtained from vegetable matter". If the PCM is produced from essentially the same vegetable material as *C. activatus*, but is used as an additive, be in food (EC, 1995, 2008; ZuV, 2015), feed (Zusatzstoffliste, 2015), or in PCP (EC, 2009), it is termed "vegetable carbon" or E153 (Table 1). While vegetable carbon is permitted in food in the EU as well as for instance in Kenya (2012), named charcoal or carbon black, the US Food and Drug Administration (FDA) only permits it in coloring cosmetics (Harp and Barrows, 2015; Lehto et al., 2017). In Switzerland, E153 in feed (Zusatzstoffliste, 2015) is only listed as sensory feed additive for ornamental fish and birds to positively influence their colours. In contrast, biochar is a real feed additive for husbandry animals. Biochar is rather new in this PCM compilation, and guidelines, amongst others as feed additive, are being developed and revised constantly as for instance the European Biochar Certificate (EBC, 2012–2022) (Table 1) or the International Biochar Initiative (IBI, 2015). Both, EBC and IBI, are currently legally non-binding, voluntary quality standards of biochar producers.

1.2. Regulated PAHs in various PCM

Several legislations in the food, feed, medical and PCP domain do not specify limits of individual PAHs (or sums thereof), but require unspecific bulk equivalent concentrations (Table 1) determined via total fluorescence intensity (EC, 1995, 2008; EPh, 2020; JECFA, 1990). The EC (2012) states that "current provisions on PAHs are too generic and not relevant to safety and should be replaced by maximum limits for individual PAHs of concern for food additive's vegetable carbon (E153)". Indeed, many environmental and human risk assessments and corresponding legislations are however based on the 16 PAHs (naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene

Table 1
European legislation regulating polycyclic aromatic hydrocarbons (PAHs) in pyrogenic carbonaceous material (PCM) of drugs, products for filtration and for coloring of food, feed and personal care products divided into different categories.

PCM category	Synonym	Production protocol	Use	PAHs regulated[a]	Extraction solvent for analysis	Legislation
Activated charcoal/ carbon	*Carbo activatus, C. medicinalis*	Obtained from vegetable matter by suitable carbonization processes intended to confer a high adsorption power	Medicines/ medical (by definition)	In a strict sense, the European Pharmacopoeia does not regulate PAHs but "fluorescent substances" to which PAHs belong	Cyclohexane	EPh (2020)
			for water/distillate purification	0.02 μg L^{-1} for the sum of FLT, BbF, Bkf, BaP, BPE, IPY in the filtrate	Not required for the granulated activated carbon but for the purified water. Extraction solvent not specified.	SN (2009)
E153	As food additive = vegetable carbon or vegetable black (EC, 1995, 2008; JECFA, 1990), in cosmetics = carbon black (EC, 2009)	Produced by the carbonization of vegetable (i.e., plant) material such as wood, cellulose residues, peat and coconut and other shells; the raw material is carbonized at high temperatures; consists essentially of finely divided carbon; may contain minor amounts of nitrogen, hydrogen and oxygen. Some moisture may be absorbed on the product after manufacture. It may be activated at high temperature in presence of steam or carbon dioxide.	Food/feed additive (by definition) for coloring and in personal care products	Food additive in EC (2012): 50 μg kg^{-1} for BaP Food additive in EFSA (2012): BaP <1 μg kg^{-1} Food additive in former but not repealed directives such as EC (1995), (EC, 2008): Single compounds not mentioned but (bulk) "polyaromatic hydrocarbons as 100 μg L^{-1} quinine sulfate equivalents" Food additive in JECFA (1990): Single compounds not mentioned but higher aromatic hydrocarbons as quinine sulfate equivalents.	Cyclohexane	(EC, 1995, 2008, 2009, 2012) (EFSA, 2012)[b] JECFA (1990)
Biochar		Porous, carbonaceous material that is produced by pyrolysis of plant biomasses	Feed additive (EBC-Feed) in this study but also applied to other matrices[c]	No limit value for $\sum PAH_{16}$, for $\sum PAH_8$ is 1 mg kg^{-1} and for benzo[*e*]pyrene and benzo[*j*]fluoranthene <1 mg kg^{-1}	Toluene	(EBC, 2012-2022)[d] and references therein

[a] Abbreviations are: naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene, (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BPE), sum of these 16 US EPA PAHs ($\sum PAH_{16}$), sum of eight US EPA PAHs ($\sum PAH_8$) are BaP, BaA, CHR, BbF, BkF, DBA, IPY, and BPE.

[b] EFSA paper is a scientific opinion.

[c] Other matrices can be soil (EBC-AgroBio, EBC-Agro, EBC-Urban) or inorganic material (EBC-Basic Materials, and EBC-Consumer Materials). For corresponding limit values we refer to the latest EBC guidelines (EBC, 2012–2022).

[d] EBC guidelines are no legislation but a quality standard compilation.

(FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*] fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenz[*a,h*]anthracene (DBA), benzo [*ghi*]perylene (BPE) and the sum of them referred to as ΣPAH_{16}) prioritized by the US Environmental Protection Agency (EPA) (EU, 2011). Some of the US EPA PAHs but also other PAH compounds are recommended by the EU or the Scientific Committee for Food (SCF) (EU, 2011). Dibenz[*a,h*]anthracene receives the highest toxicity equivalence factor (TEF) of 5 or 10 and BaP a TEF of 1 (Andersson and Achten, 2015; Nisbet and LaGoy, 1992). Hence, both compounds are prioritized by the US EPA, EU, and the SCF.

The carcinogenic BaP is the lead substance in for instance the food additive E153 (EC, 2012; EFSA, 2012) (Table 1). The EBC guideline (EBC, 2012-2022) includes eight carcinogenic PAHs (PAH_8, BaP, BaA (TEF 0.2), CHR (TEF 0.1), BbF (TEF 0.8), BkF (TEF 0.2), DBA, IPY (TEF 0.1), BPE (TEF 0.009, TEFs according to Andersson and Achten (2015)) of the 16 US EPA PAHs in EBC feed where the ΣPAH_8 must not surpass 1.0 mg kg^{-1}. Biochar for EBC feed (2012–2022) not only complies with the PAH_8 of the EFSA (2008) opinion about PAHs in food but also with the EU-registration, evaluation, authorisation and restriction of chemicals (REACH) regulation (2013) and additionally includes benzo[*e*] pyrene (BeP, TEF not specified in Andersson and Achten (2015)) and benzo[*j*]fluoranthene (BjF, TEF 0.2) (Table 1, limit of the sum is 1.0 mg kg^{-1}). The EU-REACH, 2013 itself intends to protect the health of consumers by limiting PAH concentrations (BaP, BeP, BaA, CHR, BbF, BjF, BkF, DBA) in articles, where carbon black is also listed, to <1 mg kg^{-1}. The Swiss Norm (SN, 2009) regulates FLT, BbF, BkF, BaP, BPE, and IPY in granular activated carbon for the treatment of water for human consumption. However, the SN (2009) does not stipulate the PAH content in the PCM itself, but the concentration of PAHs in the filtrate, which shall contain ≤0.02 μg L^{-1} PAHs (sum of FLT, BbF, BkF, BaP, BPE, and IPY).

1.3. (Legal) aspects of PAH analysis in PCM

While the EU legislation does not require specific analytical procedures for PAHs in food and allows laboratories to use different methods of analysis (Zelinkova and Wenzl, 2015), it does so in different ways for several of the PCM categories listed in Table 1. From generic to specific, the Council Directive 78/25/EEC from 1977 for coloring matters (E153) which may be added to medicinal products prescribes in Article 3: "The methods of analysis needed to verify that the general and specific criteria of purity adopted pursuant to the Directive of October 23, 1962 are satisfied and shall also apply for the purpose of this Directive" (EC, 1977). The Joint FAO/WHO Expert Committee on Food Additives (JECFA) and the European Commission (EC) do not set limits for PAHs in vegetable carbon (INS No. 153 = E153) but only recommend a cyclohexane extraction (Table 1) with fluorescence detection in ultraviolet light (EC, 1995, 2008; JECFA, 1990). Also, the EPh 10.0 (EPh, 2020) suggests the same extraction method as above for 2 h for fluorescent substances (such as PAHs). Both matrices, *C. medicinalis* regulated in the EPh (2020) and E153 regulated by the EC (EC, 1995, 2008) are thus to be extracted by cyclohexane and the PAHs determined by a fluorescence method in which the signal intensity is compared to the one of quinine sulfate in a sulphuric acid solution (Table 1). However, from these legislations it is difficult to align the methods because the sample to extraction solvent ratios are different and the quinine and sulphuric acid concentrations as well. Moreover, the EFSA (2012) concludes in its opinion about food additives that the fluorescence method does not allow a quantitative measurement of PAHs: "The proposed method is not specific since it is not possible to obtain a quantitative measurement of the amount of PAHs that may be present in a batch of vegetable carbon using this methodology". It also points out that the test limits are different: "The Panel also noted that in the JECFA and the European Pharmacopoeia specification the concentration of sulphuric acid used in the limit test for PAHs is 0.005 M (0.01 N), while in the EC specifications it is 0.01 M". The EFSA suggests in 2012) a validated, but yet to be established analytical method (EFSA, 2012) of appropriate sensitivity, e. g. a limit of detection for BaP of 0.1 μg kg^{-1} and, after a re-evaluation of E153 due to limited data, in 2021 again (EFSA, 2021). Even in this last report the EFSA does not address the question how PAHs should be extracted. Furthermore, it concludes wrongly that "vegetable carbon", in contrast to carbon black (which some consider synonym as the former has the same EINECS number (215-609-9) as carbon black (EC, 1995, 2008, 2009)), is unlikely to contain carcinogenic PAHs as the source material is not petrochemical (EFSA, 2012). While carbon black might exhibit higher PAHs concentrations because it is formed by reactions from petroleum (= petrochemical) vapour as well as other source gases at about 1100 °C (Marsh and Rodríguez-Reinoso, 2006b), vegetable carbon still can contain carcinogenic PAHs for reasons specified above. In summary, the above extraction procedures do not seem appropriate and in unison in quantifying PAHs in PCM.

Several researchers (Fabbri et al., 2013; Hamm et al., 2018; Hilber et al., 2012; Jonker and Koelmans, 2002a) investigated how to best extract PAHs from PCM such as (activated) charcoal, carbon black, and biochar. State of the art methods suggest toluene with an extended Soxhlet extraction suitable for PAHs in PCM, which Wang et al. (2017) confirm in their review. Substantial evidence (chapter S1, Table S1; Figures S1 – S4) for the suitability of this approach is provided in the supporting information (SI), which served as basis to extract PCM samples in this study.

1.4. Objectives

Any legislation (Table 1) can only function with analytical methods that are fit for purpose. In line with the EFSA (2012) and EFSA (2021), we argue that some of those mentioned above may not be so. Given the fact that the extraction conditions stipulated in most legislations probably are insufficient, the objective of this study was to survey different PCM products (Table 2) for PAHs with the appropriate and validated analytical method developed by Hilber et al. (2012) for biochar. Results will be presented as total concentrations, discussed in light of the different legislations, and some consequences assessed by the example of BaP and ΣPAH_8. Finally, an outlook of a potentially more appropriate extraction method is provided as a step towards more a stringent legislation.

2. Material and methods

2.1. Analytes and chemicals used for analysis

All chemicals, thus the 16 US EPA PAH including their isotopically labelled internal standards (ILIS, d_8-NAP, d_8-ANY, d_{10}-ANA, d_{10}-FLU, d_{10}-PHE, d_{10}-ANT, d_{10}-FLT, d_{10}-PYR, d_{12}-BaA, d_{12}-CHR, d_{12}-BbF, d_{12}-BkF, d_{12}-BaP, d_{12}-IPY, d_{14}-DBA, and d_{12}-BPE), the recovery standard indeno[1,2,3-*cd*]fluoranthene (IFL; 99.7% purity), the extraction solvent toluene and the material for the sample clean-up were purchased and used according to Hilber et al. (2012).

2.2. Samples, sample preparation and extraction

The 17 samples (Table 2) were categorized in activated charcoal or carbon (1–8), E153 (9–14), biochar (15), and no PCM containing matrices (16–17). Samples 1–3 are used for water and distillate filtration, 4–8 as drugs in form of capsules or powdered PCM for ingestion as *C. medicinalis*, 9–14 contain or are E153 where 9–11 belong to PCP (soap, toothpaste, facial sponge), 12 and 13 are pure food colorants, 14 is flour containing E153, and 15, the biochar, is a feed additive. Samples 16–17 are non-PCM where 16 is E151, brilliant black or laca black, another food colorant, and 17 is a control to sample 15.

Samples 2, 5, 8, 11–13, 15–16 were dried overnight at 40 °C (at

Table 2
Sample numbers, their pyrogenic carbonaceous material (PCM) category, their brand/use, benzo[*a*]pyrene (BaP) concentrations, sample and producer information and the corresponding website.

Sample no.	PCM category[a]	Brand (name)/use	Number of replicates, BaP concentrations[b] (mg kg^{-1})	Sample information and unit mass (g)	Producer	Website, date visited
1	Activated carbon or activated charcoal	Water filter	n = 3 1.35 ± 0.30	PCB 4500 L/h 10 μm carbon block filter of 24.8 cm length, diameter 7 cm containing pressed activated charcoal for water purification	Koerner AG Schmiedgasse 4 6430 Schwyz Switzerland	https://www.koerner-ag.ch/fts.php?offset=1&criteria=Aktivkohle visited Jan 12, 2022. PCB 4500 L/h disappeared on the firm's website during research and publication.
2	Activated carbon	Moonshiners Choice® distillation carbon	n = 4 0.15 ± 0.07	1 kg of activated carbon granulate	UNICOBRES OHG, Kirchweg 5 A, 36,123 Eiterfeld, Germany	https://www.destillatio.eu/aktivkohle-activekohle-aktiv-kohle-filterkohle-aromakohle-kohle-kohlepulver-carbon-active-carbon/a-410/visited Jan 12, 2022
3	Charcoal	Water filter	n = 2	Binchotan active recharge charcoal filter stick of 12 cm length and 2 cm diameter for water bottle	Black + Blum ltd 2.07 Oxo Tower Wharf Bargehouse Street London SE1 9 PH, UK	https://black-blum.com/collections/box-appetit/products/eau-good visited Jan 12, 2022
4	Activated charcoal	VITASENSE capsules *C. medicinalis*	n = 3	60 capsules at 260 mg each. Other ingredients: gelatin, vegetable, magnesium, stearate, silica	myVitaSense, Suite 36, 88–90 Hatton Garden, Holborn, London, EC1N 8 PG, United Kingdom	https://www.myvitasense.com/products/136 visited July 20, 2020
5	Activated carbon or activated charcoal	*C. medicinalis pulv.*[c]	n = 2	100 g Carbon 100%	Detrade UG, Bruchstrasse 14 d, 28,816 Stuhr, Germany	http://joannasgarden.com/Kohle-medizinisch-gemahlen-E153-100g visited Jan 12, 2022
6	Activated charcoal	NORIT Capsules *C. medicinalis*	n = 3	30 capsules at 200 mg, each and gelatine, titanium dioxide (E171) and black iron oxide (E172) as excipients	Cabot Norit Niederland B. V., Amersfoort, The Netherlands	https://www.drugs.com/uk/norit-200mg-leaflet.html visited Jan 12, 2022
7	Activated carbon or activated charcoal	NATURE'S WAY® ACTIVATED CHARCOAL capsules *C. medicinalis*	n = 2	100 capsules containing 560 mg activated charcoal, each.	Nature's Way Products, Inc. Green Bay, WI 54311 USA	https://www.amazon.de/Natures-Way-Activated-Charcoal-Aktivkohle/dp/B0006LCQ4Q?currency=EUR&language=en_GB visited Jan 12, 2022
8	Activated carbon or activated charcoal	Pulvis[c] charcoal *C. medicinalis*	n = 2	4 containers à 10 g, each containing *C. medicinalis* pulv.[c]	Köhler Pharma GmbH Neue Bergstraβe 3 - 7 64,665 Alsbach-Hähnlein, Germany	https://www.koehler-pharma.de/unsere-praeparate/produkte/kohle-pulvis-pulver visited Jan 12, 2022
9	E153	Soap	n = 2	113 g soap containing saponified coconut oil, olive oil, palm oil, terra alba (kaolin), bamboo-charcoal (concentration unknown), tea-tree oil, bergamot oil	Herbivore Botanicals, 2315 Western Avenue, Suite 310, Seattle, Wa 98,102 USA	https://clomes.ch/shop/seife-bambusholzkohle-herbivore-botanicals/visited Jan 12, 2022
10	E153	Ecodenta toothpaste	n = 2	100 mL black charcoal (concentration unknown) and Teavigo TM; ingredients: aqua, glycerin, hydrated silica, sorbitol, sodium cocoyl glutamate, aroma, sodium Pyrophosphate, charcoal powder (concentration unknown), epigallocatechin gallate, mentha arvensis (mint) oil, xanthan gum, sodium benzoate, potassium sorbate, phenoxyethanol, ethylhexylglycerin, sodium saPCMharin, CI 77499, CI 77266.	UAB "BIOK laboratorija", 02300 Vilnuis, Lithuania	https://ecodenta.lt/en/products/black-whitening-toothpaste/ visited Jan 12, 2022
11	E153	MORIHATA Binchotan facial sponge	n = 2	All-natural sponge made with pure vegetable fibers (Japanese Konjac plant roots) and ultra-fine Binchotan charcoal powder (concentration unknown)	Morihata International LTD 428 N. 13th street Philadelphia, Pennsylvania 19,123 USA	Binchotan Charcoal Facial Puff – MORIHATA visited Jan 12, 2022
12	E153	Carbo ligni food colorant	n = 2 0.15 ± 0.00	50 g wood char powder to naturally color food black	BOS FOOD Düsseldorf Food Wholesale GmbH, Gruenstr. 24c, 40,667 Meerbusch, Germany	https://www.bosfood.de/shop-detail/kategorie/lebensmittelzusatzstoffe/subkategorie/zusatzstoffe/detail/farben/produkt/carbo-medicinalis-pflanzenkohlenpulver-wasser-und-fettloeslich-ruth-50-g_50272.html visited Jan 12, 2022
13	E153		n = 2	20 g food colorant		

(*continued on next page*)

Table 2 (*continued*)

Sample no.	PCM category[a]	Brand (name)/use	Number of replicates, BaP concentrations[b] (mg kg^{-1})	Sample information and unit mass (g)	Producer	Website, date visited
		Sosa black food colorant			SOSA INGREDIENTS S.L., CL Sot d'Aluis s/nPol. Ind. Sot d'Aluies, Moia, Spain	https://www.sosa.cat/en-ww/food-colour-negro-home-gourmet visited Jan 12, 2022
14	E153	Baker's night flour food colorant	n = 2	100 g of wheat flour, wheat gluten and food colorant (biochar) at <3% (w/w)	Meyerhans Mühlen AG, Mühlering 5, 6102 Malters, Switzerland	http://www.meyerhans-muehlen.ch/documents/neue_produkte_dok/mh_15_0804_produktebroschuere_baeckernacht_proof.pdf website expired, similar product is here: https://shop.freestylecooking.ch/themen/backen/schwarzes-mehl-250g.html?sl=de visited Jan 12, 2022
15	Biochar	Carbon-enriched fodder	n = 1	1.5 kg of carbon fodder contains biochar (9–10%), wheat bran, sugar-cane molasses, alpine herbs, flax seeds, mineral nutrients, barley, wheat, and corn flakes; moisture content 35–37% (w/w)	EM Schweiz AG, Lützelflühstrasse 22, 3508 Arni, Switzerland	https://www.em-schweiz.ch/Content/Images/uploaded/Flyer_Tierfutter_HP.pdf visited Jan 12, 2022
16	no PCM, E151	Laca black	n = 3	30 g food colorant consisting of E151 brilliant black BN (concentration unknown) and E102 tartracin	SOSA INGREDIENTS S.L., CL Sot d'Aluis s/nPol. Ind. Sot d'Aluies, Moia, Spain	https://www.gourmet-versand.com/de/article13869/lebensmittelfarbe-schwarz-fettloesliches-puder-sosa-20-g.html visited Jan 12, 2022
17	no PCM	uroSAN fodder	n = 1	fodder bokashi (fermented feed additive) consisting of wheat bran, herbs, apple pomace, wheat, dextrose, flax seeds, molasses, soy oil	Niederhäuser AG, Futterwerk, 6023 Rothenburg, Switzerland	http://www.niederhaeuser.com/index.php/produkte/fermentprodukte/urosan visited Jan 12, 2022

[a] Samples 1–8 repeats the PCM category as labelled at the specific website. If it is not clear both, "activated charcoal" and "activated carbon" is mentioned. Please note that retailers may choose "activated charcoal" and "activated carbon" by chance.
[b] Benzo[*a*]pyrene (BaP) concentration only listed if above the BaP blank of 0.07 mg kg^{-1}, concentration as mean ± 1 standard deviation.
[c] pulv. = pulvis = powder.

which no PAH losses should occur (Desaules et al., 2008)), sample 2, the granulated activated carbon, was crushed, and all samples were then thoroughly homogenized before taking 1 g of each sample for extraction. For the PCM in capsules (samples 4, 6, and 7) 20 to 30 capsules were crushed and mixed before 1 g was used for extraction. The sponge (11) and the charcoal filter stick/cartridge (1, 3) were broken into pieces and milled with mortar and pestle, the soap (9) cut into pieces. The tube of sample 10 was squeezed to obtain some toothpaste for extraction. Samples 10, 14, and 17 were wet extracted and the PAH concentrations corrected to dry weight. All concentrations are reported on a (total) dry weight basis. For the samples 9–15, the PCM content was below 30% and for some samples (9, 11, 14) even below 3%. The exact content of PCM in these products was not known and could not be analysed; we provide the PCM content that the respective producers declared as indication (Table 2).

All samples were then Soxhlet extracted, in replicates of two to four except sample 15 and 17 that were only extracted once, by the method of Hilber et al. (2012). Briefly, the samples were filled into cartridges (22 mm × 80 mm, cellulose thimbles, Whatman, Buckinghamshire HP7 9 NA, United Kingdom) and spiked with deuterated PAH homologues to determine the absolute recovery of the analytes. Blank samples were empty cartridges spiked with ILIS. After 36 h of extraction with toluene at 111 °C, the boiling point of the solvent, the sample solutions were concentrated with a parallel evaporator Syncore Analyst system from Buchi (Flawil, Switzerland) to 1 mL and cleaned up by *N,N*-dimethylformamide (DMF) liquid-liquid partitioning and, if necessary, by a silica gel column.

2.3. PAHs separation and determination by GC-MS

Analysis of PAH was conducted according to Bucheli et al. (2004), which includes an on-column injection on a 2 m Siltek deactivated guard column from Restek, Bellefonte, PA, USA, followed by a 30 m Rtx-5Sil column from the same provider. The oven temperature program of a total of 56 min, the ionisation energy, the qualifier and quantifier molecules incl. those of the ILIS, the quantification method with the same range of calibration standards and the ILIS quantification method were all set according to Bucheli et al. (2004). The ILIS were added before extraction and the recovery standard IFL before sample analysis, both were quantified and related to each other to calculate the absolute recovery by comparing it with the same ratio in the calibration. A chromatogram with the mass traces of quantifier ions of all 16 compounds is provided in the SI, Figure S5.

3. Results and discussion

3.1. Method performance

The absolute recoveries of the samples fluctuated around 30% over all five extraction series and individual compounds and were slightly lower than the values in Hilber et al. (2012). However, the use of deuterated PAHs as ILIS effectively compensated for any loss of target analytes. Average blank levels (n = 6) for the $\sum PAH_{16}$ run in every sample batch ranged from 0.003 to 0.48 mg kg_{dw}^{-1}. The average precision expressed as relative standard deviations (RSD, (standard deviation (sd)/mean*100)) of the sample concentrations was 20%. This number is slightly higher than the 4–12% in Hilber et al. (2012), but still acceptable in light of the Horwitz function (Horwitz, 1982).

3.2. PAH concentrations in PCM samples

Mean concentrations of the $\sum PAH_{16}$ ranged from 0.15 to 31.5 mg

kg^{-1} (Fig. 1). In nine of the 17 samples, PAH concentrations were clearly above the highest analytical blank of 0.48 mg kg^{-1}. In the following, only these nine samples are discussed. It is further assumed that the PAH in mixed matrices, i.e., PCP containing PCM, were exclusively originating from the PCM, but related to its total mass due to missing information about the PCM fraction in the product.

The water filter (1) consisting of activated charcoal or carbon had the highest PAH concentration (31.5 mg kg^{-1}) followed by the two food colorants (12, 13; E153) with 20.8 mg kg^{-1} each (Fig. 1). Sample 16 contained no PCM but E151 and showed 13.1 mg kg^{-1} $\sum$PAH$_{16}$ and the activated charcoal in capsules belonging to *C. medicinalis* (4) had 11.1 mg kg^{-1}. The activated carbon granulate for filter distillates (2) exhibited 5.2 mg kg^{-1} $\sum$PAH$_{16}$ and the samples 5 and 6 (*C. medicinalis*), and 15, the biochar amended fodder, contained $\sum$PAH$_{16}$ of around 1.0 mg kg^{-1}.

Benzo[*a*]pyrene is listed in Table 2 for those samples with concentrations above the blank (0.07 mg kg^{-1}). Again, the water filter (1) with the highest $\sum$PAH$_{16}$ had also the highest BaP concentration with 1.35 mg kg^{-1}, followed by the activated carbon granulate for filter distillates (2) and E153 (12) where the BaP concentration was 0.15 mg kg^{-1}, each.

While there is a variety of literature about PAH sorption to activated charcoal or carbon (e.g. Brändli et al., 2008; Jonker and Koelmans, 2002b; Kupryianchyk et al., 2012; Walters and Luthy, 1984) we are not aware of any publications about their intrinsic PAH contents, be it for individual or the sum of the compounds. This may have several reasons, e.g., such analyses are not demanded by legislation (Table 1), these PCMs may be presumed to be PAH free in the first place and therefore not tested, or the applied analytical methodologies may not have been fit for purpose, thus yielding no detects. In contrast, PAH concentrations in biochar have been widely studied over the last decade, and were recently reviewed by Wang J et al. (2019a). Mean concentrations of toluene extracted biochars in their compilation (all references in Table S2 from Wang J et al. (2019a) searched for toluene extractions) was 21 mg kg^{-1} (min = 0.2 mg kg^{-1}, max = 172 mg kg^{-1}) for the $\sum$PAH$_{16}$. Large sets of biochar samples extracted with toluene and Soxhlet were investigated by Hale et al. (2012) and Hilber et al. (2017) who reported mean concentrations of 1.2 mg kg^{-1} (min = 0.1 mg kg^{-1}, max = 45 mg kg^{-1}) and 96 mg kg^{-1} (min = 1 mg kg^{-1}, max = 2000 mg kg^{-1}), respectively for the $\sum$PAH$_{16}$. Thus, the PAH concentration range of PCM quantified in the present study seems plausible.

Samples 3, 7–11, 14, and 17 had PAH concentrations below the highest blank level, which might at least partly be a result of the overall low fraction of PCM in the product. Specifically, all PCP (9–11) fall in this group. However, many cosmetic articles containing PCM are promoted in the web as for instance Brazil Beauty news (2020), Cabot (2020), GirlsCMM (2020) and some warn that the products might contain toxic pollutants, specifically PAHs (Campaign for Safe Cosmetics (2020) and Illinois Department of Public Health (IDPH, 2020)). No peer reviewed studies were found that related PCM with PAHs in PCP. Traces of PAHs in several PCM containing cosmetics obtained with an unspecified analytical method were reported, though, in a consumer protection journal (Jörg, 2016). A recent study of Wang S-W et al. (2019b) measured PAH concentrations in cosmetics without PCM and found at most a few hundred µg kg^{-1}, which are in the same range as in this study. While this outcome suggests that PCM contamination in cosmetics may be negligible even when containing PCM, the work of Wang S-W et al. (2019b) does not report on blanks, which is necessary if ubiquitous pollutants prone to cross-contamination such as PAH are quantified.

The relative concentrations of individual compounds over the ones of $\sum$PAH$_{16}$ (i.e. the PAH fingerprint) of the nine samples above the blank, grouped by PCM categories, are depicted in Fig. 2. Naphthalene with

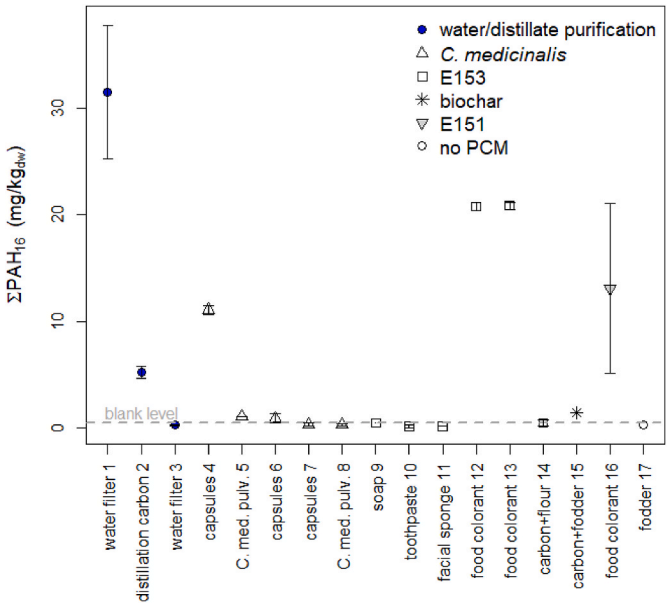

Fig. 1. Sum ($\sum$) of 16 polycyclic aromatic hydrocarbons (PAHs) assigned priority pollutants by the environmental protection agency (EPA) in the investigated pyrogenic carbonaceous materials (PCM) samples. The different PCM categories were activated charcoal (AC) to purify water or distillate (sample 1–3), AC as *Carbo medicinalis* (sample 4–8, Table 2), E153 as additive in cosmetics or food (sample 9–14), a biochar (sample 15), E151, a food additive but non-PCM (sample 16), and a non-PCM (sample 17). Sample details are provided in Table 2. Error bars show one standard deviation of the sample's replicate measurements (n = 2–4). The grey dashed line was the highest blank level (0.48 mg kg^{-1}, n = 6). Names and numbers behind them in x-axis indicate individual samples and correspond with those in Table 2.

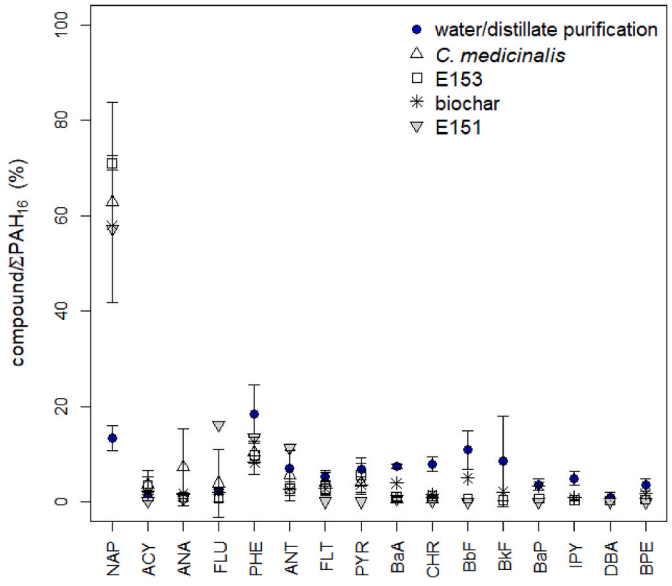

Fig. 2. Ratios of the individual polycyclic aromatic hydrocarbons (PAHs) assigned priority pollutants by the environmental protection agency (EPA) over their sum ($\sum$PAH$_{16}$) in the investigated pyrogenic carbonaceous materials (PCM). The different PCM categories were activated charcoal (AC) to purify water or distillate (sample 1, 2), AC as *Carbo medicinalis* (sample 4, 5, 6), E153 additive in cosmetics or food (sample 12, 13), a biochar (sample 15) and a non-PCM sample, E151, a food additive (sample 16). Sample details are provided in Table 2. Error bars indicate the standard deviations of the ratios of all sample replicates per category. Abbreviations are: naphthalene (NAP), acenaphthylene (ANY), acenaphthene (ANA), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BPE).

about 60% and PHE with around 15–20% contained the highest ratios of all samples. The NAP ratios of water purification samples (1, 2) were comparatively low but showed relatively high ratios for heavy PAHs as for instance BaA, CHR, BbF, BkF, and BaP of around 5–10%. Due to the limited information of these samples it can only be speculated about the reasons responsible for the difference. Explanations for this could be a different feedstock (e.g. coal as opposed to wood), specific pyrolysis and/or activation programs, the design of the pyrolysers in use, storage conditions of the PCM, etc. Investigations of 936 biochars of the EBC (EBC, 2012-2022) point towards post-pyrolysis treatment such as activation where the concentrations and fingerprints of the heavy compounds increased in comparison to light ones. Interestingly, the non-PCM E151 (16) had a similar fingerprint as the PCM samples. E151, brilliant black, is an azo-dye probably produced industrially, for which no information on PAH concentrations was found in the literature. The fingerprints of *C. medicinalis*, E153, and biochar, and even for the non-PCM E151 are similar to those of biochars reported in Hilber et al. (2012) and (Hilber et al., 2017), where NAP and PHE fractions were 40–60%, and 10–30%, respectively.

3.3. Consequences of PAHs in PCM

The water (1) and distillate (2) PCM filters contained BaP concentrations of 1.4 ± 0.3 and 0.2 ± 0.07 mg kg^{-1} (mean ± sd), respectively (Table 2). As the SN (2009) does not indicate a PAH concentration limit in the PCM itself, but in the purified water, we back-calculated the concentration in the sorbent, starting off from the maximum tolerable PAH concentration in purified water, i.e., 0.02 μg L^{-1} BaP (Table 1) in filtrated water as a worst-case scenario, by means of approximate distribution coefficients (K_D) ranges of BaP between PCM and water. The logarithmized K_D of BaP in biochar and charcoal experimentally determined by Hale et al. (2012) and Jonker and Koelmans (2002b) are 6.1 and 9.1, respectively, meaning that a BaP molecule prefers the PCM 1′000′000 to 1′000′000′000 times over the water phase. Consequently, the BaP concentration in the PCM leading to a concentration of 0.02 μg BaP in 1 L of water would amount to 20–20′000 mg kg^{-1}. Hence, sample 1 with the highest BaP concentration of 1.4 mg kg^{-1} is one to four orders of magnitude below this critical value. However, considering that actual K_D for BaP for a water filter sample consisting of activated carbon or activated charcoal might vary, and that the extraction method applied here might not yet have been fully exhaustive, a 'safety margin' of only one order of magnitude seems rather low.

While PAHs in E153 are only listed as "organic compounds" in the EC (1995) and in the (EC, 2008)and not at all in the Swiss legislation for food additives ZuV (2015), they are specifically addressed in EC (2012), where BaP should not exceed a concentration of 50 μg kg^{-1}. While 50 μg kg^{-1} BaP in EC (2012) for E153 "purity" probably addresses the quality control from a producer point of view, the EFSA opinion with its limit of <1 μg kg^{-1} for BaP (EFSA, 2012) probably concerns the consumer safety (Table 1). This is a clear discrepancy for BaP concentrations in food additives where the EFSA opinion is not legally binding but the 50 μg kg^{-1} BaP in the EC (2012) regulation is. Sample 12 (E153) showed 150 μg kg^{-1} BaP and clearly surpassed even the EC (2012) regulation. When comparing the PAH concentrations of sample 12 with the EFSA opinion concerning food (EFSA, 2008) the ΣPAH_8 of sample 12 with 1.1 mg kg^{-1} also exceeded the limit of 1 mg kg^{-1}. Although another E153 sample (13) revealed the same $\sum PAH_{16}$ concentration as sample 12, it was of no safety concern according the EC (2012) or any EFSA opinion due to the absence of BaP and consequently the ΣPAH_8 <1 mg kg^{-1} revealing the need of a differentiated evaluation concerning PAH pollution based on an adequate extraction method. Sample 15 showed around 1.0 mg kg^{-1} for $\sum PAH_{16}$ and clearly passes, with 0.3 mg kg^{-1} for the ΣPAH_8, the EBC feed quality limits of 1 mg kg^{-1} (EBC, 2012-2022) (Table 1).

4. Conclusions

In this paper, we provide indirect evidence that the current analytical methods are not appropriate to determine PAHs in PCM such as *C. activatus*, E153 (vegetable carbon), and related consumer products. Furthermore, we demonstrated on the basis of an optimized analytical method for biochar, a widely used PCM, that PAHs can be present in considerable concentrations in different types of PCM products. Some of them would even not have been allowed to be put on the market if regulations with adequate PAH quantification existed. While beyond the scope of this paper, these findings call for a more systematic methodological comparison, adaptation and harmonization of current analytical methods for PAHs in the EPh 10.0 (EPh, 2020), the JECFA (1990), EC (1995), (EC, 2008), EFSA (2012), and related ordinances. An obvious good starting point is sample extraction with toluene, but, depending on the target analytes defined by legislation, extraction solvents such as cyclohexane:acetone are worthwhile to be tested as well. Extended and aggressive extraction techniques should be preferred.

In addition, guide or threshold values for PAHs in different PCM materials and applications should be consistent with respect to the relevant target analytes (e.g. $\sum PAH_{16}$, $\sum PAH_8$, TEF, BaP), their true concentrations in the different matrices (drugs, feed, food, PCP, etc.), and relevant to the biological endpoint/species at risk. Aforementioned, an obvious example of discrepancy was BaP of 50 μg kg^{-1} and <1 μg kg^{-1} regulated in the EC (2012) and stated in the EFSA opinion (EFSA, 2012), respectively. Samples 1 and 2, the PCM for filtering, would not have been allowed to put on the market as consumer articles according to the EU-REACH regulation (EU-REACH, 2013). Another example of disproportion in legislation can be seen in five (samples 1, 2, 4, 12, 13) out of the nine samples consisting of 100% PCM and containing 5.2–31.5 mg kg^{-1} $\sum PAH_{16}$, which would even not have been allowed for soil application in Switzerland or as soil conditioner in organic farming in the EU with a limit of 4 mg kg^{-1} (ORRChem, 2005; EC, 2019a) and, except for sample 2, also not as fertilizer in the EU (EC, 2019b) where the regulation is at 6 mg kg^{-1} though they circulate as consumer products. This reveals a clear discrepancy between the legislation for soil protection and for consumer health protection, with the former being by far more stringent and methodologically more evolved.

Author contribution statement

Franziska Blum and **Isabel Hilber** analysed the samples. **Isabel Hilber** compiled and evaluated the data. **Thomas Bucheli** and **Isabel Hilber** drafted the manuscript and discussed the presentation of the data. All authors discussed and read the manuscript several times and approved the final version.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2022.119599.

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